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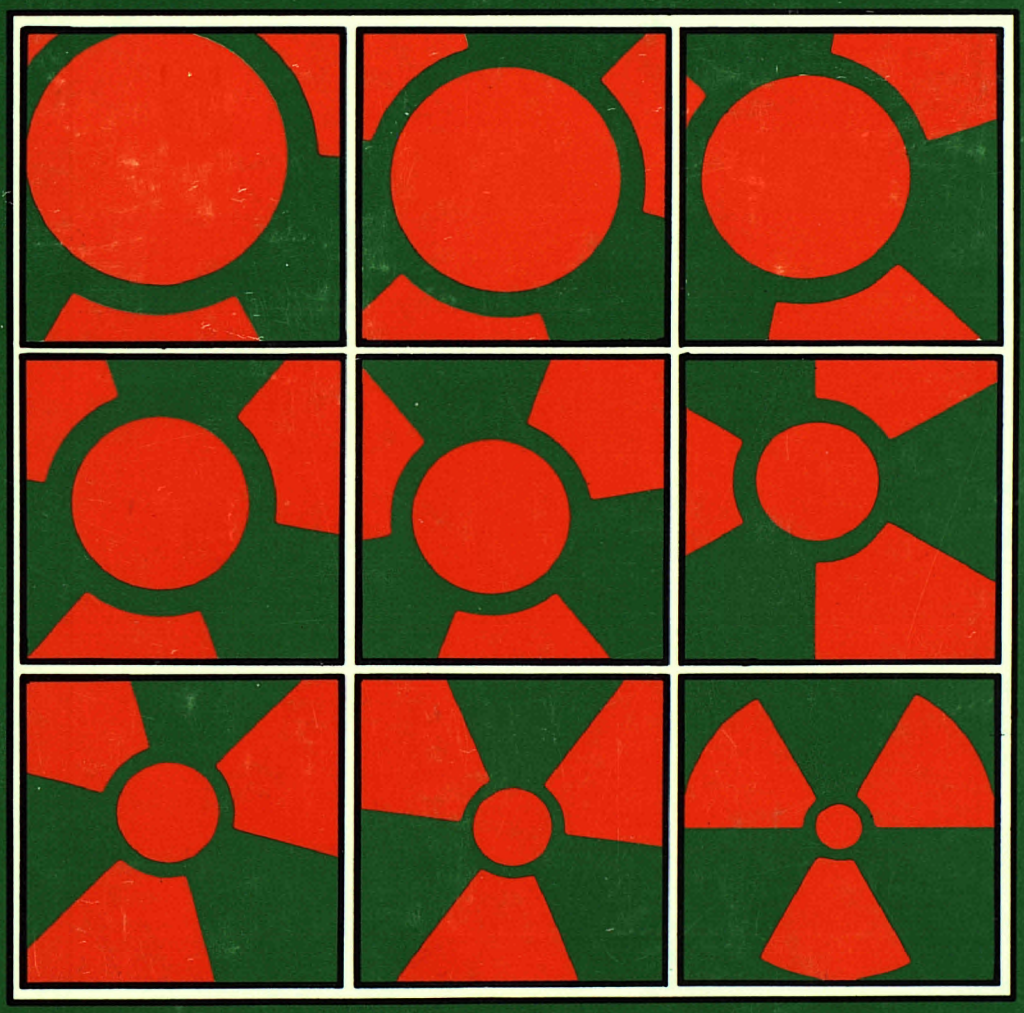
Commission of the European Communities

nuclear science and technology

Community's research and development programme on radioactive waste management and storage Shared-cost action (1990-94)

Annual progress report, 1992



Report

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FOREWORD

This report covers the progress of research work and activities started and developed during 1992 in the framework of the five-year programme (1990-1994) of the European Energy Community on "Management and Storage of Radioactive Waste". This R&D programme has been adopted by decision 89/664/EURATOM of the Council of the Ministers of the European Community on 15 December 1989.

The total amount of funding allocated to the programme is 79,6 million ECU over the five-year period.

The Council Decision, together with the technical content and the indicative Community financial contributions for the individual sections of the programme, has been published in the Official Journal of the E.C., Nr. L395, 30.12.1989, p. 28-32.

The programme is subdivided in :

- Part A : Waste management and associated R&D projects
- Part B : Construction and/or operation of underground facilities open to Community joint activities.

A call for research proposals has been launched (O.J. of E.C. Nr. C55/4, 7 March 1990) to implement Part A of the programme through shared-cost research contracts with public organisations or private firms established in the Member States. Multipartner projects have been encouraged.

Contract negotiations for the selected research proposals lead to the signature of 115 contracts for both Part A and Part B of the Programme. The number of research projects running in 1992 are 105.

The Commission is responsible for implementing and managing the programme and is assisted in this task by the Management and Coordination Advisory Committee "Nuclear Fission energy - Fuel cycle/processing and storage of waste" (see the annexed list of the Members of the Committee).

In addition to shared-cost research contracts, the programme also includes study contracts, awards of training and mobility grants, as well as international co-operation agreements with states outside the Community.

The co-operation among various teams within the Member States has considerably been promoted by the numerous multi-partner research projects.

The presentation and discussion of the work carried out during periodical progress meetings of working groups of the various projects assures the exchange of information within contractors and representatives of public and private institutions in the Community which are interested in the specific research area.

In order to provide a world wide information on the Community's activities in the field of the radioactive waste a biannual newsletter "EC-FOCUS" is edited.

In this report, the objectives, the working programme and a synopsis of progress and results obtained for each contract in 1992 are presented as prepared by the contractors, under the responsibility of the project leader(s).

The Commission wishes to express its gratitude to all scientists who have contributed to this report.

The previous annual progress reports of the programme are : EUR-11089 (for 1986); EUR-11482 (for 1987); EUR-12141 (for 1988); EUR-12761/Vol. 1 and 2 (for 1989) and EUR-14418 EN (for 1991). The overall results achieved including the progress of work for 1990 during the programme 1985-1989 have been presented and discussed at the third European Community Conference on Radioactive Waste Management and Disposal - Luxembourg, September 17-21, 1990 (Proceedings published under EUR-13389 - Elsevier Appl. Science Publisher).

S. ORLOWSKI
Head, Radioactive Waste and
Fuel Cycle Division

MEMBERS OF THE MANAGEMENT AND COORDINATION ADVISORY COMMITTEE
NUCLEAR FISSION ENERGY
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[1] This Committee was established by the Council Decision of 29 June 1984 dealing with structures and procedures for the management and coordination of Community research, development and demonstration activities (OJ N° L 177, 4.7.1984, p. 25).

PART A

WASTE MANAGEMENT AND ASSOCIATED R&D PROJECTS

A1 : STUDIES OF MANAGEMENT SYSTEMS

A2 : WASTE TREATMENT

A3 : SAFETY OF THE MULTI-BARRIER SYSTEM OF GEOLOGICAL DISPOSAL

A1: STUDIES OF MANAGEMENT SYSTEMS

Task 1

"Studies of Management Systems"

Topic 1	:	System studies
Topic 2	:	Harmonisation of radioactive waste management practices and policies
Topic 3	:	Comparative assessment of disposal practices in various management schemes for toxic and radioactive waste
Topic 4	:	Information of the public
Topic 5	:	Transmutation studies

Task 1

Topic 1 : System studies

Contract

FI2W/0037 Study on depleted uranium (tails) and on uranium residues from reprocessing with respect to quantities, characteristics, storage, possible disposal routes, and radiation exposure.

FI2W/0041 Waste management studies for large volumes of very low-level waste.

FI2W/0044 Treatment, disposal, re-use of building demolition and site cleaning wastes from nuclear facilities.

FI2W/0058 Treatment study of contaminated sodium with a view to decommissioning of FBR.

FI2W/0067 Studies of minimising transport of spent fuel.

FI2W/0119 Study of the retrievability of radioactive waste from a deep underground disposal facility.

Topic 2 : Harmonisation of radioactive waste management practices and policies

FI2W/0060 Assessment and proposal for activity limits for release of very low-level radioactive waste to landfills.

FI2W/0066 Definition of reference level for exemption of wastes, suitable for incineration.

Topic 3 : Comparative assessment of disposal practices in various management schemes for toxic and radioactive waste.

FI2W/0042 Comparison of safety assessment methods for toxic and radioactive wastes.

FI2W/0045 Study concerning the evaluation of toxic elements present in nuclear wastes.

FI2W/0061 Disposal of radioactive waste and toxic waste in underground repositories.

FI2W/0110 Use of methods and programmes developed in nuclear field for treatment and disposal of toxic and hazardous wastes.

Task 1

Topic 4 : Information of the public

FI2W/0036 Study of a communication strategy aimed at achieving a possible better understanding of the consequence of radioactive waste management in a well defined group of public.

FI2W/0043 Information of the public in the field of decommissioning waste. Study of strategies and means for specific information.

FI2W/0074 The evolution and implementation of a public information strategy on radioactive waste management.

FI2W/0105 A public information campaign to support a proposed national deep repository for low and intermediate level radioactive waste

Topic 5 : Transmutation studies

FI2W/0103 Transmutation of long-lived radionuclides by advanced converters.

FI2W/0104 Participation in a CEC strategy study on nuclear waste transmutation.

FI2W/0106 Potentialities and costs of partition and transmutation of long-lived radionuclides.

Task 1 - Studies of management systems

A. Objective

The system studies concern the evaluation of various scenarios for the management of different types of waste. Harmonisation work mainly involves the development of common waste management criteria and schemes. Waste from dismantling operations and spent fuel where these are considered as waste are included as well as the development of analytical models for minimising transport of waste. An additional topic is the evaluation of the possibilities offered by transmutation to reduce the inventory of long-lived radionuclides. Information of the public in all fields of radioactive waste management and disposal is a further topic.

B. Research performed under previous programmes

System studies have been performed by comparing various management schemes for particular categories of wastes or groups of waste streams; the comparisons were based on evaluation of costs and radiological consequences to workers and the public. The management alternatives were studied for :

- solid plutonium contaminated waste,
- alkaline liquid wash waste from fuel reprocessing and zircaloy-hulls,
- reactor waste (waste from normal operation of light-water reactors),
- waste management implications of direct spent fuel disposal and disposal after reprocessing.

Activities in the field of harmonisation of practices covered a review on "Objectives, standards and criteria of radioactive waste disposal in the European Community", the development of criteria for exemption from regulatory control for radioactive waste not linked to the nuclear fuel cycle, and first approaches to waste equivalence.

C. Present programme (1990-1994)

Studies are performed under five headings corresponding to specific research topics.

Topic 1 : System studies

The system studies are based on the comparison of possible management schemes, with the definition of waste inventories at origin, an analysis of the subsequent steps in the possible management routes (treatment, transport, interim storage and disposal), evaluation of costs and determination of radiological consequences. The sensitivity of each scenario to modifications in waste quantities, release limits, and waste acceptance criteria is also evaluated.
The main waste streams concerned are radioactive waste arising from decommissioning of nuclear installations, tailings from uranium-treatment, spent fuel declared as being waste and very low level waste candidate to being exempted from regulatory control.

Topic 2 : Harmonisation of radioactive waste management practices and policies

The main field of activity is the development of the scientific basis for developing criteria for exemption of particular waste streams from regulatory control. Particular disposal routes considered are incineration and disposal at industrial waste burial sites.

Topic 3 : Comparative assessment of disposal practices in various management schemes for toxic and radioactive waste

Studies are performed which compare radioactive waste management schemes to management practices for waste streams involving radioactive isotopes in material not linked to the nuclear fuel cycle and toxic waste mixed with radioactive elements. Particular attention is paid to disposal of toxic and mixed waste in salt formations.

Topic 4 : Information of the public

Studies on strategies allowing efficient information to be given to the public, and on how a good degree of penetration through various media may be reached are in progress. Development of information materials (booklets, visual aids, etc.) is also part of the activities.

Topic 5 : Transmutation studies

After having established the inventory of long-lived radionuclides produced for a given reactor capacity in considering the spent fuel as a waste, the possibilities of reducing the inventory of long-lived actinides and fission products by partitioning and transmutation are calculated. The conventional routes are irradiation in thermal reactors with MOX-fuel and a mix of light-water-reactors and fast breeder reactors, with long-lived radionuclides added in a homogeneous or heterogeneous way. Advanced possibilities considered are spallation devices and reactors with special fuel types.

Title:	Study on Depleted Uranium (Tails) and on Uranium Residues from Reprocessing with Respect to Quantities, Characteristics, Storage, Possible Disposal Routes, and Radiation Exposure
Contractors:	NUKEM GmbH 8755 Alzenau, FRG (Co-ordinator) WasteChem Ltd., Manchester/UK (Partner)
Contract N°:	FI2W-CT90-0037
Duration of Contract:	March 01, 1991 - Oct. 31, 1992
Period covered:	Jan. 01, 1992 - Oct. 31, 1992
Project Leader:	Dr. H.J. Wingender (NUKEM); J. Doran (WasteChem)

A. OBJECTIVES AND SCOPE

The objectives of the study are to:

- determine the quantities and rates of accumulation of depleted uranium tails arising from enrichment of natural uranium in the past and the foreseeable future (until about 2010 A.D.),
- allocate these data to the storages currently in existence,
- characterise the substances with respect to their chemical, physical, and radiological properties,
- identify and quantify possible ways to use and/or to dispose of these quantities.

Estimates of radiation and dose rate levels will be made for the different treatment steps. Similar investigations will be performed for reprocessed uranium as it is and for the tails generated by re-enrichment of the reprocessed uranium. Based on a predefined 20 GWe nuclear capacity scenario, the results for the three types of residues (see Figure 1), ie. uranium tails, reprocessed uranium, and tails from the re-enrichment of this will be compared and conclusions derived.

B. WORK PROGRAMME

1. Basic data evaluation
2. Investigation of use or disposal of the materials
3. Relating the data to a predefined scenario
4. Safety considerations
5. Comparison and conclusions.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The investigation has proceeded generally in line with the initial schedule. Difficulties with respect to source data availability - initially faced - and resulting deviations from schedule could be cancelled out with some effort. In consequence, the contractor had to exceed the original budget. A draft version of the final report has been submitted for comment to the CEC in December 1992.

Progress and results

C.1 Basic Data Evaluation

The study refers to experience from the UK, the Netherlands, Belgium, and the FRG. The data covers the following items:

- reprocessed uranium (U_{re})
- tails uranium from the enrichment of natural uranium (U_{nat}) or U_{re}.

The respective information had been communicated in the 1991 progress report. In 1992 the data has been detailed to some degree and essentially confirmed.

C.2 Possible Use or Disposal of the Materials

The possibilities to make use of uranium tails from U_{re} have been looked at discerning applications in the non-nuclear and in the nuclear domain (table I). Use of U in the non-nuclear field is recommendable for tails from natural U enrichment only. It is to be emphasised that using U does not mean its disappearing: the material re-emerges as scrap when the equipment containing U-devices is decommissioned.

The following conclusions have been drawn with respect to the possibilities to use U-tails and reprocessed uranium:

° The non-nuclear use of uranium will have a minimal effect on reducing the stocks of depleted or reprocessed uranium

° Basically tails uranium and reprocessed uranium with todays assays represent a stockpile of U235 which facilitates some conservation of natural uranium

° Tails uranium ($U_{nat,tails}$) is a very suitable material for use in MOX fuel elements and in Fast Breeding Reactors

° According to is residual U235 content, reprocessed uranium is suitable for repeated energy production, either as-is in CANDU reactors or after a new enrichment, in LWR's. However the usefulness of the material depends on its composition, which is determined by its history as reactor fuel. New loading and burn-up strategies can move the limits of qualification for re-use. New selective enrichment methods might necessitate new valuations.

Ways to store or to dispose of the materials have been investigated taking into consideration their chemical, physical, and radiological properties as well as the quantities to be expected. One particular issue governing the result of this consideration has become the inherent energy potential.

For relatively short term storage, uranium hexafluoride (UF_6) might be the most appropriate compound, as it is a basis for many conversion steps (fig. 2). For long term storage exceeding 50 years and for final disposal uranium dioxide (UO_2) is preferable because of its chemical stability, density, non-volatility and low chemical toxicity compared with UF_6.

Despite the currently perceived adverse economics (and, to some extent, public perception of nuclear power) of the use of tails in fuel fabrication for LWR's and FBR's, the present stock represents, not waste, but a very important strategic stockholding of energy. Such tails stocks in the UK have been calculated to represent more available energy than the total reserves of coal in the UK. Future energy resources will need to keep pace with demand from the world population, which is estimated to double before the middle of the next century, and reserves of fossil fuels are diminishing. Apart from the beneficial environmental effects, nuclear power will continue to provide a necessary part of our energy production. Thus, the UK position is clear; tails stocks will be stored as a usable energy source and utilised as demand dictates.

No re-use outlets for U_{re} have been found, other than return to customers or enrichment for fuel fabrication. No disposal of U_{re} either for retrieval or non-retrieval has taken place, but this would only be done if the re-enrichment option were seriously uneconomically viable and U_{re} considered as waste. However disposal options would be evaluated.

C. 3 Scenario Relation

In order to relate the data and results to a more general scale, a scenario of reactor capacity of 20 GWe was chosen. The respective through - put of uranium (3,5 % enriched in U_{235}) amounts to 600 metric tons of uranium metal equivalent per year, and this is roughly the amount of reprocessed uranium in this scenario, too.

The respective data of the scenario are shown in table II for a particular example. It is to be emphasised that - in reality - there will be spectra

- of residual enrichment in spent fuel,
- of initial enrichment in fresh fuel,
- of blending uranium fuel and mixed oxide fuel,
- of enrichment demands according to fuel poisoning and
- of storing/processing strategies of the materials.

Whatever the activities are, in the end the amounts of U_{re} or/and of $U_{tails,nat}$, $U_{tails,re}$ will be present and to be dealt with.

C. 4 Safety Considerations

Tails materials mainly consist of U_{238} and their specific activity is lower than that of natural uranium.

Reprocessed uranium on the other hand contains some constituents which alter the radiation behaviour of the material in relation to natural or enriched natural uranium. As can be seen by the figures of the tables I to III in annual progress report 1991, these constituents are some newly formed uranium nuclides, which do not exist in natural or enriched uranium. They are generated by nuclear processes during irradiation of the fuel elements in the reactors; their quantitative proportion depends on the burn up.

In addition to this, there are traces of impurities, consisting of fission products mainly being gamma emitters.

In order to allow an assessment of the changed radiation properties of reprocessed uranium compared with those of natural or enriches natural uranium some, dose rate calculations have been carried out.

The following parameters have been varied:

- Initial enrichment of the reprocessed fuel elements (3.2 % to 4.4 % U235)
- Final burp up (33 to 50 GWd/tHM)
- Storage time after cooling and reprocessing (three months to two years).

The calculation of the gamma dose rate caused by fission products is based on separation factors stated in the literature.

Summing up it may be said, that

- the gamma dose rate level of reprocessed uranium is higher than that of natural uranium or enriched natural uranium
- the gamma dose rate level of reprocessed uranium depends on the burn up history of the former fuel element; the higher the burn up the higher the dose rate in reprocessed uranium
- the gamma dose rate level of reprocessed uranium generated by uranium and its decay products increases during a period of ten years after reprocessing; after this time it remains constant.
- this effect is superimposed by the influence of fission products always being present in reprocessed uranium; gamma dose rate of fission products diminishes with time. Its magnitude depends on the separation factors achieved during the reprocessing.

C.5 Conclusions

In the nuclear fuel cycle of Light Water Reactors two materials arise whose utilisation today is not fixed definitely. These materials are the tails of the enrichment of either natural or reprocessed uranium and the reprocessed uranium itself.

Real consumption of depleted uranium in the non nuclear field is minimal. The re-use of the materials in the nuclear fuel cycle is associated with various conditions, which are not easy to predict, i.e. the reloading and burn-up strategies for Light Water Reactors leading to qualitative changes of the spent fuel composition, the supply and the price of natural uranium influencing the enrichment conditions (e.g. the tails assay), or the success of the development of new technologies as selective uranium enrichment (e.g. LASER techniques as AVLIS or MLIS).

The accumulating amounts of these materials in question have been estimated, their characteristics investigated, and possibilities for further treatment considered. These comprise an intermediate storage as well as a final disposal.

Depleted uranium (tails and reprocessed) can be stored for several decades as produced, i.e. as uranium trioxide or hexafluoride: Adequate storage capacity is available. But there are also processes practicable and proven to convert these original materials into less reactive compounds better suited for intermediate or final disposal.

According to the expected extension of the burn-ups in the future the isotopic composition of reprocessed uranium will change. As a result the emitted radiation of the materials will cause higher dose rates which must be taken into account when handling these materials.

Regarding the variety of influences on quality and quantity of depleted uranium, it is very difficult to make long term statements whether these materials should be classified for use or for final disposal. Considering the anticipated success in selective enrichment methods, an intermediate storage for the next few decades seems to be a good policy.

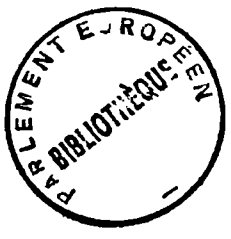


Table I: Possibilities to use reprocessed uranium and tails of natural and reprocessed uranium enrichment

Non-nuclear domaine:	
U(metal)	: - ballast weights - counterbalance weights - X-ray/gamma ray shielding - alloying constituent
(compounds)	: - catalysts - ceramic colours/dyes - chemical reagents - ceramic material constituent
Nuclear domain	
U(fuel)	: - light water reactors - breeding reactors - CANDU reactors

Table II: Scenario related data

Scenario parameters:		
- 20 GWe electricity generating capacity equivalent to		
- 600 metric tons of U metal annual fuel demand at		
- 3.5 Wt % enriched in U235		
natural U data resulting:		
- feed (U_{nat} demand)	:	3880 tons/year
- product (fuel)	:	600 tons/year
- tails (0.2 % tails assay)	:	3280 tons/year
- actual enrichment capacity examples:		
° Almelo	:	25 % of scenario
° Gronau	:	16 % of scenario
° Capenhurst	:	39 % of scenario
° Eurodif	:	337 % of scenario
reprocessing data resulting:		
- spent fuel reprocessed	:	600 tons/year
- U_{re} arising (3.5 % - 2.5 % = 1 % residual enrichment)	:	585 tons/year
- capacity example: THORP	:	1200 tons/year nominal 700 tons/year planned
reprocessed U data resulting:		
- feed (demand of U_{re})	:	2900 tons/year
- product (fuel, 3.8 wt% U235)	:	600 tons/year
- tails (0.2 % tails assay)	:	2300 tons/year

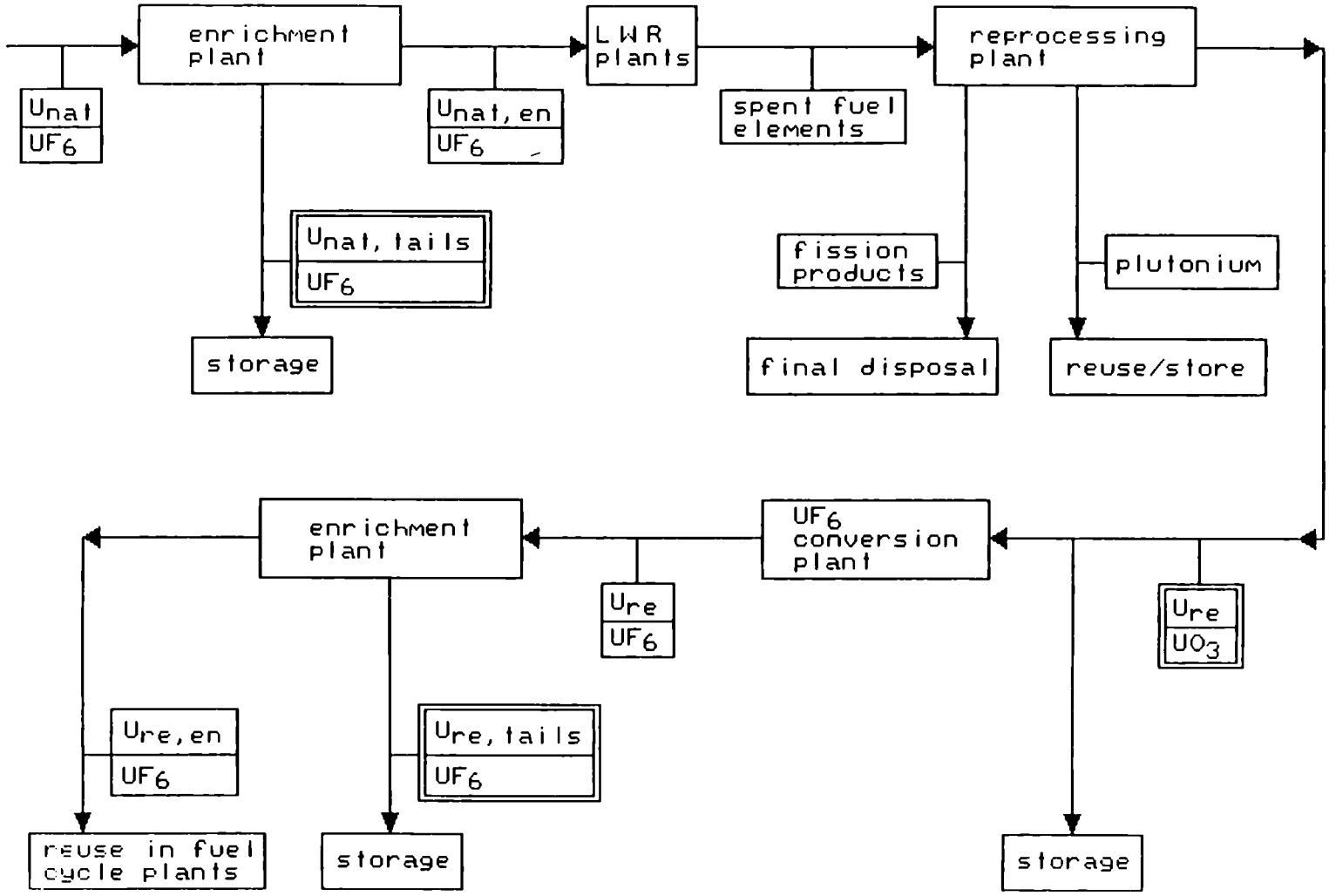


Figure 1: Source of Arisings of Uranium Tails and Reprocessed Uranium in the Nuclear Fuel Cycle

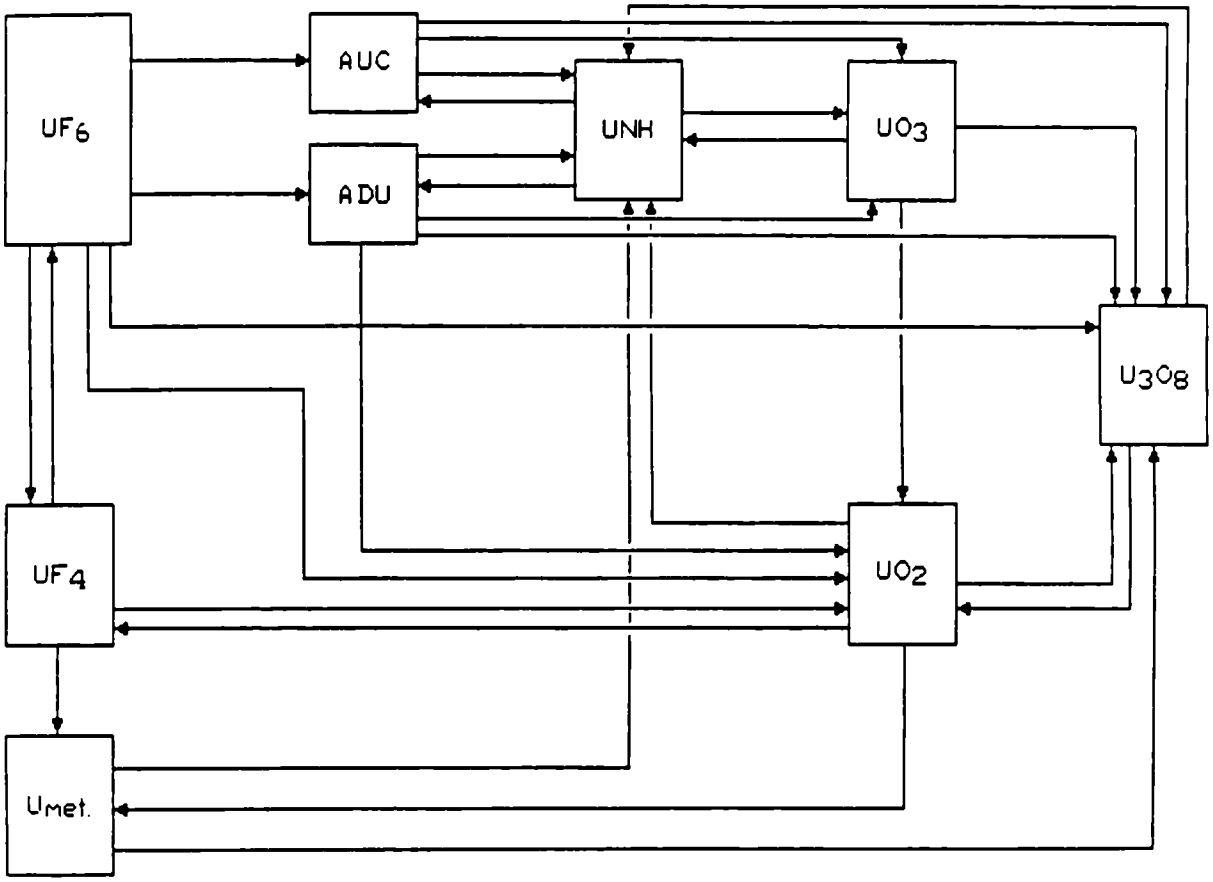


Figure 2: Uranium and the most known compounds

AUC: ammonia uranyl carbonate
ADU: ammonia di-uranate
UNH: uranyl nitrate

Title	:	Waste Management Studies for Large Volumes of Very Low-Level Waste
Contractor	:	Intera Information Technologies, United Kingdom
Contract n°	:	FI2W-CT90-0041
Duration of contract	:	March 1991 - September 1992
Period covered	:	January 1992 - September 1992
Project Leader	:	G.M. Smith

A. Objectives and Scope

A significant proportion of the radioactive material which arises on decommissioning of nuclear facilities contains only small amounts and low concentrations of radionuclides, either as surface contamination, or as activation products within the body of the material. The objective of this study is to investigate the implications for waste management systems of various levels and forms of exemption criteria and the corresponding implications for routing low-level waste materials arising from decommissioning. Following a review of the existing information on the volumes and radionuclide contents of the most significant low level materials which arise during decommissioning, and the current legislative background relevant to the disposal, recycling or reuse of such materials, the study will investigate the full range of radiological implications of adopting alternative clearance levels now under consideration. A number of related factors, such as volumes of materials which would require disposal as "radioactive" waste, the timing and the degree of dismantling, and the requirements for waste packaging are also addressed.

B. Work Programme

B.1. Characterisation of the waste arisings, the options for the management of the arisings, and the exemption principles and criteria within which the options have to be applied.

B.2. Ranging of parameters which characterise the system identified in B.1., particularly those associated with the formulation of exemption.

B.3. Evaluation of the radiological impacts following adoption of the relevant sets of parameter values characterising the system.

B.4. Evaluation of the implications for routing of wastes following adoption of alternative formulations and levels for exemption by means of a comprehensive assessment and sensitivity analysis.

C. Progress of work and obtained results

State of advancement

The work carried out during the year 1992 has been focused on the completion of item 2 and development of the items 3 and 4.

- Following on from the review of various waste management procedures, appropriate representations of these were made to assess the potential for waste material to give rise to a wide range of radiation doses to workers and members of the public. This involved aggregating the individual procedures (eg. dismantling, transport, smelting operation, post-disposal impact from landfill) into overall options (eg. unrestricted and restricted disposal, recycling) whose impacts are required to be quantified.

- Available information on waste streams (eg. PWR contaminated steel, Magnox activated concrete) were collated. These were represented mathematically in terms of radionuclide contents, and the distribution of activity throughout the mass or volume.

- Preliminary calculations were conducted of the annual individual and collective doses to workers and public for unit activity concentrations of each radionuclide, or for total activity, resulting from the various management procedures.

- Given the information gathered on the composition of the various waste streams and the representations of the management options, their respective radiological impacts were calculated, as was their sensitivity to factors such as the assumed exemption level and delay prior to dismantling.

Summary of the overall study

A significant proportion of the radioactive waste which arises on decommissioning of nuclear facilities contains only small amounts or low concentrations of radionuclides, either as surface contamination, or as activation products within the body of waste materials.

The primary objective of this study is to investigate the implications for overall waste management systems of various levels and forms of exemption criteria, and the corresponding implications for routing of low-level wastes arising from decommissioning. In addition, consideration has been given to related topics such as the amount of the radioactive waste to be disposed of given various levels of exemption, and monitoring requirements. The work was divided into four topic areas :

1. Literature search and analysis of existing work on low-level decommissioning waste arisings,
2. Review and mathematical representation of the options for managing large volumes of low-level and potentially exempt material,

3. Review of forms and levels of criteria practicable in the context of large scale exemption,
4. Assessment and analysis of the radiological impact of adopting various management options, and their dependence on important parameters such as exemption level and delay after reactor shutdown.

In the context of the arisings of decommissioning waste, numerous recent studies conducted by government agencies, international bodies and operators have been reviewed. The options for the management of very low level waste arisings include interim or partial measures, eg. deferred decommissioning and decontamination, as well as unrestricted and restricted final disposal and recycling. In the context of exemption principles and criteria, the recommendations of international agencies (the International Commission on Radiological Protection and the International Atomic Energy Agency) have been reviewed, as well as those of national authorities within and outside the European Community.

The majority of the high volume low level wastes from decommissioning comprise the concrete and steel structures of nuclear power plants. Given the magnitudes of exemption criteria being considered in such contexts (expressed as limits on activity concentrations) there is considerable scope for the unrestricted disposal or reuse of very large fractions of the substantial concrete structures of most nuclear facilities, along with significant fractions of the potentially active steels and other metals outside the areas of greatest radioactivity. The volume of materials which has to be treated as radioactive waste is a function of many factors. These include particularly the delay prior to dismantling, the decontamination factor for the various affected surfaces and the exemption criteria assumed. Notably the adoption of higher concentration limits (around 50 Bq g^{-1}) implies arisings of hundreds of m^3 whereas lower values (around 1 Bq g^{-1}) imply thousands of m^3 per major facility.

A major interest concerns how the radiological impacts of adopting various management strategies for potentially exemptible decommissioning waste are dependent on factors such as the exemption limits adopted and the delay assumed between facility shutdown and dismantling, waste disposal or recycling. Extensive calculations have been undertaken to investigate this issue, on the basis of exemption for options giving rise to individual doses less than 10 μSv per year and collective doses less than 1 man Sv. A detailed explanation of the assumptions made and parameter values adopted in the assessment has been provided. Consideration has been given to the problem of defining the practice which is being exempted. In a sensitivity analysis gross activity concentration limits have been varied within the range 0.1 - 10 Bq g^{-1}, in line with current international and national consensus, and delays between shutdown and waste processing up to 100 years have been considered.

Given the cautions nature of the assessment of individual doses, the results presented here confirm the considerable scope for exempting large fractions of both concrete and steel waste arising from decommissioning. Collective doses do not appear to be a significant factor in choices between management options.

The volumes of, and the annual individual doses associated with, material which is potentially exemptible, are both approximately linearly dependent on the numerical value of the exemption limit in the region of 1 Bq g^{-1}, being somewhat sub-linear at higher levels. This follows from the best available data on the distribution of activity throughout the various waste streams.

For some waste streams and management options, allowing the radionuclide inventory to decay prior to removal from the facility occasionally leads to an increased radiological impact per unit activity concentration owing to the ingrowth of some long lived radiotoxic nuclides, notably Am-241, and because older material at the same activity concentration tends to contain longer-lived radionuclides.

For some exposure modes it is important to consider whether the distribution of individual doses associated with a given volume of waste should be addressed or allowed for in evaluations of impact, or whether average values are sufficient, especially in the light of the generally low doses involved. This reflects the absence of clear guidance in recommendations for exemption criteria on how to deal with uncertain exposure conditions. For some wastes and some exposure modes the distributions of dose do not appear to be very wide. However, in some cases it is possible, though unlikely, that individual doses may be an order of magnitude or more higher than those estimated on the assumption of exposure to average material in the volume being considered.

Useful guidance on waste stream characterisation and corresponding VLLW exemption can be provided generically. The results presented here illustrate what is practicable in terms of assessment. Possibilities arise for the application of partial exemption of special exemption justified on a case by case basis, rather than blanket exemption at a higher level which could be harder to justify.

Such assessments can be used to direct procedures and plans on a site-specific basis. However, better radiological control in management of decommissioning VLLW requires improved characterisation of the high volume waste streams involved. Particularly important is the distribution of radionuclide concentrations throughout the considered volumes, as this largely determines how much of the total waste volume can be considered for exemption.

Title:	Treatment, Disposal, Re-Use of Building Demolition and Site Cleaning Wastes from Nuclear Facilities
Contractors:	NUKEM GmbH, FRG (Coordinator); WasteChem Ltd., UK; SGN, F
Contract No:	FI2W-CT90-0044
Duration of contract:	February 91 - December 92
Period covered:	January 92 - December 92
Project Leaders:	H.J. Wingender (NUKEM); J. Doran (WasteChem); S. Goetghebeur (SGN)

A. OBJECTIVES AND SCOPE

The study concerns waste materials arising from building demolition and from site cleaning activities associated with decommissioning of nuclear facilities. The study does not consider wastes such as dismantled and/or disassembled process equipment, radioactive process inventories, etc., as these wastes are assumed to have been removed from the facilities prior to building demolition and site cleaning.

The objectives are:

- Establish an overview of building demolition and site cleaning wastes arising from various types of fuel cycle facilities (enrichment, fuel manufacturing, power reactors, reprocessing, waste treatment, spent fuel encapsulation).
- Consider sampling, monitoring and analysis tools enabling the characterization and classification of these wastes.
- Classify these wastes according to a 3 class scheme (release for unrestricted use, release for restricted use only, radioactive waste) and describe possible ways of re-use or disposal.

Information from FRG, UK and France is to be used. Three partners contribute to the study (NUKEM: enrichment, fuel fabrication, reactors, fuel encapsulation; SGN-F: reprocessing, waste treatment; WasteChem-UK:enrichment, fuel fabrication, reactors, reprocessing, waste treatment).

B. WORK PROGRAMME

The programme of the study is structured according to following tasks:

B.1 Collection and compilation of waste data and characterization (3 partners)
B.2 Investigation of sampling, monitoring and analysis tools (NUKEM)
B.3 Material classification and investigation of re-use and disposal possibilities (3 partners)

For standardization purposes, the information obtained is to be re-arranged in such a way that it reflects the waste arisings from a 20 GWe fuel cycle scenario (equivalent to 600 metric tons of heavy metal per year).

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

With the completion of the study in December 1992, a report has been prepared which needs only editorial revision.

As mentioned in the last annual report considerable difficulties occurred. The problem of completing the report in the given time frame and the limited finances was difficult. However, with extra efforts the report was completed, keeping to the original timescale.

Progress and results

C.1 Determination of the waste arisings

The total waste arising from the demolition of the scenarios building structures is listed in Table I. The main portion of waste arising is generated by reactor demolition, i.e. 85% when the demolition starts as soon as possible after shut down. The lower portion in the case of UK results from a different strategy. Here, the reference strategy entailed the removal off site of the plant and buildings external to the biological shield within 10-14 years of shut down. Total building waste arising must remain the same irrespective demolition timing - only the categorized waste will change. The demolition and the removal of remaining structures occurs after 100-135 years. Approximately 5% reduction of the total building waste arising accrues from fuel encapsulation replacing reprocessing at the back end of the fuel cycle. Approximately 90% of the wastes contain reinforced concrete, 8% steel, 1,5% brickwork and 1% of other materials.

A unified scheme for demolition waste estimation is difficult, since the regulations and the strategies practiced and/or envisaged are different from country to country and from plant to plant. Therefore, the listed waste arising data are strongly dependent on the model used.

Two main types of building demolition strategy are considered: total demolition and step by step demolition. The first case employed in France: the materials with and without radioactive material are mixed. The average specific radioactivity is below the limits given by the regulations. However, a release of this material for unrestricted use is not possible. These waste materials must be disposed of in a near-surface landfill. The second case, as employed in FRG and UK: parts of floors and walls are removed at first which contain radioactivity. Then the remaining building structures are demolished.

The amount of contaminated soil is difficult to estimate. Experience only exist for older plants in which such waste could be generated. In newer plants, such waste can be excluded or the amount is insignificant compared to the volumes produced by other sources. Therefore, this waste arising was not considered.

The secondary waste expected during the demolition phase is also small. The part with radioactive impact is less than 1% of the total radioactive waste arising and was not considered.

The determination of the expected radionuclide content, distributions, concentrations, and dose levels necessitates several assumptions along with suitable models. The only detailed experience exists in the ease of power reactor decommissioning. Here, the activation of the material by neutron irradiation can be precisely determined.

For calculating the surface contamination the operating data, the release rates of radioactive material and the possiblity for transfer of radioactive material was considered. The quantities expected are evaluated according to former decommissioning studies and/or experiences from the plant operation.

The radioactive impact is conservatively calculated. A more precise estimation would be possible with increasing experience on nuclear plant decommissioning, especially for the front end and back end plants.

Assumptions for calculating the radioactive impact and surface contamination are made with a relative high uncertainty. One uncertainty results from the assumption of how to decontaminate the surfaces before the safe enclosure period, especially for plants on which there is no decommissioning experience. The other uncertainty results from the mass correlation of contamination corresponding to surface contamination.

C.2 Sampling, Monitoring and Analysis Tools

The wastes with beta and gamma radioactive constituents can be suitably monitored (radionuclide content, distributions, concentrations, and dose levels) for release of these materials into the environment. Particularly in the case of non-destructive analysis techniques (NDA) for large radioactive waste packages, the experiments and the routine measurements demonstrate the applicability of a monitoring system. Detectors and measuring systems are also suitable for localization of the contamination on building structures. When a gamma emitter is utilized as a lead-nuclide the survey technique can be used for measuring the surface contamination. With the application of the contamination register system (cataster), an effective waste management system can be established to survey the waste arising from the initial phase to the removal of the material from the surfaces, to the packaging of the material.

In the case of alpha radioactive contaminated waste, a suitable NDA monitoring system does not exist. Surface measurements are unsuitable for crushed material. In this case, samples are used together with laboratory analysis. But, this method is unsuitable for routine monitoring because of the complex techniques and is time consuming. Sampling techniques have the disadvantage of being unable to estimate the activity at locations between the points on the sampling grid. The developed statistical methods are only useful when hidden "hot spots" can be excluded. A combination of NDA measurement with sampling collections could solve this problem when a lead-nuclide as a gamma emitter can be used in the NDA measurement. The developed measurement systems based on neutron detection are utilized in the area for waste treatment and for checking the limits of near-surface disposal.

In both cases, i.e. (beta, gamma) and alpha radiation monitoring cannot be used at the present time because the material throughput is not high enough to process the large amount of waste. The delay would significantly increase the total cost of the project. For routine operation, new measurement systems must be developed to treat large amounts of waste. A key role in this scheme is played by the application-oriented user interface while measurements and testing routines must become more and more automated and interconnected.

C.3 Material Classification

The classification of the waste material governs the categorization of the material as:

- radioactive waste
- ready for restricted use

- ready for unristricted use

Two main groups must be considered when classifying the waste material according to the specific radioactivity content and surface contamination: 1. beta, gamma and 2. alpha radioactivity. Each group has its own limits given by the respective national regulations, needs its own measurement methods to control the waste material, and has its own strategy in waste management.

For compilation of waste arisings from the 3 countries mentioned, a more general scheme for waste classification (pre-classification) is used according to the following definitions: very low level waste (VLLW), low level waste (LLW), and intermediate waste (ILW) and high level waste (HLW).

In the case of VLLW, the radioactive content and the surface radioactivity are below the exemption limits and the waste material can be handled as "free of radioactivity".

The significant proportion of the waste material which arises on plant demolition contains only a small amount of low concentration of radionuclides within the body of waste material.

Wastes with higher activity are only generated by dismantling the biological shield when the demolition phase is started after a short safe enclosure period. Therefore, HLW does not arise in UK consideration. All these waste materials are suitable for final disposal and no extra classification in ILW and HLW is needed for this study.

Based on the uncertainties for calculating the waste quantities and the different exemption limits in the three countries, detailed analysis is difficult. For this reason, no detailed consideration was given to calculation and estimation of waste arising in respect of the different exemption limits given by the separate authorities in the participating countries.

Presently, large quantities of waste material classified as for unrestricted use are disposed of. A transportation to public landfills is already a complicated process. Therefore in the future, these wastes could be used unrestrictively for road construction, dam building etc.. However, it must be demonstrated , that no accumulation and/or no mobilization of radioactivity can occur and produce any harmful effects on the human environment.

In the context of waste treatment, disposal, and re-use, a major interest of this study concerns how these waste materials do not need to be disposed of, but rather to be re-used as restricted and unrestricted material. Numerous studies have been reviewed to investigate the waste arisings and the options for classification. Table I gives an idea of the waste proportions when considering optimistic options of waste management mentioned in research.

No special strategies and procedures are considered to minimize the radioactive waste arising (pre-sorting, decontamination procedure, incineration, etc.). An effective minimization of radioactive contaminated waste can be implemented by doing an effective decontamination of the building structures in the beginning of the demolition phase, as well as during the different steps of the waste treatment phases. It is worth noting that the decontamination procedure can become too costly; thus, the direct disposal of the contaminated material may be then preferred. Therefore, for evaluating the waste amounts, the radioactive material should be also classified by criteria related to different waste treatment procedures.

Table I: Building Waste Material from Scenario Fuel Cycle Plants

	Total Waste Arising		Un-restricted Use		Restricted Use		Radioactive Material	
	m^3	Mg	m^3	Mg	m^3	Mg	m^3	Mg
Front End Plants								
FRG	90,400	246,000	90,300	245,800	-	-	84	240
UK	110,00	386,500	109,700	386,200	110	300	-	-
Reactors								
FRG[1]	1126,000	3110,000	1121,000	3100,000	500	2,300	2,740	7,520
UK[2]	60,840	187,400	60,390	183,900	450	3,500	-	-
Back End Plants								
FRG[3]	26,800	75,300	26,700	75,200	15	45	5	10
UK[4]	203,700	596,600	20,370	59,700	183,290	536,000	-	-
F[4]	78,000	202,600	-	-	78,000	202,600	-	-

1) Building demolition as soon as possible
2) Building demolition 100 years after shut down for reactors, 50 years for other fuel cycle plant
3) Building waste from encapsulation plant
4) Building waste from reprocessing plant

Title :	Treatment Study of Contaminated Sodium with a View to Decommissioning of FBR
Contractors :	CEA - SIEMENS - FRAMATOME
Contract N° :	F12W - CT90-0058
Duration of the contract :	from April 1991 to April 1993
Period covered :	January 1992 - December 1992
Project Leader :	C Latgé (CEA - coordinator) N. de Seroux (Framatome) Mr. Hanebeck (Siemens)

A. OBJECTIVE AND SCOPE

In the Fast Breeder Reactor (FBR) decommissioning studies, sodium management is a major problem. Sodium becomes an important waste which must be taken into account in the final process. To handle this specific topic, a cooperative working group has been formed, with the French "Commissariat à l'Energie Atomique" (CEA), FRAMATOME and SIEMENS. CEA is the project leader.

The scope of work is based on a step by step approach, using available data and experimental results with regard to the sodium inventory, sodium purification and waste treatment.

The aim of this particular development program is to highlight optimized scenarios for sodium destruction and recycling, based on a technical and an economical approach. Moreover a Research & Development (R&D) orientation will be provided to improve the selected scenario and to allow a better understanding of fundamental processes.

B. WORK PROGRAMME

To perform the above scope of work, five main stages have been defined :

a : Inventory of the sodium needs :
The sodium balance, based on sodium needs for future FBR programs and existing wastes to be treated, is the starting point from which the problem is tackled and from which the scenarios to be highlighted later on are set.

b: Assessment of sodium behaviour and characteristics :
From an estimated contamination, provided by mathematical models which have been validated using experimental data, it is possible to predict the behaviour and characteristics of the sodium to be treated.

c: Sodium purification :
Purification processes are examined with regard to the predicted quantities of contaminated sodium and the associated storage and transportation techniques. The R&D axes are defined, according to the required level of knowledge in the waste treatment domain.

d: Analysis of the scenarios and their main parameters :
Using the previous steps as a reference, the main parameters of the scenarios are reviewed, with both a technical and an economical vision. This twofold approach allows the working group to highlight arguments to select and describe the scenarios to be analysed.

e: Optimized scenarios :
These processes, having been defined as suitable scenarios for sodium treatment, will be described. Further needs for R&D programs will be highlighted, to improve the processes

efficiency.

C. PROGRESS OF WORK AND OBTAINED RESULTS

C.I. STATE OF ADVANCEMENT

The cooperative working group was assigned in April 1991 the task of sodium management in the decommissioning studies environment.
A first semestrial report was published on November, 1991, /1/ and is included in the Annual Progress Report 1991, /2/.

Two semestrial reports were published on April, 1992, /3/ and on September, 1992, /4/.

The Reference /3/ describes the activation and the contamination assessments of the sodium to be treated after the final shutdown of the FBR.
Then it lists the sodium purification processes : physical processes such as filtration and cristallization, or chemical processes such as molecular adsorption and isotopic exchange.
It describes also available disposal processes for contaminated sodium. Sodium is converted in an inert waste which is sent to a definitive storage.

The Reference /4/, following the results of the previous work, gives an analysis of the main parameters for the choice of the scenarios for the sodium treatments, either to reuse it, or to dispose it.
For the primary sodium, it details the storage conditions, the transportation possibilities and the scenarios following several axes : reuse, disposal, long term storage.

The same work has been carried out for the secondary sodium.

The milestones with regard to the sodium treatment in a decommissioning framework are presented on figure 1.

C.II. SODIUM ACTIVATION AND CONTAMINATION

The pollution due to the radioactive elements consists in :

Primary sodium :
- primary sodium activation coming from the neutronic flux within the core.
- continuous contamination coming from tritium of control rods releases going through the clads and from corrosion products of the steels.
- uncontinuous contamination coming from caesium of spent fuel subassemblies releases.

Secondary sodium :
- secondary sodium activation from the neutronic flux during its way through the intermediate heat exchangers in the vessel (only sodium 24).
- continuous contamination coming from tritium of primary sodium going through the pipes of the intermediate heat exchangers.

A computer programme, CORONA, from CEA - France allowed us to assess the sodium activation and contamination level at the final shutdown of a FBR after a thirty years operating time.

We have noted fast decay of activation and contamination level when the reactor operation

is ended and a reduction by a factor of 5000 is quickly obtained in one year. Some radioactive elements, like Iodine 132, have very short half life and they are not to be taken into account in our case. The short decay time of the sodium 24 brings a large contribution to the general decay.

After the quick decay of the sodium 24, the secondary sodium activation and contamination is mainly due to the tritium. The long half life of this element cannot allow to expect significant modifications in time.

Figure 2 gives the main activation and contamination levels to take into account at the final shutdown for the primary and the secondary sodium. We did not consider : elements with half life under 1 year, corrosion products (their concentrations stay very low) and gazeous products.

C.III. SODIUM TREATMENT

In the view of sodium reuse or easy disposal, several purification processes have been listed following the different elements being in the sodium.

- the filtration of oxygen and hydrogen is carried out by solubility decreasing by the cooling of a secondary flow of sodium. They are crystallized and retained by filtration. FBR are fitted out with cold traps (figure 3) which include these functions. The final concentration can be very low, under 1 ppm for O and under 0.5 ppm for H.

- the filtration of the tritium is carried out with cold traps. The tritium can be crystallized by cooling like the isotope hydrogen and retained by filtration or can be fixed by isotopic exchange with hydrogen. The final concentration can be very low, as for H.

- the control of the sodium purity is carried out with a plugging indicator : its principle is to measure a sodium flow through a calibrated hole during a cooling phasis. The reading of the flow/temperature curve indicates the purity level of the sodium.

- the filtration of the solids particles such as metallic or fuel particles can be carried out by the cold traps. Specific filters in sintered metal are also very efficient (near micrometer squale).

- the purification of caesium is made by adsorption on carbon material sorbent (mainly RVC type : Reticulated Vitreous Carbon). Efficiency is very good and it has been tested successfully at KNK and RAPSODIE.

- in case of water/sodium reaction in steam generators, the purification of sodium hydroxide (caustic soda) can be carried out with cold traps.

- corrosion products such as Mn 54 and Co 60 can be eliminated by adsorption on a nickel support but the efficiency is low.

- caesium, Mn 54 and Co 60 concentration level can be easily assessed by gamma spectromeasure.

Several sodium disposal processes have been examined. Three main processes have been distinguished :
- reaction with steam : good efficiency but not adapted to large volume,
- alcohol process : good efficiency but not adapted to large volume,
- dissolution in water : good efficiency, adapted to large volume.

For these 3 processes, the successive phases are : conversion of the sodium in caustic soda, neutralization with acids, drying in salts, mixing with epoxy resins and definitive storage. Only one process has been developed up to an industrial scale : the water process NOAH .

NOAH process has been developed and patented by CEA. A pilot plant has been operated to validate the process and 2 tonnes of sodium have been disposed. NOAH process is chosen in DESORA plant at RAPSODIE for the operation of the primary sodium disposal (37 tonnes).

NOAH process principle (figure 4) consists in injecting small quantities of sodium in a large water flow in a vessel. The sodium is quickly scattered in the water and the conversion of the sodium is very soft. The results of the conversion is hydrogen which is released in the atmosphere after several filtrations, and aqueous caustic soda which is sent to a liquid waste centre.

Caustic soda can be purified in cesium with resins at this step. This can avoid to purify the activated sodium in cesium with RVC filters of which the use is quite expensive.

The main interests of the NOAH process are :
- operation in one step
- good monitoring of the sodium quantity reacting at any time
- process developed at an industrial scale.

C.IV. ANALYSIS OF PARAMETERS OF THE SCENARIOS

Three parameters having an influence upon the choice of the scenarios are analysed hereafter :
- buffer sodium storage,
- transportation of sodium and soda,
- long term sodium storage.

Buffer sodium storage :

EFR (European Fast Reactor) plant is fitted out with seven sodium tanks. Their total capacity is sufficient to store all the primary sodium but four of them need biological shielding addings to take into account the radioactivity.
SPX plant is fitted out with six sodium tanks but their total capacity is insufficient to store all the primary sodium and three of them need biological shielding addings to take into account the radioactivity.
There is no problem to store the secondary sodium for the two plants.

Transportation of sodium and soda

Sodium transportation is expensive because heating and inert gas covering are necessary. But soda volume is four times larger after the conversion than the sodium volume.
Eventually, the sodium transportation cost has been assessed lower than the soda transportation cost per reactor plant.
The main transportation condition to fulfill, with regard to the regulations, is to have a dose rate under 10^{-4} Sv/h at 2 meters of the transport tank. Transported quantities per travel vary following the purification level and the storage decay. For example, for a total load of 21 tonnes per travel, there are 12 tonnes of sodium and 9 tonnes of biological shielding when the sodium has not been purified and has not been stored, and there are 19 tonnes of sodium and 2 tonnes of biological shielding when the sodium has been purified at 98 % in caesium and has been stored 5 years.

Long term storage :
Sodium can be stored for a transition period, waiting a reuse in FBR or an other solution.
Storage can allow to differ large costs for disposal and to decrease the sodium activity by time decay.
Storage time is the sole mean to decrease the sodium 22 activity.
But long term storage brings cost penalty if the sodium has to be finally disposed. Its decay effect is negligible if the cesium is not purified by carbon traps.

C.V. MAIN SCENARIOS DESCRIPTION

The possible scenarios for the sodium treatments, taking into account the previous work, are then analysed, either to reuse it, or to dispose it.
The scenarios can be separated in two groups :
- there is one or several FBR to fill up in sodium --> scenarios of sodium reuse
- there is no FBR to fill up in sodium --> scenarios of sodium disposal or sodium sale in industrial field when it is desactivated.

The possible scenarios are summarized in figure 5. The selected steps are : storage, purification, processing, final destination.

a) Primary sodium :

After reactor final shutdown, primary sodium can be disposed with the NOAH process or can be reused in nuclear or industrial field.
If the sodium has to be disposed, it can be converted in the reactor site and aqueous caustic soda has to be transported, or it can be converted in the liquid waste site after its transportation.
In each case, caesium and tritium purification has to be considered.

a1) Sodium reuse :
Several scenarios have been examined :
- reuse of sodium with activity below 10 Bq/g, in industrial field,
- reuse of non purified sodium in a new plant
- reuse of sodium purified at 98% and stored during 5 years, in a new plant
- reuse of non purified sodium but stored during 30 years, in a new plant
- reuse of sodium purified at 99% and stored during 5 years, in a new plant
- reuse of sodium with activity below 10 Bq/g, in a new plant
The new plant can be on the same site than the old one or in an other site.

Sodium reuse can bring two main advantages :
- cost saving :
If the sodium can be reused in new FBR, new sodium buying is avoided.
If the sodium can be reused in industrial field, it is sold to a customer.
In these two cases, no major waste storage cost has to be considered.
- time saving :
New sodium delivery can necessitate several months from the supplier. If the old and new FBR are on the same site, reusable sodium can be delivered in few days. If the old and new FBR are not on the same site, reusable sodium can be delivered in one month.

Sodium reuse in industrial field necessitates high purification means (division of the caesium and tritium content by 10 000) and long term storage (30 years due to the so-

dium 22 decay) to decrease the total activity below 10 Bq/g.
These conditions are difficult to reach. Industrial sodium price is also lower than the nuclear one. But the purification and storage cost can be covered by the sodium sale and that can avoid waste storage cost.

Sodium reuse in nuclear field with activity above 10 Bq/g implies specific biological shielding measures during the sodium drying of the old plant, transportation, filling up and testing of the new plant. The plant has to be put in controlled areas several months earlier, due to the filling up and hydraulic testing phases.
It is also possible to use sodium with activity below 10 Bq/g to avoid specific biological shielding measures.

a2) Sodium disposal :
Sodium cannot be disposed directly. It has to be converted in a stable element being able to be treated in liquid waste centres. The conversion of 2000 tonnes of sodium generates large volumes of aqueous caustic soda, about 8000 tonnes. This soda can be used to neutralize acid liquid wastes from reprocessing centres or can be treated directly as a waste.
Sodium disposal is the sole way if no new plant is expected or if sodium sale is not possible in industrial field.

The better cost balance has to be established between the plant capacity (cost of the plant) and the operation duration (cost of the operation). In the case of EFR, we have considered 2 years of operation for the disposal plant with a disposal capacity of 1000 t/y.

Several scenarios have been examined :
- disposal of no purified sodium on the reactor site and transport of purified soda to a treatment center,
- disposal of sodium purified at 98% on the reactor site and transport of no purified soda to a treatment center,
- transport of no purified sodium from the reactor site to a treatment center and disposal of the sodium,
- transport of sodium purified at 98% from the reactor site to a treatment center and disposal of the sodium.

The operation can be carried out in the old plant site or in the liquid waste centre. Transportation cost has to be considered following the purification level.
The disposal plant can be designed : either in several modules to be mobile between old sodium plants, or as a fixed plant on one site.

Sodium disposal operation is the most unfavourable economical way because :
- if there is a new plant to fill up, the total cost is the addition of the disposal cost and the new sodium cost,
- if there is no new plant, sodium reuse cost in industrial field is not upper than sodium disposal cost.

b) Secondary sodium :

Secondary sodium is contaminated only by tritium, which is a beta emitter. No biological shielding is necessary for the operators.
SPX secondary sodium activity will be about 2,5 10^3 Bq/g at the final shutdown.
EFR secondary sodium, which is continuously purified in operation, will have an activity bellow 10 Bq/g at the final shutdown.

b1) Secondary sodium reuse :

Several scenarios have been examined :
- reuse of not purified sodium in secondary loops
- reuse of purified sodium with activity below 10 Bq/g, in secondary loops
- reuse of purified sodium with activity below 10 Bq/g, in industrial field

Sodium can be easily reused in a new plant because no modification has to be carried out. If the sodium activity is above 10 Bq/g, controlled areas have to be foreseen earlier.
This reuse has the same interest than for the primary sodium one : cost saving and time schedule reduction. A purification, if it is necessary, is made with cold traps.
EFR secondary sodium can be reused directly without purification because its activity is below 10 Bq/g.

b2) Secondary sodium disposal :

Two scenarios have been examined :
- disposal of sodium purified at 98% on the reactor site and transport of soda to a treatment center,
- transport of sodium purified at 98% from the reactor site to a treatment center and disposal of the sodium.

Sodium disposal is the sole way if no new plant is expected or if sodium reuse is not possible in indutrial field.
Tritium purification has to be made in sodium to allow low tritium concentration in soda.
NOAH process has been also selected for the sodium conversion.
Secondary sodium disposal brings the same cost disvantages than the primary one.

C.VI. NEXT STEP

Next step will consist to carry out a cost assessment of the different scenarios. They will be compared together and classified. Proposed scenarios will be highlighted in relation to the main technical conditions.

References :

/1/ CCE - Gestion et stockage des déchets radioactifs - Traitement du sodium contaminé - Rapport semestriel N°1 - NOVA X 005 807 000
/2/ CCE - Community's research and development programme on radioactive waste management and storage - Annual Progress Report - EUR 14418 EN
/3/ CCE - Gestion et stockage des déchets radioactifs - Traitement du sodium contaminé - Rapport semestriel N°2 - NOVA X 006 067 000
/4/ CCE - Gestion et stockage des déchets radioactifs - Traitement du sodium contaminé - Rapport semestriel N°3 - NOVA X 006 123 000

Figure 1 : Main Milestones

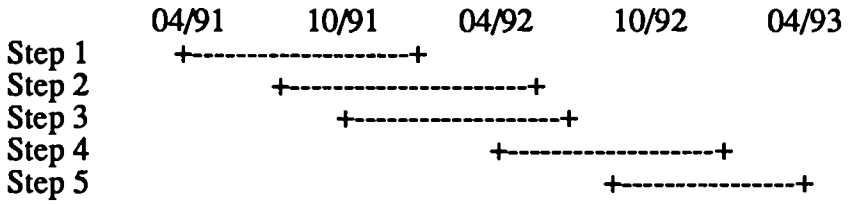


Figure 2 : sodium activation and contamination levels

		PRIMARY SODIUM		SECONDARY SODIUM	
Radio-element	Period	Activity in Bq/kg	Total activity in Bq	Activity in Bq/kg	Total activity in Bq
Na 22 (β^+, gamma)	2,62 years	$1{,}33.10^7$	$4{,}4.10^{13}$	-	-
Cs 134 (β^-, gamma)	2,1 years	$1{,}25.10^7$	$4{,}1.10^{13}$	-	-
Cs 137 (β^-, gamma)	30 years	$8{,}95.10^7$	$2{,}9.10^{14}$	-	-
Tritium (β^+)	12,3 years	$3{,}35.10^7$	$1{,}1.10^{14}$	$2{,}5.10^6$	$3{,}2.10^{12}$
TOTAL		15.10^7	$4{,}9.10^{14}$	$2{,}5.10^6$	$3{,}2.10^{12}$

EFR secondary sodium activity will be under 10 Bq/g in tritium because it will be continuously purified during operation.

Figure 3 : cold trap

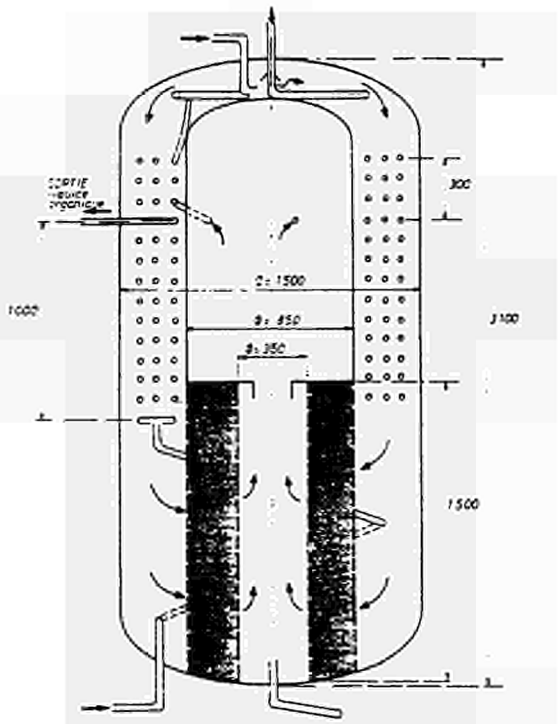


Figure 4 : sodium disposal NOAH process

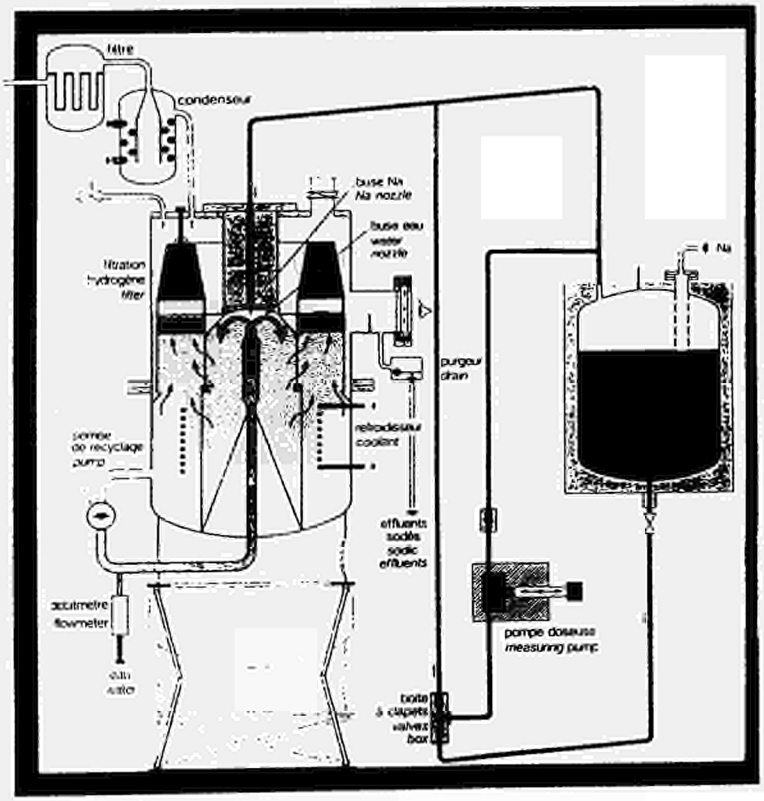
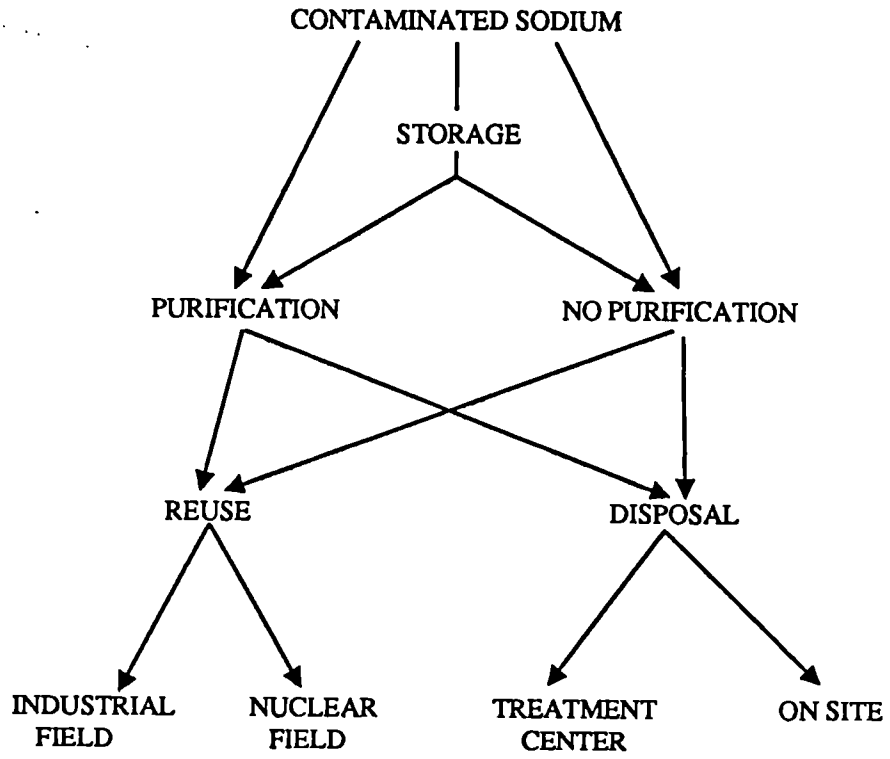


Figure 5 : scenario ways



Title	Studies of Minimising Transport of Spent Fuel
Contractor	BAeSEMA
Contract N°	FI2W-CT90-0067
Duration of contract	September 1991 to February 1993
Period covered	January-December 1992
Project leader	Jonathan B. Taylor

A. OBJECTIVES AND SCOPE

The aim of the work is to establish a methodology and software tools for examining the implications for cost, environmental impact and safety of minimising the transport of spent fuel using multi-attribute utility analysis and linear programming techniques.

The objectives are therefore :

- to define two realistic, illustrative "base case" scenarios for the management of spent fuel and a framework for analysing their cost, transport requirements and environmental impact using an enhanced version of the DISPOSALS model
- to define the data needed for analyses, and collect data for illustrative cases
- to enhance, test and document the DISPOSALS model
- to carry out illustrative analyses and report on the results

B. WORK PROGRAMME

1. Task 1 : Formulation of the Problem

The costs and environmental impacts which need to be taken into account will be identified and a high level design document setting out the structure of the analytic model will be prepared.

2. Task 2 : Data requirements

A report describing the model's data requirements will be produced.

3. Task 3 : Data Collection

The best available data meeting the requirements identified in Task 2 will be collected and a summary report produced.

4. Task 4 : Model Development

Building upon the previous DISPOSALS work, a revised model will be developed to enable the illustrative analysis to be carried out.

5. Task 5 : Illustrative Analysis

Using the revised model an illustrative study will be carried out based on the scenarios developed under Task 1.

C. PROGRESS OF WORK AND OBTAINED RESULTS

The status of progress has not been forwarded to the Commission for 1993.

Title:	Study of the retrievability of radioactive waste from a deep underground disposal facility
Contractor:	ECN
Contract no:	FI2W-CT92-0119
Duration of contract:	July 1992 to July 1993
Period covered:	July 1992 to December 1992
Project leader:	J. Prij

A. *OBJECTIVES AND SCOPE*

Retrievability of radioactive waste emplaced in a deep repository in a geological formation has received increasing attention during recent years. Arguments in favour of keeping waste retrievable are that more suitable sites might be found, that technological advances and/or reduced fission material availability would give an incentive for extracting valuable materials from the waste, or that an economically feasible way could be found to transmute long-lived radionuclides to short-lived ones.

The Member States of the European Community have not, up to date, included provisions for retrievability in their regulatory framework or in recommendations for disposal of waste. Other countries, like the United States, ask for an access to conditioned waste to be guaranteed for some decades.

Two conditions govern the option to retrieve radioactive waste packages from a deep repository:

- the packages should not be damaged (by pressure from the host rock, or due to corrosion, or other processes)
- the position of the package and the nuclide inventory must be known, and this knowledge has to be kept alive.

As those two conditions can be met for a few centuries at the best, provisions for retrievability makes sense only for up to 300 years (a widely used design limit for corrosion resistance of over-packs). During these few centuries, retrievability may be realised by keeping the access to the waste packages open, by maintaining in operational condition the access shafts and the main galleries. A second possibility is to dispose the waste in a suitable overpack and abandon the repository after backfilling, closing and sealing. In this case the waste will have to be re-mined from the surface. Although this re-mining will be very costly it is obvious that there will be a point in time, where the cost of keeping the repository in operating condition will be higher than those of re-mining from the surface to reach the waste packages in a closed repository. By way of illustration this break-even point is represented in Figure 1.

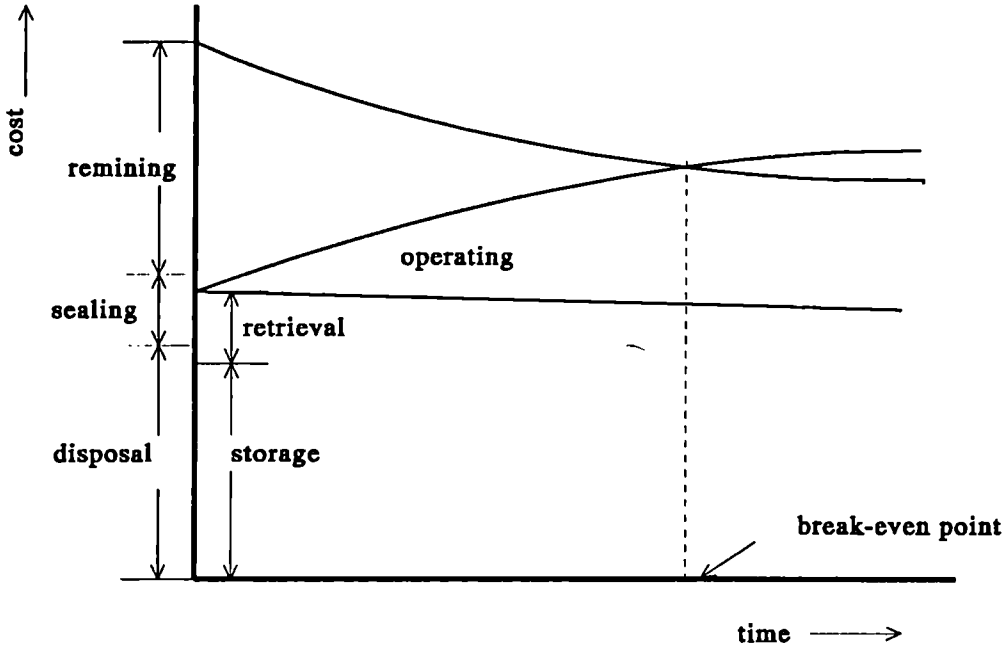


Figure 1 *Cost comparison for retrievable storage and re-mining after final disposal.*

The objective of this study is to collect existing data on retrievability of heat-generating long-lived waste and to produce an un-biased set of data on implications in terms of cost when deciding adoption of a retrievability strategy.

B. WORK PROGRAMME

Present state of the retrievability option

Existing information on retrievability of radioactive waste will be collected in EC-Member States and other countries having a nuclear energy production programme. This review will include regulations, recommendations and even opinions as long as they have been expressed in open literature or in open working documents of national or international bodies. Attention will be paid to aspects of non-proliferation in the case of direct disposal of spent fuel being declared as waste.

Overview of expected modifications as a consequence of opting for retrievability

This overview will examine aspects concerning design and fabrication of waste packages, design of the repository, operation and maintenance of the repository and associated equipment, surveillance and control of the installation, and maintaining a documentation system when changing from a final disposal concept to retrievability.
For these factors an estimation of additional costs and occupational exposure will be attempted. Evaluations with regard to radiation protection and long term safety to the environment will be made without carrying out detailed performance assessment calculations.

Detailed evaluations for a reference disposal scenario

A detailed evaluation under realistic conditions will be made in performing a comparison between the costs of retrieval of the waste from a suitable deep underground repository (including the annual costs of keeping the repository open) and the costs of re-mining the waste from a final deep underground repository (including the costs of closing and sealing).

The assumptions and boundary conditions are:

- The study is restricted to HAW (high level radioactive waste). The quantity of HAW is based on 20 GW installed nuclear power (in standard LWR NPP's) operating for a period of 30 years (scenario and data as in studies /1/ and /2/).
- Two types of waste management strategies will be considered:
  . direct disposal of all spent fuel
  . disposal of the HAW from reprocessing all the spent fuel
- One loading sequence of the waste into the repository will be considered.
- The disposal concepts will be chosen based on current state of the mining and disposal techniques.
- Three types of host rock will be considered: clay, granite and rock salt.
- One retrieving and one re-mining strategy will be selected.

The activities to be carried out are:

- select feasible final disposal and retrievable storage concepts for each of the three host rock formations,
- assess the feasibility of the selected options: concise safety evaluations will be performed with regard to radiation protection and long term safety to the environment,
- select a feasible retrieval and re-mining concept for each of the three host rock formations,
- determine the total costs of each of the options selected:
  . for the retrievable options the total costs are the annual costs to guarantee the retrievability, and the costs of the retrieval
  . for the final disposal concepts selected the total costs are the costs of closing and the costs of re-mining.
- evaluate the costs in present day value and determine for each of the host rocks the break-even point at which re-mining is more favourable from an economical point of view. This evaluation will be based on the present-day society and present day estimates of the economical parameters such as interest rates.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

A literature search has been performed trough the regular documentation systems on existing literature on the topic of retrievable storage of radioactive waste.
A general inventory has been made of the consequences of retrievable storage and a start has been made with the conceptual planning for storage and disposal facilities in the three host rocks mentioned.

Progress and results

Very little has been published on the topic of retrievability for EC and other relevant European countries and therefore other, more informal, sources of information will have to be used in the next part of the inventory.

The design of the repository for both retrievable and re-minable storage will be based in the concept of storage in galleries which will be backfilled with a suitable medium. A general lay-out of the repository is represented in Figure 2.

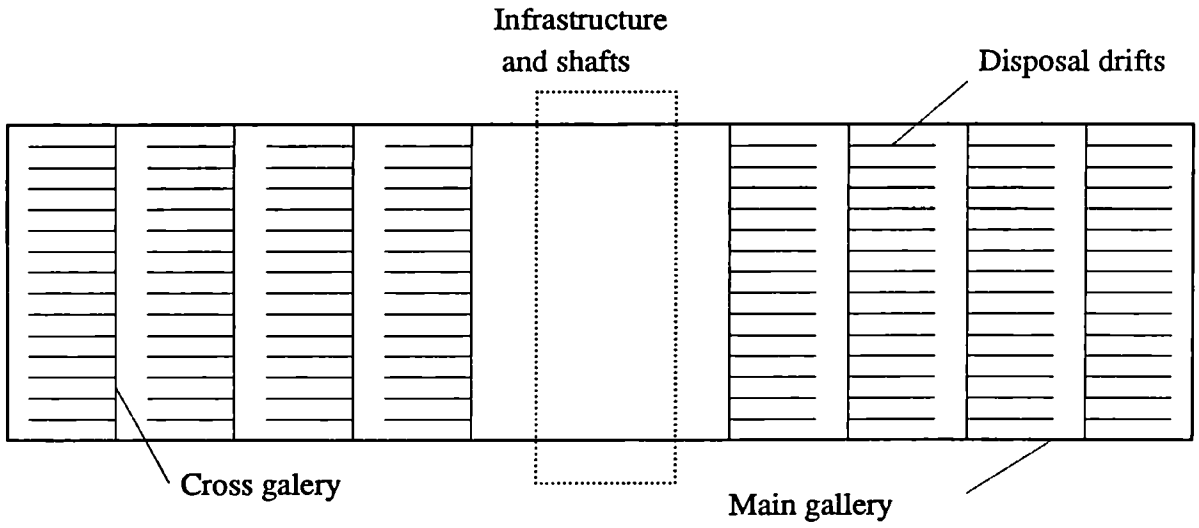


Figure 2 *Lay-out of the mine building.*

In this way the decay heat will be fed into the surrounding rock and not primarily into the ventilation system. This concept implies that an overpack is required which withstands the rock pressure.
For the current study it has been assumed that a Pollux container satisfies the requirements for mechanical integrity and corrosion resistance. An additional reason for the use of a heavy

overpack is the radiation protection during the storage and retrieval operation.
The major problem arising from the disposal concept chosen is that the containers have to be retrieved or re-mined from the surrounding medium under high temperature conditions. Temperature calculations will have to show if artificial cooling is sufficient to create a workable environment or if a form of remote control has to be used.

References

/1/ J. Malherbe: Management of radioactive waste from reprocessing including disposal aspects, EUR-13116 (1991), Office for Official Publications of the EC, Luxembourg.

/2/ P. Ashton et al: Analysis of scenarios for the direct disposal of spent nuclear fuel-disposal conditions as expected in Germany, EUR-12953 (1990), Office for Official Publications of the EC, Luxembourg.

Title : **Assessment and proposal for activity limits for release of very low-level radioactive waste to landfills**

Contractor : CEA/IPSN, France, and ONDRAF/NIRAS, Belgium
Contract No. : FI2W/CT-90/0060
Duration of contract : April 91 - March 93
Period covered : January 92 - December 92
Project leader: P. Guetat (CEA/IPSN, coordinator), L. Baekelandt (ONDRAF/NIRAS)

A. OBJECTIVES AND SCOPE

In the frame of studies dealing with exemption of particular streams from regulatory control, the project aims to establish acceptance criteria for municipal and industrial landfill for unconditional exemption.

Correspondances between levels of exposure and levels of radioactivity will be established.

From this work, it will be possible to derive specific and surface activity levels corresponding to acceptance criteria for landfill for the two types of exemption.

B. WORK PROGRAMME

Three steps have been defined :

Phase 1, F and B : Analysis of landfill disposal practices of industrial and municipal waste.

A particular attention is paid to the regulatory context and on working conditions encountered in the different installations.

Evaluation of the waste streams, at the level of some to hundred $Bq.g^{-1}$ for the most radiotoxic nuclides.

Phase 2, F : Development of a radioprotection code CERISE, to establish the relations between exposure and radioactivity of waste, including a data bank for dose conversion factors.

Evaluation of the exposures resulting of the water pathway using the code GEOLE (geosphere) and the code ABRICOT (biosphere).

Separate calculations will be pursued for workers and public.

Phase 3, F and B : Establishment of the correspondance between exposure and specific and surface activities of the wastes.

Proposal of levels of radioactivities for the waste acceptance in the different types of landfill and for different dose criteria.

Final report.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

CEA

Phase 1 and 2 are finished now.

Informations and data concerning low level radioactive waste streams produced in different nuclear facilities were collected.

Phase 3 is well in advance. Evaluation of worker and public exposures resulting of waste treatments has been already pursued starting with the evaluations of basic parameters.

Dust measurements are being made on landfill sites.

ONDRAF

Phase 1 is almost completed. The description of the legal context (of regional concern) will be updated in function of the most recent modifications published in the official journal.

Dose calculations, as foreseen in phase 3, have been performed, using the code CERISE, and based on parameters derived from the actual management of landfills for industrial (hazardous and inert) waste.

The water pathway, using the code GEOLE, will be evaluated within the next weeks.

Progress and results

CEA

Scenarios of exposures were defined after visits of landfills. FIGURE 1 shows the selected scenarios.

The first radiological impacts for workers and members of the public have been performed with the code CERISE for these scenarios including different pahways : external irradiation, contamination, inhalation and ingestion, /2/. This code is modified to be in a more user friendly form.

For the water pathway, the code ABRICOT and the code GEOLE are used.

Three types of landfills are examined : large and small landfills for municipal waste (CET 2a et CET 2B) and one for industrial waste (CET 1).

Measurements of dust concentrations on site and in the vicinity of site are presently performed to specify the choice of the values used in inhalation scenarios. While waiting, preliminary results are given in TABLE I to III.

The case of a landfill including a cell only filled with low level radioactive waste will be examined (specific landfill).

ONDRAF

The study was performed on the same base as in France, with the following remarks :

- two types of landfills were selected :
  - class 1 landfill for hazardous industrial waste (100,000 tonnes/year)
  - class 3 landfill for inert industrial waste (33,000 tonnes/year)
- two campaigns of measurements of dust on a class 1 site were performed during the year 1992.
- the transport pathway was also considered.

The various scenarios studied are summarized in FIGURE 2.

The maximal doses resulting of exposures to waste of unit specific activity (1 Bq/g) for workers and population are given in TABLE IV.

For both countries, the next step is the final evaluation of the activities derived from the individual dose criteria to propose the radioactivity levels for the waste acceptance in the different types of landfills, and the writing of the final common report.

REFERENCES

/1/ Presentation of the objectives, methodology and the project progress status in Brussels (October 1991).

/2/ GUETAT P., RENAUD P., SANTUCCI P., ASSELINEAU J.M., "CERISE : Code d'Evaluations Radiologiques Individuelles pour des Scénarios en Entreprises et dans l'Environnement." CEA/IPSN Report SERGD 92/03 (1992), for advance report of this CEC contract.

TABLE I (FRANCE)

Maximal individual dose for workers in landfill and for 1 Bq.g^{-1} (in Sv.y^{-1}).
(e.i. : external irradiation e.c. : external contamination fire : trench fire inh. : inhalation)

Radionuclides	CET 1 (50,000 tonnes/year)		CET 2a (150,000 tonnes/year)		CET 2b (15,000 tonnes/year)	
^{3}H	1,37.10^{-12}	(ing.,inh.)	1,72.10^{-11}	(fire)	5,46.10^{-11}	(fire)
^{14}C	4,50.10^{-9}	(inh.	4,44.10^{-10}	(fire)	1,40.10^{-9}	(fire)
^{32}P	3,35.10^{-9}	(e.i.)	1,57.10^{-9}	(e.i.)	4,57.10^{-9}	(e.i.)
^{35}S	3,55.10^{-11}	(ing.)	8,25.10^{-11}	(fire)	3,22.10^{-10}	(fire)
^{36}Cl	1,64.10^{-9}	(e.i.)	6,15.10^{-11}	(fire)	1,90.10^{-8}	(fire)
^{54}Mn	6,06.10^{-6}	(e.i.)	2,18.10^{-6}	(e.i.)	5,45.10^{-6}	(e.i.)
^{55}Fe	3,54.10^{-11}	(inh.)	1,27.10^{-11}	(inh.)	1,16.10^{-10}	(inh.)
^{60}Co	1,99.10^{-5}	(e.i.)	6,64.10^{-6}	(e.i.)	1,66.10^{-5}	(e.i.)
^{59}Ni	7,51.10^{-11}	(e.i.)	2,66.10^{-11}	(e.i.)	1,43.10^{-10}	(inh.)
^{63}Ni	3,38.10^{-11}	(inh.)	1,22.10^{-11}	(inh.)	1,15.10^{-10}	(inh.)
$^{90}Sr+$	1,08.10^{-8}	(e.i.)	3,54.10^{-9}	(e.i.)	1,51.10^{-8}	(e.i.,inh.)
^{94}Nb	1,22.10^{-5}	(e.i.)	4,06.10^{-6}	(e.i.)	1,05.10^{-5}	(e.i.)
^{99m}Tc	1,20.10^{-9}	(e.i.)	2,58.10^{-8}	(e.i.)	1,60.10^{-8}	(e.i.)
^{99}Tc	1,28.10^{-10}	(inh.)	7,15.10^{-11}	(inh.)	4,92.10^{-10}	(inh.)
$^{106}Ru+$	1,52.10^{-6}	(e.i.)	5,20.10^{-7}	(e.i.)	1,31.10^{-6}	(e.i.)
$^{108m}Ag+$	1,31.10^{-5}	(e.i.)	4,38.10^{-6}	(e.i.)	1,10.10^{-5}	(e.i.)
$^{110m}Ag+$	2,12.10^{-5}	(e.i.)	7,10.10^{-6}	(e.i.)	1,77.10^{-5}	(e.i.)
$^{125}Sb+$	2,99.10^{-6}	(e.i.)	1,00.10^{-6}	(e.i.)	2,50.10^{-6}	(e.i.)
^{125}I	8,10.10^{-9}	(e.i.)	3,58.10^{-9}	(e.i.)	1,16.10^{-8}	(e.i.)
^{129}I	1,14.10^{-8}	(e.i.)	9,36.10^{-9}	(fire.)	3,97.10^{-8}	(fire)
^{131}I	2,18.10^{-6}	(e.i.)	8,28.10^{-7}	(e.i.)	1,99.10^{-6}	(e.i.)
^{134}Cs	1,19.10^{-5}	(e.i.)	3,98.10^{-6}	(e.i.)	9,97.10^{-6}	(e.i.)
$^{137}Cs+$	4,21.10^{-6}	(e.i.)	1,40.10^{-6}	(e.i.)	3,52.10^{-6}	(e.i.)
^{147}Pm	4,53.10^{-10}	(inh.)	1,81.10^{-10}	(inh.)	1,56.10^{-9}	(inh.)
^{151}Sm	2,22.10^{-10}	(inh.)	7,85.10^{-11}	(inh.)	7,51.10^{-10}	(inh.)
^{152}Eu	1,08.10^{-5}	(e.i.)	3,60.10^{-6}	(e.i.)	9,01.10^{-6}	(e.i.)
^{154}Eu	9,46.10^{-6}	(e.i.)	3,16.10^{-6}	(e.i.)	7,90.10^{-6}	(e.i.)
$^{226}Ra+$	2,05.10^{-5}	(e.i.)	6,84.10^{-6}	(e.i.)	1,73.10^{-5}	(e.i.)
$^{235}U+$	2,15.10^{-6}	(inh.)	7,44.10^{-7}	(inh.)	5,50.10^{-6}	(inh.)
$^{238}U+$	1,60.10^{-6}	(inh.)	5,08.10^{-7}	(inh.)	5,02.10^{-6}	(inh.)
$^{237}Np+$	4,18.10^{-6}	(inh.)	1,45.10^{-6}	(inh.)	1,09.10^{-5}	(inh.)
$^{238}Pu+$	2,89.10^{-6}	(inh.)	1,02.10^{-6}	(inh.)	9,82.10^{-6}	(inh.)
$^{239}Pu+$	2,89.10^{-6}	(inh.)	1,02.10^{-6}	(inh.)	9,82.10^{-6}	(inh.)
$^{240}Pu+$	2,89.10^{-6}	(inh.)	1,02.10^{-6}	(inh.)	9,82.10^{-6}	(inh.)
$^{241}Pu+$	4,35.10^{-8}	(inh.)	1,53.10^{-8}	(inh.)	1,47.10^{-7}	(inh.)
^{241}Am	2,92.10^{-6}	(inh.)	1,03.10^{-6}	(inh.)	9,85.10^{-6}	(inh.)
^{244}Cm	1,74.10^{-6}	(inh.)	6,12.10^{-7}	(inh.)	5,89.10^{-7}	(inh.)

TABLE II (FRANCE)

Maximal individual dose in a small ordinary landfill (CET 2b 15,000 tonnes/year) and for 1 Bq.g^{-1} (in Sv.y^{-1}).

Radionuclides	WORKER (Sv.y^{-1})	PUBLIC non aquatic pathway (Sv.y^{-1})	PUBLIC aquatic pathway (Sv.y^{-1})
^{3}H	5,46.10^{-11}	7,77.10^{-10}	2,29.10^{-9}
^{14}C	1,40.10^{-9}	9,39.10^{-9}	1,29.10^{-9}
^{32}P	4,57.10^{-9}	1,13.10^{-10}	-
^{35}S	3,22.10^{-10}	1,43.10^{-11}	-
^{36}Cl	1,90.10^{-8}	3,03.10^{-8}	1,81.10^{-7}
^{54}Mn	5,45.10^{-6}	3,54.10^{-10}	-
^{55}Fe	1,16.10^{-10}	4,47.10^{-12}	-
^{60}Co	1,66.10^{-5}	1,30.10^{-6}	3,86.10^{-13}
^{59}Ni	1,43.10^{-10}	8,83.10^{-11}	1,93.10^{-10}
^{63}Ni	1,15.10^{-10}	2,28.10^{-10}	1,06.10^{-10}
$^{90}Sr+$	1,51.10^{-8}	7,76.10^{-7}	5,71.10^{-9}
^{94}Nb	1,05.10^{-5}	3,14.10^{-6}	2,65.10^{-7}
^{99m}Tc	1,60.10^{-8}	5,65.10^{-16}	-
^{99}Tc	4,92.10^{-10}	2,81.10^{-7}	9,95.10^{-6}
$^{106}Ru+$	1,31.10^{-6}	9,28.10^{-10}	-
^{108m}Ag	1,10.10^{-5}	3,25.10^{-6}	2,72.10^{-9}
^{110m}Ag	1,77.10^{-5}	1,39.10^{-10}	-
$^{125}Sb+$	2,50.10^{-6}	5,57.10^{-8}	-
^{125}I	1,16.10^{-6}	8,35.10^{-10}	-
^{129}I	3,97.10^{-8}	7,83.10^{-8}	3,42.10^{-8}
^{131}I	1,99.10^{-6}	9,99.10^{-10}	-
^{134}Cs	9,97.10^{-6}	8,38.10^{-8}	-
$^{137}Cs+$	3,52.10^{-6}	8,66.10^{-7}	5,27.10^{-21}
^{147}Pm	1,56.10^{-9}	8,04.10^{-12}	-
^{151}Sm	7,51.10^{-10}	3,07.10^{-11}	-
^{152}Eu	9,01.10^{-6}	1,63.10^{-6}	-
^{154}Eu	7,90.10^{-6}	1,05.10^{-6}	-
$^{226}Ra+$	1,73.10^{-5}	5,37.10^{-6}	4,23.10^{-8}
$^{235}U+$	5,50.10^{-6}	2,67.10^{-7}	3,48.10^{-8}
$^{238}U+$	5,02.10^{-6}	1,40.10^{-7}	3,02.10^{-8}
$^{237}Np+$	1,09.10^{-5}	1,27.10^{-6}	1,01.10^{-6}
$^{238}Pu+$	9,82.10^{-6}	1,65.10^{-7}	-
$^{239}Pu+$	9,82.10^{-6}	2,06.10^{-7}	9,01.10^{-11}
$^{240}Pu+$	9,82.10^{-6}	2,05.10^{-7}	7,31.10^{-13}
$^{241}Pu+$	1,47.10^{-7}	4,33.10^{-9}	-
^{241}Am	9,85.10^{-6}	1,44.10^{-7}	-
^{244}Cm	5,89.10^{-7}	1,72.10^{-7}	-

TABLE III (FRANCE)

Maximal individual dose in an industrial waste landfill (CET 1 50 000 tons/year) for 1 Bq.g^{-1} and for 1 Bq.cm^{-2} (in Sv.y^{-1}).

Radionuclides	Maximal individual dose for 1 Bq.g^{-1} (Sv.y^{-1})	Maximal individual dose for 1 Bq.cm^{-2} (Sv.y^{-1})
^{3}H	$1,37.10^{-12}$	$3,60.10^{-11}$
^{14}C	$4,50.10^{-9}$	$2,52.10^{-9}$
^{32}P	$3,35.10^{-9}$	$6,08.10^{-8}$
^{35}S	$3,55.10^{-11}$	$2,11.10^{-9}$
^{36}Cl	$1,64.10^{-9}$	$1,28.10^{-8}$
^{54}Mn	$6,06.10^{-6}$	$4,75.10^{-7}$
^{55}Fe	$3,54.10^{-11}$	$5,82.10^{-10}$
^{60}Co	$1,99.10^{-5}$	$1,30.10^{-6}$
^{59}Ni	$7,51.10^{-11}$	$7,24.10^{-10}$
^{63}Ni	$3,38.10^{-11}$	$3,93.10^{-10}$
$^{90}Sr+$	$1,08.10^{-8}$	$9,98.10^{-8}$
^{94}Nb	$1,22.10^{-5}$	$9,05.10^{-7}$
^{99m}Tc	$1,20.10^{-9}$	$2,40.10^{-10}$
^{99}Tc	$1,28.10^{-10}$	$4,13.10^{-9}$
$^{106}Ru+$	$1,52.10^{-6}$	$2,35.10^{-7}$
$^{108m}Ag+$	$1,31.10^{-5}$	$9,45.10^{-7}$
$^{110m}Ag+$	$2,12.10^{-5}$	$1,51.10^{-6}$
$^{125}Sb+$	$2,99.10^{-6}$	$2,57.10^{-7}$
^{125}I	$8,10.10^{-9}$	$4,91.10^{-8}$
^{129}I	$1,14.10^{-8}$	$1,97.10^{-7}$
^{131}I	$2,18.10^{-6}$	$2,32.10^{-7}$
^{134}Cs	$1,19.10^{-5}$	$9,29.10^{-7}$
$^{137}Cs+$	$4,21.10^{-6}$	$3,73.10^{-7}$
^{147}Pm	$4,53.10^{-10}$	$2,98.10^{-9}$
^{151}Sm	$2,22.10^{-10}$	$4,14.10^{-10}$
^{152}Eu	$1,08.10^{-5}$	$6,38.10^{-7}$
^{154}Eu	$9,46.10^{-6}$	$7,00.10^{-7}$
$^{226}Ra+$	$2,05.10^{-5}$	$1,41.10^{-6}$
$^{235}U+$	$2,15.10^{-6}$	$1,64.10^{-7}$
$^{238}U+$	$1,60.10^{-6}$	$1,42.10^{-7}$
$^{237}Np+$	$4,18.10^{-6}$	$1,36.10^{-6}$
$^{238}Pu+$	$2,89.10^{-6}$	$9,01.10^{-7}$
$^{239}Pu+$	$2,89.10^{-6}$	$9,00.10^{-7}$
$^{240}Pu+$	$2,89.10^{-6}$	$9,01.10^{-7}$
$^{241}Pu+$	$4,35.10^{-8}$	$1,80.10^{-8}$
^{241}Am	$2,92.10^{-6}$	$1,22.10^{-6}$
^{244}Cm	$1,74.10^{-6}$	$6,00.10^{-7}$

TABLE IV (BELGIUM)

Maximal individual dose for 1 Bq.g^{-1} (in Sv.y^{-1}).

Radionuclides	Class 1 (100,00 tonnes)		Class 3 (33,000 tonnes)	
	Workers	Population	Workers	Population
^{3}H	8,28.10^{-12}	1,22.10^{-11}	2,61.10^{-12}	4,08.10^{-12}
^{14}C	3,68.10^{-9}	1,40.10^{-9}	1,18.10^{-9}	4,67.10^{-10}
^{32}P	2,63.10^{-8}	0,00	6,44.10^{-9}	0,00
^{35}S	3,58.10^{-9}	0,00	1,14.10^{-9}	0,00
^{36}Cl	1,61.10^{-8}	5,30.10^{-10}	4,65.10^{-9}	1,77.10^{-10}
^{54}Mn	1,06.10^{-5}	7,23.10^{-25}	7,95.10^{-6}	2,41.10^{-25}
^{55}Fe	2,81.10^{-10}	2,18.10^{-17}	8,88.10^{-11}	7,26.10^{-18}
^{60}Co	3,23.10^{-5}	1,66.10^{-9}	2,42.10^{-5}	5,55.10^{-10}
^{59}Ni	8,41.10^{-10}	1,62.10^{-11}	2,51.10^{-10}	5,41.10^{-12}
^{63}Ni	1,67.10^{-10}	2,60.10^{-11}	5,22.10^{-11}	8,66.10^{-12}
$^{90}Sr+$	5,88.10^{-8}	4,37.10^{-8}	1,21.10^{-8}	1,46.10^{-8}
^{94}Nb	1,97.10^{-5}	7,75.10^{-7}	1,48.10^{-5}	2,58.10^{-7}
^{99m}Tc	3,12.10^{-8}	0,00	2,34.10^{-8}	0,00
^{99}Tc	6,60.10^{-9}	4,21.10^{-8}	2,11.10^{-9}	1,40.10^{-8}
$^{106}Ru+$	2,45.10^{-6}	1,31.10^{-22}	1,84.10^{-6}	4,37.10^{-23}
$^{108m}Ag+$	2,13.10^{-5}	6,46.10^{-7}	1,60.10^{-5}	2,15.10^{-7}
$^{110m}Ag+$	3,45.10^{-5}	8,53.10^{-29}	2,59.10^{-5}	2,84.10^{-29}
$^{125}Sb+$	4,86.10^{-6}	5,96.10^{-13}	3,65.10^{-6}	1,99.10^{-13}
^{125}I	1,92.10^{-8}	0,00	9,53.10^{-9}	0,00
^{129}I	5,22.10^{-8}	1,20.10^{-8}	1,40.10^{-8}	4,00.10^{-9}
^{131}I	3,85.10^{-6}	0,00	2,89.10^{-6}	0,00
^{134}Cs	1,94.10^{-5}	2,11.10^{-14}	1,45.10^{-5}	7,04.10^{-15}
$^{137}Cs+$	6,83.10^{-6}	8,51.10^{-8}	5,12.10^{-6}	2,84.10^{-8}
^{147}Pm	5,31.10^{-9}	4,53.10^{-17}	1,68.10^{-9}	1,51.10^{-17}
^{151}Sm	4,25.10^{-10}	6,25.10^{-12}	3,57.10^{-10}	2,08.10^{-12}
^{152}Eu	1,75.10^{-5}	5,15.10^{-8}	1,31.10^{-5}	1,72.10^{-8}
^{154}Eu	1,54.10^{-5}	1,03.10^{-8}	1,15.10^{-5}	3,42.10^{-9}
$^{226}Ra+$	3,33.10^{-5}	1,33.10^{-6}	2,50.10^{-5}	4,42.10^{-7}
$^{235}U+$	3,97.10^{-6}	9,30.10^{-8}	3,23.10^{-6}	3,10.10^{-8}
$^{238}U+$	3,08.10^{-6}	5,86.10^{-8}	2,56.10^{-6}	1,95.10^{-8}
$^{237}Np+$	7,74.10^{-6}	3,05.10^{-7}	6,31.10^{-6}	1,02.10^{-7}
$^{238}Pu+$	5,66.10^{-6}	5,84.10^{-8}	4,75.10^{-6}	1,95.10^{-8}
$^{239}Pu+$	5,66.10^{-6}	9,08.10^{-8}	4,75.10^{-6}	3,03.10^{-8}
$^{240}Pu+$	5,66.10^{-6}	9,04.10^{-8}	4,75.10^{-6}	3,01.10^{-8}
$^{241}Pu+$	8,49.10^{-8}	2,51.10^{-9}	7,12.10^{-8}	8,38.10^{-10}
^{241}Am	5,70.10^{-6}	7,65.10^{-8}	4,78.10^{-6}	2,55.10^{-8}
^{244}Cm	3,39.10^{-6}	1,10.10^{-8}	2,85.10^{-6}	3,66.10^{-9}

FIGURE 1.

Shematic description of landfill scenarios for France.

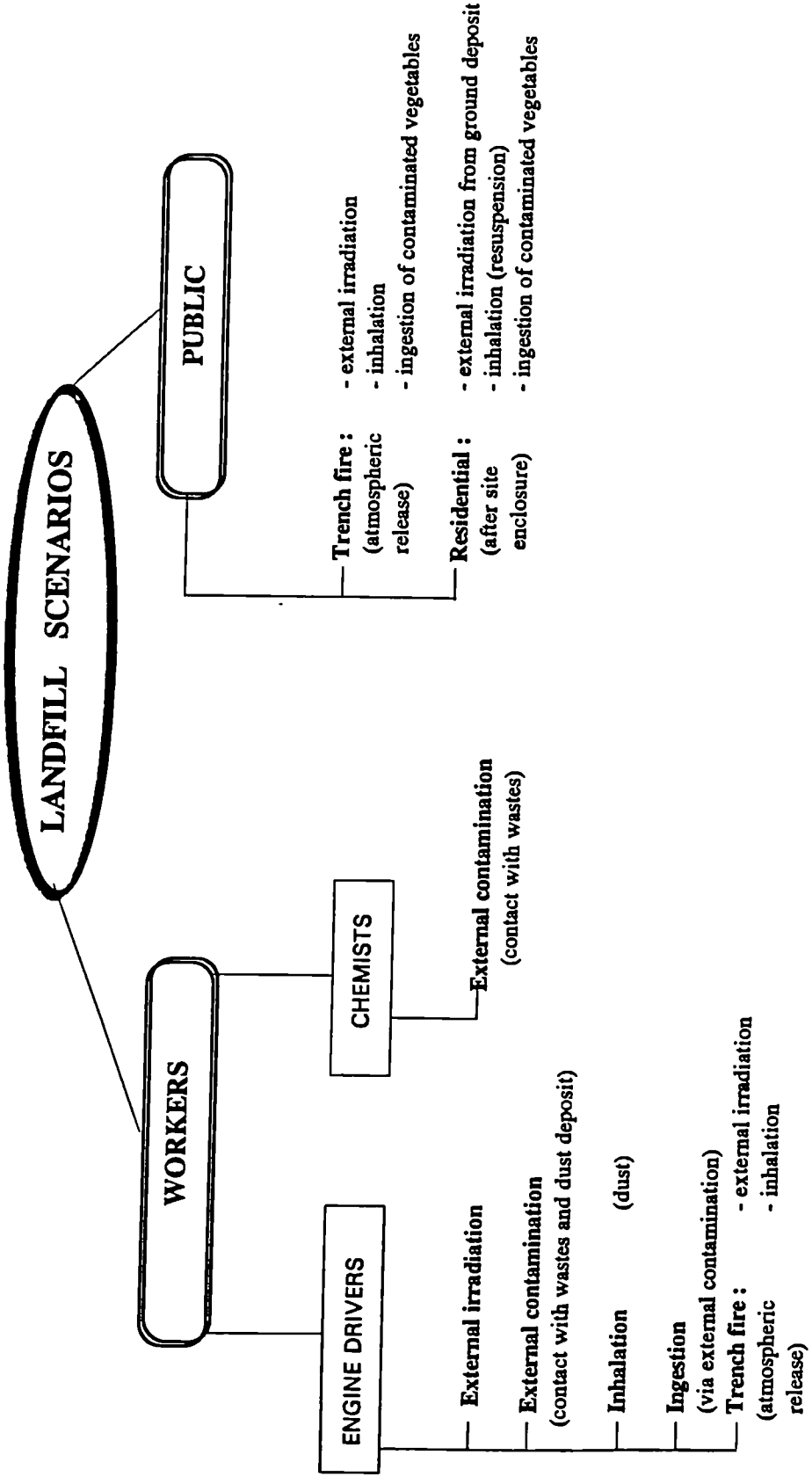
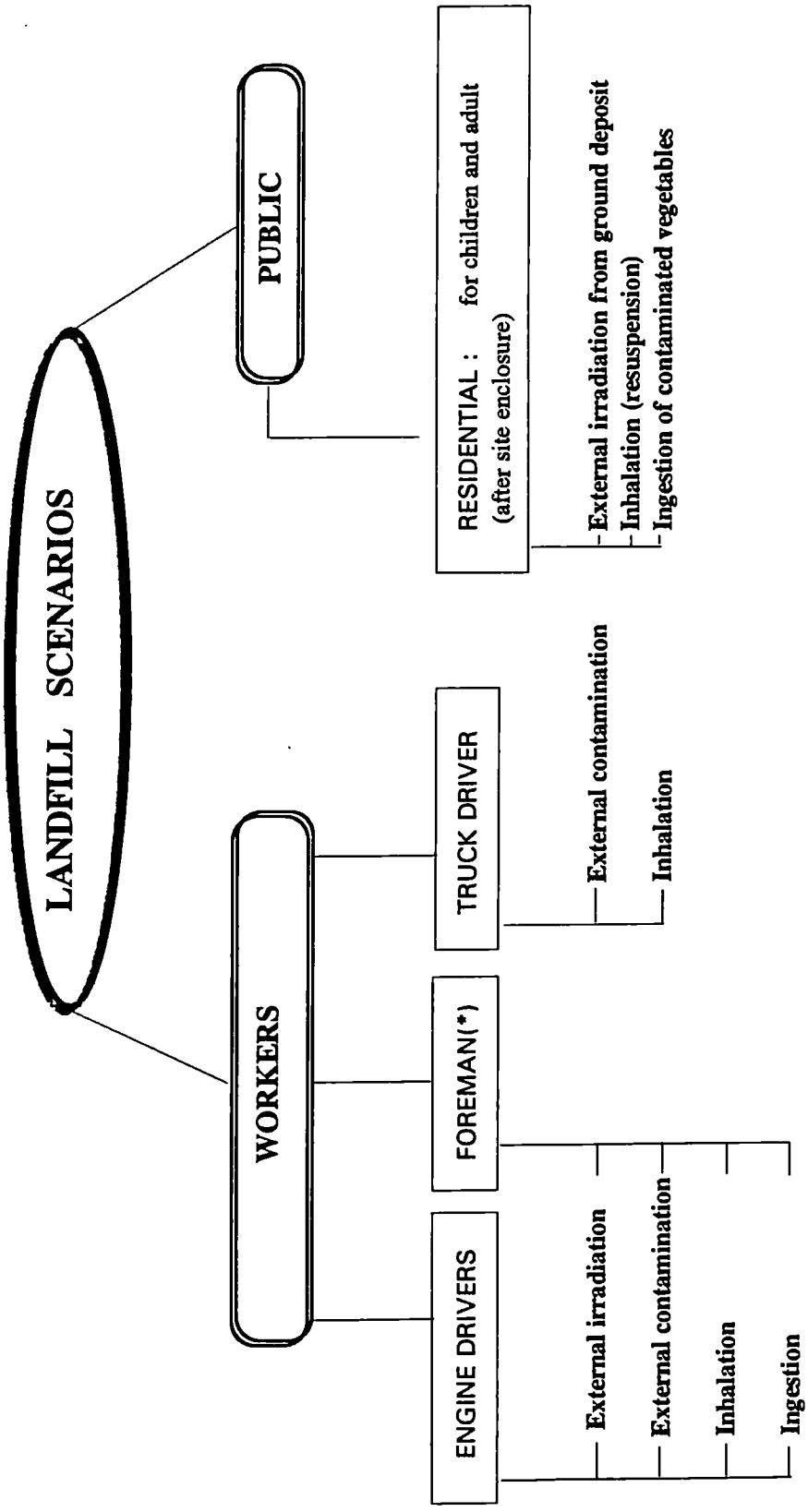


FIGURE 2.

Shematic description of landfill scenarios for Belgium.



(*) not for class 3 landfill

Title	: DEFINITION OF REFERENCE LEVEL FOR EXEMPTION OF WASTES SUITABLE FOR INCINERATION
Contractors	: CEA, IPSN/CEN-FAR, France and Empresarios Agrupados, Madrid, Spain
Contract n°	: FI2W-CT90-0066
Duration of contract	: 1 January 1991 - 30 June 1993
Period covered	: 1 January 1992 - 31 December 1992
Project leader	: O. Cahuzac (coordinator - CEA) - F. Andaluz (EA)

A. OBJECTIVES AND SCOPE

In the frame of studies intented for groups of experts to develop common criteria for exemption of particular waste streams from regulatory control, the project aims to give correlations between waste activity levels and the individual doses due to their incineration.

The approach for establishing radiological protection criteria for the incineration of very low radioactive waste involves :

- The identification of possible waste management scenarios including : sources terms, incinerator data, composition of wastes streams, mode of disposal or reuse of the residues.
- The establishement of dose levels corresponding to incineration of very low radioactive burnable material in a classical installation.
- The establisment for each scenario defined, of environment pathways and dose assessments.

From this work, it will be possible to derive activity concentrations corresponding to acceptable level for incineration whithout special precaution.

CEA/IPSN (France) and EA (Spain) took part on this study, EA investigating specially biological and organic wastes produced in Spain.

B. WORK PROGRAMME

Four steps are envisionned :

1. Data Acquisition and Analysis :

1.1 Data collect and analysis of base information on incinerator types, processes and working conditions.

1.2 Definition of the characteristics of burnable very low level radioactive wastes and expected quantities.

2. Analysis

Sampling and dust in situ measurement.

3. Evaluation of the radiological impact :

3.1. Definition of scenarios corresponding to significant pathways for workers and members of public.

3.2 Adaptation of computer code CERISE to specific case of incineration.

3.3 Assessment of individual doses for the workers and radiological impact to the public as a function of quantities, waste activities and incinerator and site characteristics.

4. Correlation between activity levels and individual doses

4.1. Individual doses caused by unitary activity concentration of the waste in the considered scenarios.

4.2 Determination of the average activity of the wastes corresponding to the individual dose exemption level.

4.3 Determination of practical limits by groups of the nuclides

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

A collect of data about incineration of municipal waste, hospital waste and industrial waste are available. Complementary information will be necessary for workers operational conditions in cement works.

Scenarios and radiological impacts have been carried out for municipal and hospital wastes.

Progress and results

1.Data acquisition and analysis

CEA

During 1992, efforts have been made on the following topics:

-Review in available experience concerning incinerator exploitation, treatment of fumes, workers operational conditions in the plant and handling of by-products (storage and recycle).

-Thorough examination of the current literature, specially to collect the data useful to determine, for each radionuclide, the distribution factor of radioactivity between gas, fly ash and bottom ash and eventually dechloruration residues.

-Investigation on the conditionning of the fly ash. As required in a recent CCE directive, and because toxic elements are concentrate in the fly ash, it is not anymore possible to eliminate these ashes in a landfill without immobilisation. The national regulation concerning the elimination of this ashes is not presently issued. By lack of experience, the scenarios will be elaborated from the literature informations.

EA

During 1992 efforts have been made in order to:

-know technical data and operational aspects of the spanish incineration plants for both urban and clinical wastes: processes and changes undergone by materials (wastes), process parameters, operational conditions of the workers and treatment of by-products.

-obtain practical data (from the experience) about generation rate of by-products (gas, fly ashes and bottom ashes)

-obtain values of the radioactivity distribution factors between gas and ashes. Values have been taken from the current literature because of the lack of the experimental data.

-know the treatment given to the fly ashes stream in the spanish incinerators. Actually the fly ashes stream is added to the bottom ashes stream and disposed together, because there is not a national regulation concerning the immobilization of the fly ashes. Nevertheless provisions for treatment and stabilization of the fly ashes with special cement and others additives before disposal are being considered in the projects of the new plants in construction, in order to comply, in the future, with the recent CCE directive.

2.Analysis

Information has been collected from the gas exploitation of different plants in view to determine the distribution of radionuclides in gas, fly ash, bottom ash and residues of dechloruration. The use of these data is difficult in a generic study because of the dispersion of the data.
Some experiments carried out at Grenoble on CeO_2 and CsCl samples shows that respectively 74% and 89% of the contaminants are collected in the bottom ash. CeO_2 is representative of PuO_2 or UO_2 and CsCl is representative of moderatly volatile contaminants. These experiments have been worked out only at 550° and it will be necessary to make investigation with higher temperature

3.Evaluation of the radiological impact

CEA

In view of establishing evaluation of radiological impact, the computer code CERISE has been revised, especially concerning the data file on dose factor ; other ameliorations are envisaged.

Preliminary impact assessment have been performed for the individual during all operational activities : incinerator exploitation, storage or recycle of by-products. The different pathways considered are presented in table I and preliminary results in table II.

Definition of scenarios which can result in exposure to people, choice of parameter values have been performed for municipal incinerator, hospital incinerator and industrial incinerator excepted for the scenarios concerning the fly ash which requires more information (see 1.).

Calculation is carried out for municipal incinerator : the different pathways considered are presented in table I and preliminary results are compiled in table II.

EA

-The CERISE computer code methodology has been analysed and several test performed for training.

-Exposure scenarios conditions and pathways for workers of an incinerator of clinical wastes and for the public in the surroundings have been defined. Values of the exposure parameters have also been determined.

-Radiological calculations have been performed for the relevant posts and situations in the considered scenarios.

-The exposure scenarios, posts and pathways are presented in table III.
Preliminary results are showed in table IV.

4.Correlation between radioactivity levels and individual doses.

Not yet treated.

incinerator workers	
-wastes loading	-external exposure -inhalation
-ashes disposal	-external exposure -inhalation
landfill workers	
-chimist	-hand contamination -face contamination -ingestion transferred by hand contamination
track conductor	-external exposure -inhalation
road construction workers	-external exposure -inhalation
population	-exposure to the incinerator plume -external exposure due to deposits on the ground -ingestion of contaminated vegetables

TABLE I

PATHWAYS IN THE CASE OF INCINERATION

OF VERY LOW LEVEL WASTES IN A MUNICIPAL INCINERATOR

	INCINERATOR Bq.g-1	LANDFILL $Bq.g^{-1}$ *	ROAD CONSTRUCTION $Bq.g^{-1}$*
H3	1.25E+05	3.16E+12	4.06E+09
C14	2.88E+03	1.04E+09	1.62E+08
P32	2.66E+03	8.92E+07	3.78E+06
S35	3.16E+04	1.06E+09	9.54E+08
CR51	6.61E+03	1.10E+03	1.54E+02
MN54	2.29E+02	3.68E+01	3.48E+00
CO60	7.44E+01	5.97E+01	5.46E+00
FE59	1.62E+02	5.32E+02	6.34E+01
NI63	3.07E+06	2.56E+08	6.07E+05
SR90	1.53E+04	3.34E+05	6.08E+03
ZR95	1.31E+02	2.13E+01	2.34E+00
TC99	6.47E+05	4.18E+06	1.00E+20
AG110M	7.00E+01	1.13E+02	1.08E+01
I129	6.21E+01	3.96E+03	3.60E+02
I131	2.94E+02	1.15E+02	4.72E+01
CS137	2.99E+02	5.52E+01	5.03E+00
PB210	9.07E-01	2.47E+04	2.25E+01
PO210	2.71E+03	2.89E+05	4.49E+01
RA226	1.09E+02	1.75E+04	1.59E+03
NP237	1.78E+02	1.47E+05	6.23E+02
TH229	4.06E+01	1.02E+05	1.42E+02
AM241	3.47E+02	1.88E+03	1.21E+00
U233	5.79E+02	1.44E+07	2.02E+03
PU239	3.47E+02	8.64E+06	1.21E+03

*only for bottom ashes

TABLE II

DERIVED LEVEL OF ACTIVITY FOR THE CASE OF MUNICIPAL

INCINERATOR

The reference levels used to calculate the activity levels are:

- 10 μSv/y for the public
- 50 μSv/y for workers or for the public concerned with low probability scenario

EXPOSURE SCENARIOS	PATHWAYS
ON INCINERATOR	
-post of furnace loader	-External Exposure -Inhalation
-post of ash worker	-External Exposure -Inhalation
ON SANITARY LANDFILL	
-post of equipment operator (exposure similar to the ash worker	-External exposure -Inhalation
ON INCINERATOR SURROUNDINGS	
-individual of the public	-Inhalation } (exposure to the plume) -Immersion } -External exposure(from deposits on the ground) -Ingestion (of contaminated vegetables)

TABLE III

EXPOSURE SCENARIOS AND PATHWAYS DUE TO THE INCINERATION OF VERY LOW LEVEL RADWASTE

TABLE IV

UNITARY DOSES CAUSED BY THE INCINERATION OF BIOLOGICAL SOLIDS AND ORGANIC LIQUIDS (CONTAINING 1Bq/g)

IN THE DIFFERENT SCENARIOS OF THE PRACTICE (Sv/a) AND DERIVED ACTIVITIES (Bq/g)

	ANNUAL DOSES IN THE SELECTED SCENARIOS Sv/a					
	FURNACE LOADER	ASH WORKER	PUBLIC.INCIN.			
NUCLIDE	TOTAL DOSE	TOTAL DOSE	TOTAL DOSE	MAXIM DOSE Sv/a	LIMITATIVE SCENARIO	DERIVED CONCENTRATIONS
P-32	2.56E-13	3,20E-16	1,44E-10	1,44E-10	public	6,94E+04
S-35	3.33E-13	4,17E-16	1,76E-11	1,76E-11	public	5,68E+05
I-125	9,25E-11	1,38E-10	8,63E-10	8,63E-10	public	1,16E+04
FE-59	7,73E-09	5,79E-10	2,73E-12	7,73E-09	furnac.loader	1,29E+03
CA-45	1,49E-12	1,86E-12	7,97E-13	1,86E-12	ash worker	5,38E+06
H-3	2,92E-14	3,65E-17	1,62E-11	1,62E-11	public	6,17E+05
C-14	1,01E-12	1,26E-15	5,43E-10	5,43E-10	public	1,84E+04
TOTAL	7.83E-09	7,19E-10	1,59E-09	7,83E-09	furnac loader	

Title:	Comparison of Safety Assessment Methods for Toxic and Radioactive Wastes
Contractor:	Intera Information Technologies Ltd.
Contract No.:	FI2W-CT90-0042
Duration of Contract:	March 1991 - February 1993
Period Covered:	January 1992 - December 1992
Project Leader	Graham Smith (Intera) and Carlos Torres (IMA/CIEMAT)

A. Objectives and scope

The need for safety assessments of waste disposal stems not only from the increasing implementation of regulations requiring the assessment of environmental effects but also from the more general need to justify decisions on protection requirements. Just as waste disposal has become more technologically based, through the application of more highly engineered design concepts and through more rigorous and specific limitations on the types and quantities of the waste disposed, consequently the assessment procedure become more sophisticated. It is the overall aim of this study to improve the predictive modelling capacity for post-disposal safety assessments of land-based disposal facilities through the development and testing of a comprehensive yet practicable assessment framework.

Within this project the disposal of toxic, radioactive and mixed hazardous wastes is considered. The term "toxic wastes" is interpreted broadly to include any kind of liquid or solid non-radioactive waste which could give rise to some detrimental environmental effects, post-disposal. The associated work programme is being undertaken jointly by Intera Information Technologies, Environmental Division, United Kingdom, and Instituto de Medio Ambiente of Centro de Investigaciones Energéticas Medioambientales y Tecnológicas (IMA/CIEMAT), Spain.

B. Work programme

B.1. To review the different waste types and to compare and contrast concepts and methods adopted for their land based disposal.

B.2. To review the kinds of criteria adopted for authorising disposals, in so far as they relate to post-disposal environmental impact.

B.3. To review the different assessment methods which have been used to assess post-disposal environmental impacts and to evaluate the advantages and disadvantages of alternative assessment methods.

B.4. To identify the types of post-disposal impact which might arise and use a scenario analysis, according to a well defined procedure, to determine how such impacts may arise.

B.5. To develop a practicable framework for assessment of post-disposal safety for disposal of wastes to land-based facilities taking full account of existing methodological developments.

B.6. To test the application of the proposed framework on a representative set of example disposals. Illustrations will reflect realistic problems of environmental assessment.

C. Progress of work and obtained results

State of advancement

The following programme items have been successfully completed during 1992 without need for modification of the work programme:

- the identification of the types of post-disposal impact which might arise and the determination of how such impacts may arise.
- the development of a practicable framework to assess post-disposal safety for the disposal of wastes to land-based facilities taking account of existing methodological developments.
- the identification of suitable example disposals to demonstrate the application of the proposed framework.

The items which remain to be completed by February 1993 are:

- the testing of the proposed framework on the representative set of example disposals.

Progress and results

1. Identification of post-disposal impacts (B.4.)

1.1. Procedure for the identification of post-disposal impacts

To allow the identification of impacts and how they arise, it is necessary to develop a conceptual model of the disposal system, its environmental setting and the associated release, transport and exposure mechanisms and media. To aid this, the scenario analysis approach outlined in Figure 1 can be used.

The first step is to identify the release and transport media, exposure points, and human and environmental effects. The mechanisms by which the associated release, transport and exposure may occur are then considered (ie the links between the media, exposure points, or human and environmental effects). All the possible features, events and processes (feps) which have been identified are then screened in order to reduce the number to be assessed in detail. Criteria such as low probability or low impact can be used as a screening mechanism. Simple scoping calculations (for example /1/ and /2/) of certain feps can be used to make preliminary assessments of impacts to aid screening. Each possible combination of feps is termed a scenario. These scenarios are identified and the number reduced by grouping them into categories (those with the same impact, those causing pollution of the same media, etc.). Finally those scenarios for which detailed modelling should be undertaken due to their high probability of occurrence, high impact, etc. are identified.

1.2. Post-disposal Impacts

How post-disposal impacts arise and their nature will vary depending upon: waste characteristics; disposal facility characteristics; geosphere factors; environmental factors; human factors. Therefore, without consideration of a particular waste and a particular site, it is only possible to make general comments about pathways and impacts. The main pathways for contaminants to escape from the disposal facility are: groundwater; gas; intrusion (human/biotic); and erosion (by water/wind/ice). Once contaminants have reached the biosphere there are a large number of pathways by which they can reach man. For example, Figure 2 shows the range of possible pathways for contaminants discharged from groundwater into the biosphere.

Impacts can be considered in terms of impacts on humans and impacts on the general environment. In some cases it is assumed that the protection of humans will ensure the protection of other species (eg /3/). However, the concept of considering risks to both humans (individuals and groups) and to ecosystems is being introduced in some countries, for

example the Netherlands /4/. In addition to the consideration of biotic health effects, it is also relevant to consider the effect of contaminants on resources such as water supplies and land.

2. Development of the assessment framework (B.5.)

In light of the aims of the project, it was proposed to develop a general assessment framework which:

- is applicable to all waste types and land-based disposal facilities.
- is applicable to varying levels of data availability.
- is quantitative in its approach.
- has a range of possible end points.
- allows the comparison of the environmental impacts of different disposal options and waste types.

It was concluded from a review of assessment methods carried out earlier in the project /5/, that the use of the quantitative performance assessment approach was most suitable. This approach is considered to have several advantages over other approaches mainly due to its ability to quantify the behaviour of the disposal system. The framework illustrated in Figure 3 was developed. It consists of the following steps:

- Collect and collate data. This involves collecting any site specific data which might be available concerning the waste and associated contaminant characteristics, the facility design, the geosphere, the biosphere, and the associated physical, chemical and biological processes.
- Review the criteria relating to post-disposal safety which are relevant to the site, waste and contaminants being considered. This review should take into account the specific objectives of the assessment and should identify relevant end points for the assessment.
- In light of the criteria, review the data collected in Step 1, identify any gaps in the data and obtain the necessary data.
- Develop conceptual model(s) of the system by identifying possible features, events and processes (feps) using the approach described in Section 1.1.
- Screen the possible feps which have been identified in Step 4 in order to reduce the number to be assessed in detail (see Section 1.1).
- Identify scenarios and reduce the number for further detailed consideration (see Section 1.1).
- Select/develop mathematical code(s) to represent relevant scenarios and their associated processes at a level of detail appropriate to the available data and relevant safety criteria. A variety of codes could be used depending on the nature of the scenarios, processes, data and criteria.
- Obtain any further site and/or generic data which are necessary for the mathematical code(s).
- Verify and validate the code(s).
- Taking account of the uncertainties through the use of statistical and expert elicitation techniques, use the code(s) to estimate the end points defined in the safety criteria identified in Step 2.
- Compare the results with the relevant criteria.

The level of detail incorporated into applications of this framework will depend on a variety of factors such as the resources available, the level of understanding of the disposal system and its processes, and the perceived severity of the existing or potential environmental problems. The above sequence should be seen not as a once-through process, but as an

iterative procedure, with each iteration taking account of changes in conceptual assumptions and data values arising from the previous iteration. Iterations might require the repetition all the steps or just particular steps in the framework.

Steps 7 to 10 of the framework require the application of computer codes which can be used to assess the scenarios chosen for detailed modelling. It was decided to develop an example code which could be used within steps 7 to 10 of the assessment framework and could also be used to demonstrate the benefits of the quantitative approach adopted. Rather than develop a code which only considers only one aspect of the disposal system, it was decided to develop an integrated assessment code with characteristics similar to those illustrated in Figure 4.

As a starting point, it was decide to use an existing code, VANDAL (Variability ANalysis of Disposal ALternatives). VANDAL has been developed as part of the radioactive waste disposal assessment methodology of Her Majesty's Inspectorate of Pollution of the UK Department of the Environment (UK DoE) /6/. It allows the simulation of the release of radionuclides from a disposal facility, their transport in the geosphere and the biosphere, and eventual uptake by humans. It includes a groundwater flow module, a radionuclide release (vault) module, a radionuclide transport module, and a compartmental biosphere module /7/. VANDAL has the ability to run in either deterministic mode (all parameters fixed) or probabilistic mode (some parameters sampled).

It was recognised that certain developments would have to be introduced to VANDAL to allow the development of a code for the assessment of both radioactive and toxic waste disposals. In particular, it was considered that there was a need to represent the effects of chemical and biological processes in toxic waste disposal facilities. Therefore a review of such processes was undertaken and consideration was given to their possible representation in the example assessment code. In addition, a sub-contract was let to RM Consultants of Abingdon, UK, by Intera and IMA/CIEMAT to allow RM Consultants to assist with the specification and implementation of the developments. As a result of the review of chemical and biological processes and additional input from Intera, IMA/CIEMAT and RM Consultants, a list of possible developments was outlined to improve the code's modelling capabilities. The developments were then prioritised based on their perceived importance and ease of implementation within the budgetary and time restraints of the project. The developments which were undertaken can be divided into three broad categories:

- source term developments (introduction of a new gas generation module).
- flow and transport developments (introduction of a new gas transport module).
- biosphere developments (introduction of a more flexible module which allows consideration of gas migration in the biosphere).

The resulting new code has been called the SACO (Safety Assessment COmparison) code. All modifications have been tested and documented to ensure the correct operation of the code. SACO has been developed as a modular code, thus providing the user with the flexibility to replace or omit modules of his/her choice. In particular, this allows for the future development of both new and existing modules to replace/provide an alternative to existing modules.

More details concerning the development of the assessment framework are given in /8/.

3. Identification of Suitable Test Cases (B.6.)

Identification of suitable example disposals to demonstrate the application of the proposed framework has been undertaken. The tests will include appropriate demonstrations of the enhancements made to the assessment code, and will be designed specifically to reflect realistic problems of environmental assessments, for example any lack of comprehensive waste and site characterisation data. Tests will be undertaken for radioactive, hazardous (non-radioactive) and municipal waste, and shallow and deep disposal facilities.

It is proposed to consider three broad categories of test case; a shallow unengineered disposal case, a shallow engineered disposal case, and a deep engineered disposal case. For both shallow cases, disposal of radioactive, hazardous and municipal waste will be considered, whilst for the deep case, disposal of radioactive and hazardous waste will be considered. It is proposed, where possible, to use data from international intercomparison exercises which have been established in order to test and compare the performance of assessment codes. The provisional list of data sources and their associated exercises is given in Table I.

List of publications

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/1/ IAEA, Technical Reports Series No. 332 (1992)

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Table I: Proposed Data Sources for Test Cases

	Shallow Unengineered	**Shallow Engineered**	**Deep Engineered**
Facility Design	NSARS Level 1 (1)	NSARS Level 1	PSACOIN Level 1a (2)
Waste Type			
- Radioactive	NSARS Level 1	NSARS Level 1	PSACOIN Level 1a
- Hazardous	To be determined	To be determined	To be determined
- Municipal	To be determined	To be determined	Not required
Geosphere	NSARS Level 1	NSARS Level 1	PSACOIN Level 2 (3)
Biosphere	NSARS Level 1 & PSACOIN Level 1b (4)	NSARS Level 1 & PSACOIN Level 1b	PSACOIN Level 2 & PSACOIN Level 1b

Notes:

1. See reference /9/
2. See reference /10/
3. See reference /11/
4. See reference /12/

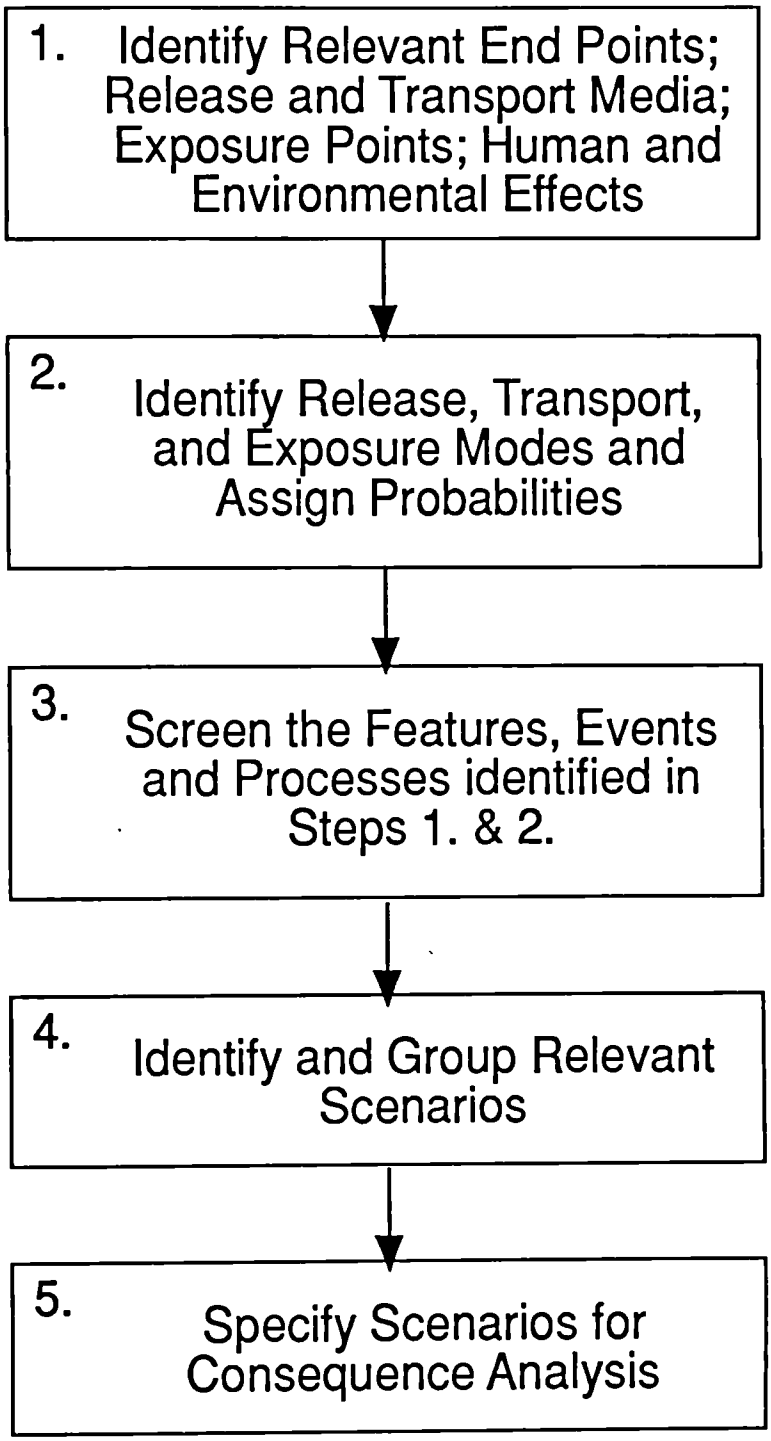

Figure 1: Scenario analysis technique for the analysis of post-disposal impacts

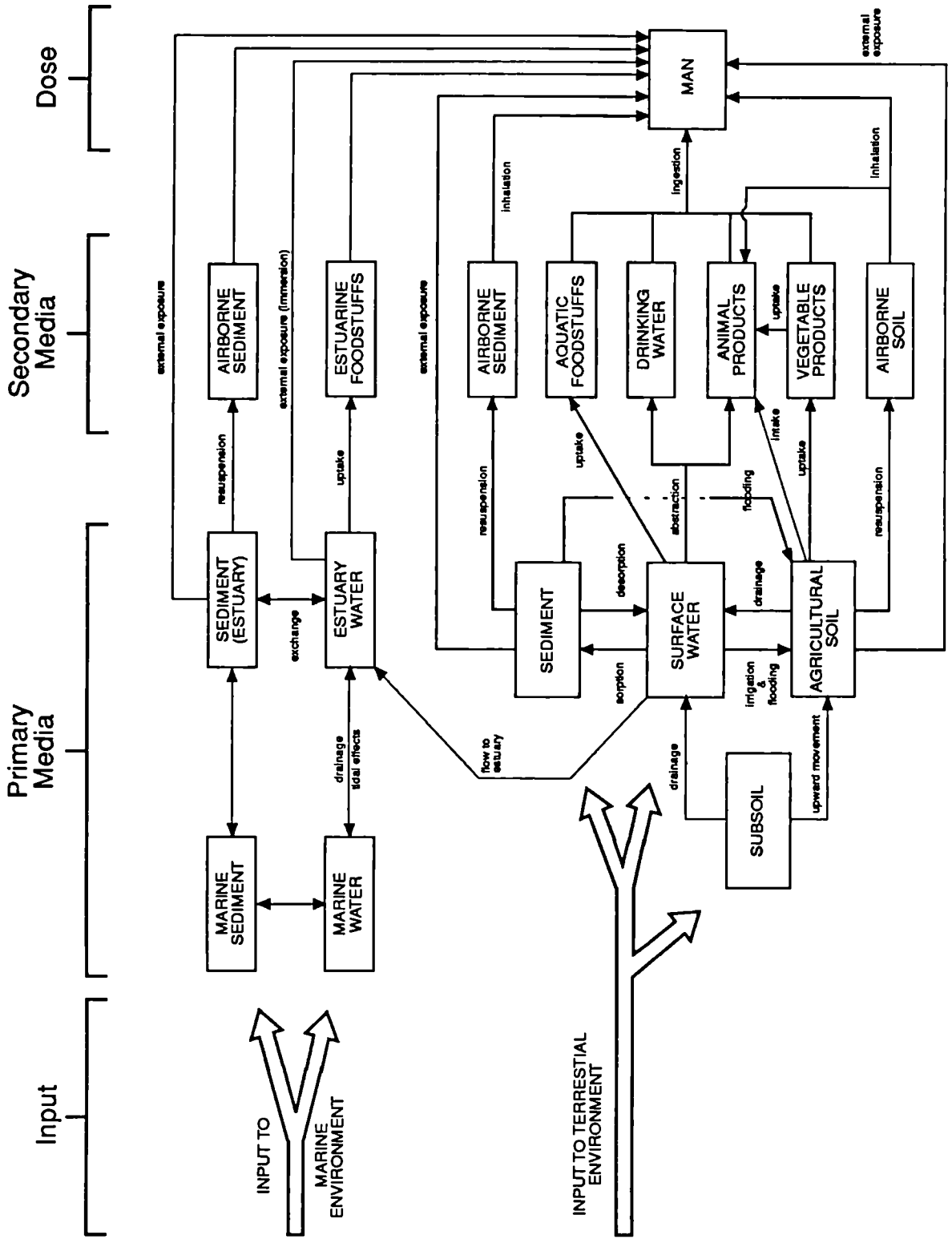

Figure 2: Contaminant transport pathways in the biosphere and associated exposure mechanisms

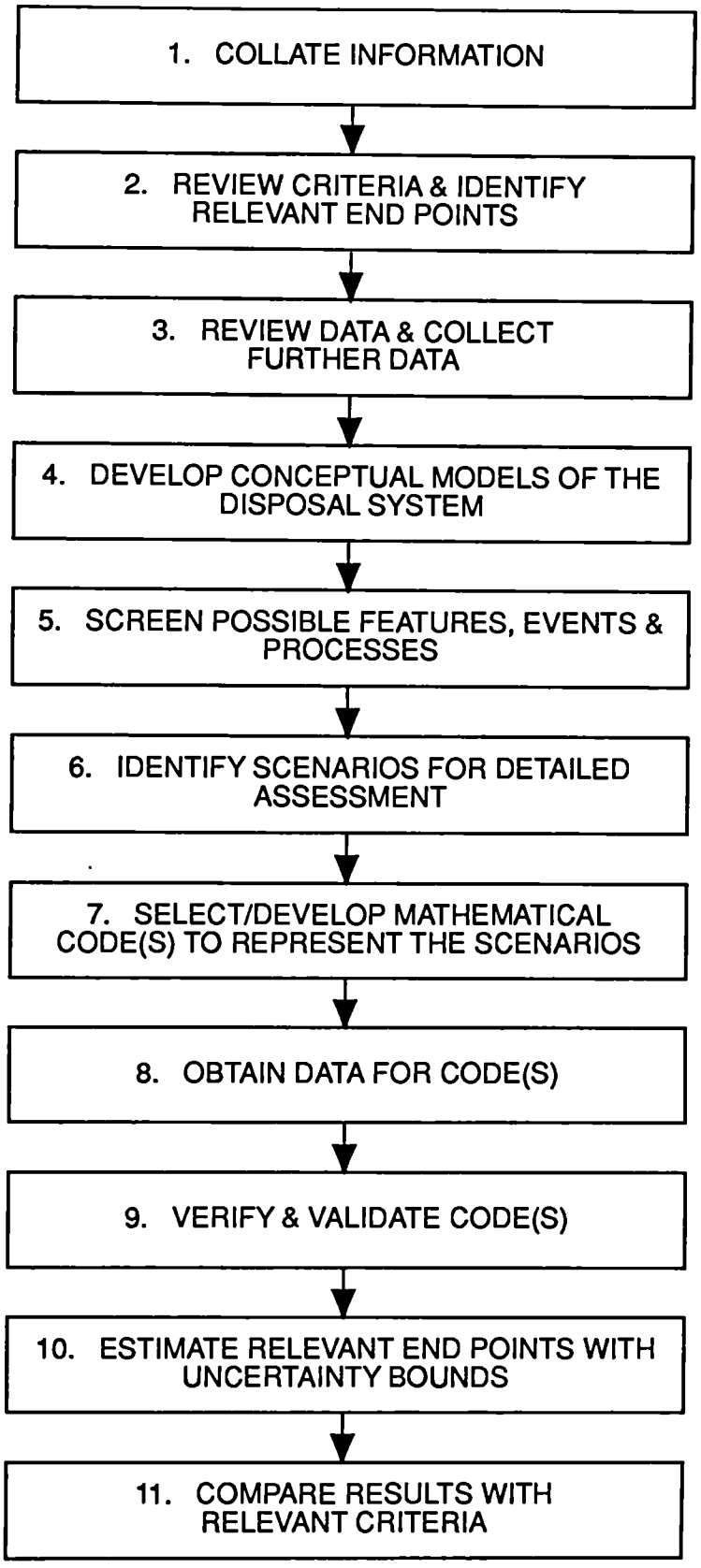

Figure 3: The assessment framework

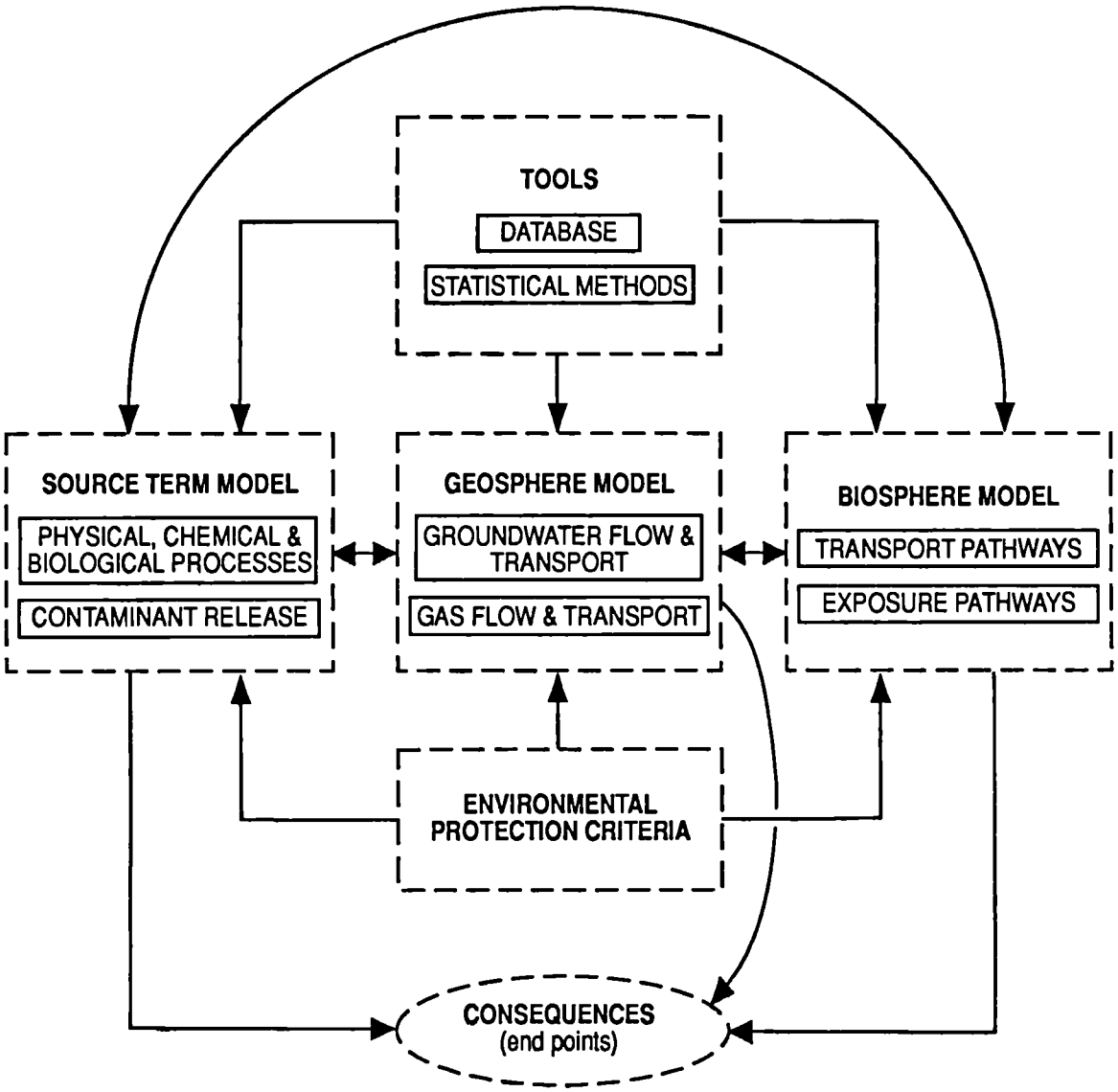

Figure 4: Structure of the proposed assessment code

Title : Study concerning the evaluation of toxic elements present in nuclear wastes

Contractor : ONDRAF/NIRAS, BRUSSELS

Contract nr : FI2W-CT90-0045

Duration of contract : from 01.04.1991 to 31.03.1993

Period concerned : 01.01.1992 to 31.12.92

Project leader : A. De Goeyse

A. Objectives and scope.

The management of radioactive waste is mainly determined by the safety conditions of the final disposal. Those safety conditions must cover the radiological aspects but also the chemical toxicity aspects coming either from the radioactive isotopes or from the non radioactive components of the waste.

The aim of the study is to make an evaluation of those chemical elements and of their quantity in the different waste streams.

The different waste streams will be identified systematically (per producer and per category) making a segregation between them based on the production process (operational, technological, dismantling, packaging, conditionning,...).

The chemical properties of the identified waste streams will be included in a general databank covering the identification and quantification, the physico-chemical properties, and the radiological characterization of the nuclear wastes.

To define the field of the inventory and to structure the inquiry, we take advantage of the experience of similar works performed in other European countries.

The evaluation and characterization of the chemical toxicity of nuclear waste is performed in collaboration with Indaver N.V. (Antwerp-Belgium), a mixed treatment plant company for chemical waste.

B. Work programme.

1. Selection of toxic elements, in particular heavy metals, in function of the actual local, national and european legal context.
2. Evaluation of the presence of these toxic elements in the nuclear wastes, and structuration of the collected information based on the following criteria : - type of producer
   - type of process
3. Definition of toxic elements/limits (orders of magnitude) acceptable for the admission of waste on a shallow land burial, referring to the operation criteria for conventional landfilling of industrial waste.
4. Definition of measurements or evaluation methods to identify and quantify the toxic elements in nuclear wastes.
5. Preventive actions to avoid the use of toxic elements in the nuclear installations.

C. Progress of work and obtained results

State of advancement

To collect the information on heavy metal content of radioactive waste at the most efficient way, ONDRAF-NIRAS opted for an inquiry system.

Therefore a form was developped, covering systematically the different characteristics of the waste like specific identification parameters, origin, quantities, physico-chemical properties (with a special attention for the heavy metals) and radiological properties.

To make the compilation by producers easier, the form is translated in informatical language, using lotus software.

The systematic inquiry has been presented to the selected producers. In a first step, the producers defined the waste fluxes and in a second step some fluxes were chosen as test case to complete the form.

Both steps occured in close collaboration between producers and ONDRAF-NIRAS.

Because the present management of radioactive waste in Belgium is not really based on the concept of "waste flux", the above mentionned first step tooks much more time than originally expected and is still current for some of them.

Therefore, some producers started on a parallel way a compilation of available information on the presence of heavy metals in [current waste, in packaging, or in structures] possibly concerned by dismantling.

As already mentionned, the available data on heavy metals in radioactive waste is actually quite limited as well for production waste as for dismantling waste (dismantling programs are not yet finalized).

As a result of this situation, some assumptions, projections and extrapolations will be needed to obtain a global evaluation of the amounts at stake.

Progress & Results.

1. Revue of foreign studies on chemical aspects of radioactive waste.

   Three studies of first interest were reviewed and are shortly presented hereafter, pointing out the most important conclusions.

1.1. Switzerland : "Inventar chemisch-toxischer Stoffe in nuklearen Endlogern und ihre Freisetzung in die Umvelt" (Technischer Bericht 85-61 NAGRA 1986). This study, performed by Electrowatt and Motor-Colombus, was requested by the federal authorities for agreement on final burial of radioactive waste (project Garantee).

   An inventory of ecotoxical substances was performed, based on a list provided by the federal ministry of environment and using 3 criteria :

   - presence in more than 500 kg per site
   - reactivity (corrosion, explosion)
   - solubility/volatility

   The use of this criteria combined with the specifications of the swiss management of radioactive waste reduced to a few heavy metals the list of substances to be checked. A specific study of Cadmium was performed and the conclusion, extrapolable to other metals is that the presence of chimiotoxic substances in radioactive waste does not influence the safety of final depositories in such a way that measurable effects on man and environment can occur.

1.2. Canada : "An assessment of the long term impact of chemically toxic contaminants from the disposal of nuclear fuel waste" (AECL-8367, Atomic Energy of Canada limited 1987).
   This specific study on nuclear fuel started with a list of 58 selected elements. Through a selection procedure (exclusion system) based on natural abundance in the geosphere/biosphere, the solubility and the comparison between chemical and radiological toxicity, a final list of 12 elements (only metals) was selected for long term assessment.
   The conclusions of the study, based on a stochastic approach are restricted to a qualitative level.

   Depending on the type of conditioning and the pathway, only chromium, molybdenum and lead exceed acceptable levels of concentrations in some simulations, with a probability less than 0,02.

   The main conclusion, on a management point of view, is that 4 factors affect the results :

   - 3 factors (elemental inventory, release rate and toxicity) have an influence on the magnitude of impact

   - 1 factor (elemental mobility in the geosphere) has an impact on the frequency of occurance of impact.

1.3. USA : "The management of mixed low-level radioactive waste in the nuclear power industry" (prepared for the National Environmental Studies Project, Nuclear Waste Management and Resources Council by Rogers & Associates Engineering Corporation with Nuclear Waste Management, Inc., 1990).
This study, as mentionned by the authors themselve, is more interesting for the approach used than for the results : the startpoint of this study is that a nuclear power plant is not a producer of waste, but a producer of steam. Further, this production does not require any chemical process. As a logic consequence, waste and specially mixed waste produced in a nuclear power plant, is a direct consequence of the toxic products introduced as raw material on the plant, taking any possibility of contamination into account.

In the context of the legislation in force in the USA, a qualitative comparison of disposal performance for mixed waste was made between two types of disposal facilities :

- the first one is licensed under the radioactive legislation
- the second one is licensed under the radioactive and chemical legislation.

The conclusion of this qualitative comparison, for the options and pathways selected by the authors, is that no significant difference of safety efficiency can be shown.

2. Heavy metals in radioactive waste.

Near the systematic inquiry, the Belgian power plants (owned by the company Electrabel) performed a preliminary study on heavy metals present - or possibly present - in radioactive waste.
Informations provided by other producers pointed also out the presence, for example, of mercury in lab-waste, in such concentrations that it could be classified as toxic waste in the non-radioactive sector.

2.1. Heavy metals in rods.

An inventory of silver, cadmium, antimony, beryllium and boron in control, poison and source rods was performed, giving the following results for the whole life of the 7 reactors :

- 23168 kg Ag
- 1521 kg B
- 8 kg Be
- 1449 kg Cd
- 28 kg Sb

2.2. Heavy metals in evaporator concentrates, filters and resins.

4 heavy metals are present in the waste selve :

- chromium, cobalt and nickel come from the corrosion of pipes
- boron is used as neutronic poison.

1 heavy metal, zinc, is used in galvanisation of drums used for the packaging of conditionned waste.
The following quantities are annually produced :

3150 kg B
0,33 kg Co
22 kg Cr
30 kg Ni
4000 kg Zn

2.3. Heavy metals in decommissioning waste : zinc and copper.

The following amounts are to be considered with caution, because they are the results of :

- total inventories without evaluation of decontamination possibilities (exemption levels are not yet legally defined)
- estimations of surfaces which could be contaminated in case of major accident.

A major accident could result in a contamination of 46.600 kg of zinc for the 7 reactors (41.300 kg for the reactor buildings and 5.300 kg for the space between inner and outer containment).
A total amount of 81.000 kg of copper is present in the heat zone of reactor Tihange 3 (motor pumps and cables).

3. Admission criteria for heavy metals on landfill.

A comparison was performed between the legal norms in force and the effective acceptance criteria applied on the reception of industrial waste.

Because the owner of such an installation has to complete with the norms in any time, even in the future, for example after closure of the site (concentration of pollutants in leachate), the acceptance criteria are often more restrictive than the law actually in force, and are based on regional norms under development, foreign or international norms.

Title:	Disposal of Radioactive Waste and Toxic Waste in Underground Repositories
Contractor:	GSF-Forschungszentrum für Umwelt und Gesundheit, GmbH; Stichting Energieonderzoek Centrum Nederland (ECN)
Contract No:	FI2W-CT90-0061
Duration of contract:	from March 1st, 1991 to February 28th, 1994
Period covered:	January 1st - December 31st, 1992
Project Leader:	Th. Brasser (GSF - Coordinator) A. van Dalen (ECN)

A. OBJECTIVES AND SCOPE

The initial objective of a mutual research project between GSF and ECN is to delineate the statutory boundary conditions pertaining to an underground emplacement of hazardous wastes. At the same time the wastes of relevance to disposal are to be characterized according to type, composition, origin, toxicity, and volume, while taking the particularities of the situation in both countries into due consideration. Assumed potential hazards to the environment emanating from disposal are to be assessed on the basis of these data. The current strategies for an underground storage of hazardous wastes are described and compared with the concepts for the final disposal of radioactive wastes. Reference is taken to the special R&D topics of final disposal, such as the selection of the host rock, investigation of the geomechanical and hydrogeological situation, transport methods, backfilling and sealing techniques as well as the more complex subjects, such as the spreading of toxic agents and the safety analysis. This mutual project is to combine the basic knowledge of the repository concepts for the disposal of radioactive and hazardous wastes.

B. WORK PROGRAMM

2.1 Consideration of legal stipulations for the underground disposal of toxic wastes, based on the aims, requirements, techniques and safety concepts of radioactive waste disposal.

2.2 Description of the types of waste, their composition, origin, toxicity and assessment of their potential hazards to the environment emanating from the emplacement.

2.3 Description of strategies for underground disposal of toxic wastes and comparison with the concepts for radioactive waste disposal.

2.4 Compilation of special requirements on the disposal of toxic wastes in deep geological formations, summarizing those results which can be generally adopted from the R&D work in the field of radioactive waste disposal.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Federal Republic of Germany

2.1 Legal Stipulations

2.1.1 Execution of waste management legislation in the new Bundesländer

Waste disposal in the five new federal states will continue to present considerable difficulties during the next five years. With the acceptance of the environmental law for the Federal Republic of Germany, however, the basic legal conditions have been established for environmentally compatible waste management in the acquired regions.

In conformance with the criteria presented by the Federal Minister of the Environment, Nature Conservation, and Reactor Safety (BMU), an inventory has been completed on the infrastucture for waste disposal in the new Bundesländer. The necessary legislative measures are in progress there, and the concepts for these Bundesländer are being extended.

Under the provisions of the immediate programme for environmental protection, measures are being implemented by the German Federal Government in the field of waste management and funded with a total volume of 819 Mio DM for 1991 and 1992.

The support of large-scale industrial demonstration projects is also of substantial importance. In this connection, of course, only individual projects have hitherto received immediate support, because the lead time for planning of such projects is very long in the new federal states, too. In individual industrial areas, however, this measure will result in the amelioration of a number of waste problems.

In all of the new federal states, the ministries of the environment which have been established are already operative. The entire structural organization will be completed shortly. The associated environmental authorities are likewise being established with specification of the fields of competence by means of regulatory statutes in conjunction with the law relating to waste management or ordinances relating to competence.

The status of execution differs among the various federal states; especially in Sachsen-Anhalt and Thüringen, planning data are already available.

2.1.1.1 Sachsen-Anhalt

A preliminary consultant draught of a general concept for planning of problem waste disposal has already been submitted. The expected agreements concerning problem wastes in the future will result in the following planning requirements for waste disposal facilities:

- 2 CPT (chemical-physical treatment plants)
- 2 HWI (hazardous waste incineration plants)
- 1 HWL (hazardous waste landfill)
- 1 UWR (underground waste repository)

2.1.1.2 Thüringen

The following facilities are currently being planned for processing and disposal of problem wastes in Thüringen:

- 2 HWI (locations: Rositz and Kirchheiligen)
- 3 HWL (Rehestädt, Aga; search for the location of an additional facility)
- 1 UWR (Merkers / Springen)
- 4 CPT (Rositz; three additional locations currently being discussed)

The underground repositories already planned in Sachsen-Anhalt (Zielitz) and in Thüringen (Springen) are described in section 2.3.2 of this report.

2.2 Characterization of wastes

2.2.1 Radioactive wastes

On behalf of the German Federal Minister for the Environment, Nature Conservation, and Reactor Safety (BMU), the German Federal Board of Radiation Protection conducts an annual survey of the quantities of radioactive wastes occurring in the Federal Republic of Germany. The first survey was performed in 1984.

By means of the interrogation, the unconditioned as well as conditioned radioactive wastes are determined with respect to polluter or plant. The survey of spent fuel elements is conducted by the BMU itself. In 1990, the new federal states were included in the survey for the first time.

The inventory of unconditioned radioactive wastes with negligible heat generation in the Federal Republic of Germany totals 14 875 m^3 at present; of this total, almost 75 per cent originates from the old federal states. The preponderant share of these wastes is still located in or at the respective nuclear power stations.

So-called transient wastes involve radionuclides with short half-lives, which have disintegrated to such an extent after a corresponding decay period that conventional disposal is possible.

A total volume of 1584 m^3 is currently present in the Federal Republic of Germany.

The inventory of unconditioned radioactive waste which generates heat was about 73 m^3 at the end of 1990. These wastes originate exclusively from the reprocessing of spent fuel elements at the reprocessing plant in Karlsruhe (WAK).

No heat-generating, unconditioned radioactive wastes were present in the new federal states by the end of 1990.

The inventory of conditioned radioactive wastes with negligible heat generation was about 50 000 m^3 at the end of 1990. Of this total, only about 150 m^3 originated from the old federal states. The average rate of waste production was about 4200 m^3/a from 1984 to 1989; some 6900 m^3 of waste was incurred in 1990. The major shares of waste originate from large research installations (about 40 per cent) and from nuclear power stations (about 33 per cent). Some 800 m^3 originates from the new federal states; of this total, some 700 m^3 has been deposited in the final repository for radioactive wastes in Morsleben (ERAM). The major portion of the conditioned wastes incurred is still in intermediate storage in or at the nuclear power stations (about 90 per cent). Hence, no intermediate storage facilities were required in the new federal states. The utilization factor for the existing and operating intermediate storage facilities is currently about 43 per cent.

About 93 m^3 of conditioned, heat-generating waste was produced in the Federal Republic of Germany in 1990. The wastes originated especially from research institutions (about 44 m^3) and from reprocessing of spent fuel elements (about 35 per cent). The total amount of conditioned heat-generating wastes was 367 m^3 at the end of 1990.

No conditioned, heat-generating, radioactive wastes were present in the new federal states at the end of 1990. Only small quantities are expected to occur annually after discontinuation of operations at the reprocessing plant (RPK) in the future. Major inventory changes can be expected only after vitrification of fission product solutions from the RPK, or after the return of heat-generating wastes from foreign reprocessing of spent fuel elements from German nuclear power stations. Intermediate storage facilities must be constructed for this purpose.

2.2.2 Chemical toxic wastes

Especially wastes which require surveillance, but also other materials which must be deposited underground, may contain a wide variety of different components, and the composition varies from one batch to another. Potential hazards to humans and to the environment result from the discrete, individual constituents of the respective wastes. Consequently, the present classification of wastes with respect to origin or major components is too coarse. By means of waste analysis, therefore, the potential environmental hazards associated with the wastes must first be determined.

The wastes destined for underground disposal in rock salt formations can be subdivided into two main categories:
- wastes of mineral origin, as well as refining products
- wastes from conversion and synthetic processes,

as well as other types of wastes, to the extent that they fail to satisfy the classification criteria for disposal at the surface.

The wastes just indicated possess different chemical-physical and toxicological properties. Consequently, the chemical characterization and toxicological appraisal of these wastes with respect to the associated potential hazard as well as the assessment of their behaviour in the long term are of vital importance for disposal.

Because of a great lack in data availability in the course of the current project the most important UWR-relevant wastes are chemically characterized.

The object of the characterization of UWR-relevant wastes is, as far as possible, the complete detection of the sample material. The task was limited to the determination of inorganic parameters.

All samples were subjected to pressure solubilization, total solubilization, and solubilization with aqua regia. A few samples were solubilized by silicon fusion. All solubilizates were examined by ICP-AES; a very broad element spectrum was thereby determined.

2.3 Concepts

2.3.1 Radioactive wastes

Morsleben (Sachsen-Anhalt)

In 1970, the Bartensleben salt mine was selected by the former German Democratic Republic from ten salt mines under consideration for use as a final repository for radioactive wastes at Morsleben (ERAM). It was transferred to the legal entity of the former nationalized combine "Kernkraftwerk Bruno Leuschner, Greifswald", as a dependent plant department. The Morsleben final repository is located north-northwest of Morsleben in the county of Haldensleben in Sachsen-Anhalt.

In the Bartensleben salt mine, the extraction of potassium salts began in 1912; predominantly rock salt was produced after 1969. The salt was mined by panel working with chambers 100 m long, 30 m wide, and 30 m high, with a total cavity volume of 5 Mio m^3.

After detailed suitability studies, the site permit was granted in 1972. In 1974, permission was granted for the construction of a final repository, subject to a provision for conversion of the shaft plant as well as research and development work on transport and final disposal techniques. The construction phase was followed by commissioning with trial operation in 1978. In 1981, the first permit was granted for continuous operation with a validity of five years; this was followed by a second permit for continuous operation on 22nd April 1986.

On 1st July 1990, the Omnibus Act Relating to the Environment of the German Democratic Republic became effective. Thus, among other items, the Nuclear Energy Act for the Federal Republic of Germany also became effective

in the German Democratic Republic. The final repository for radioactive wastes in Morsleben (ERAM) received the legal status of a national final repository in conformance with § 9a, clause 3 of the Nuclear Energy Act.

As a result of the reunification of the two German countries on 3rd October 1990, the competence for operation of the final repository was transferred to the BfS. On 7th November 1990, the BfS commissioned the German Association for the Construction and Operation of Final Repositories for Waste Materials (DBE) with the management of the final repository.

After the decision by the German Federal Adminstrative Court dated 25th June 1992, there are no further legal obstructions to the continuing operation of the ERAM. The legal action for discontinuation of operation was ultimately rejected, and decisions to the contrary by the District Court in Magdeburg during the precedent year have thus been reversed. The BfS is now committed to continued operation of the ERAM as a federal final repository, in compliance with § 9a, clause 3 of the Nuclear Energy Act.

Preparations are under way for the final disposal of radioactive wastes by the BfS and DBE. The final disposal is to commence after specification or examination of the operating conditions, the costs incurred, as well as the product requirements. In the final repository at Morsleben, priority is to be given to radioactive wastes from the new federal states, but wastes from the old federal states also are to be deposited there.

Erzbergwerk Konrad (Lower Saxony)

On 31st August 1982, the PTB, the competent agency at the time, filed an application with the state government of Lower Saxony for initiating the Konrad project evaluation procedure in compliance with § 9 b of the Nuclear Energy Act. At the end of March 1986, the PTB then submitted a plan which was in its opinion complete to the Environmental Ministry of Lower Saxony (NMU). Within the scope of advance participation by state authorities, this plan, together with a summary, was submitted to about 80 state authorities with the request to provide preliminary opinions on the completeness of the plan.

The initial results of the advance participation by state authorities and the results of the examination of the plan for completeness and examinability of the zoning documents by the NMU and its experts led to a revision of the plan which was terminated with the submission of the March 1989 version.

On 1st November 1989, the new Radiation Protection Ordinance became effective. On this basis, the plan was revised again and submitted with the April 1990 status to the zoning authority on 31st May 1990. In the joint opinion of the NMU and its experts, as well as the BMU and BfS, a basis now existed for continuing the project evaluation procedure. In a letter dated 15th June 1990, the NMU confirmed for the BfS the maturity of the zoning documents for exposition.

On 8th May 1991, the exposition of the zoning documents was announced by the NMU, after the German Federal Constitutional Court, in a decision dated 10th April 1991, demanded compliance by Lower Saxony with the instructions of the BMU to conduct the public participation. During the period from 16th May to 15th July 1991, the documents were displayed for inspection at five locations. The time for discussion began on 28th September 1992.

Gorleben

Since 1979, the Gorleben salt dome has been under investigation to determine its suitability as a final repository for all types of solid and consolidated radioactive wastes.

The mine for exploration of the Gorleben salt dome is located in eastern Lower Saxony, in the community of Gartow, in the county of Lüchow-Dannenberg.

The Gorleben salt dome is one of many salt structures of the North German lowlands. It consists of thick stratigraphic sequences of Zechstein salt, which have undergone intensive folding in the course of halokinesis.

The objectives of the surface exploration in Gorleben were as follows:

- investigation of the hydrogeological conditions of the overlying and adjacent formations,
- obtaining of site data for appraisal of the operational and long-term safety of the projected final repository, and
- determination of appropriate shaft construction sites.

Besides some 150 exploratory boreholes and wells for long-term pumping tests, 4 deep wells with a depth of about 2000 m as well as 44 salt dome top wells have been drilled for exploring the salt dome.

The evaluation of results obtained from the wells has been supplemented by reflection seismic and seismological measurements.

The underground exploration phase is currently in progress in the Gorleben salt dome. This phase comprises the excavation of shafts 1 and 2, the development of the mine lay-out necessary for the exploration, as well as the accompanying geoscientific investigations.

Until 1994, the underground exploration is still restricted to the excavation of the shafts. The exploratory measures are an absolute prerequisite for a project evaluation procedure.

2.3.2 Chemical toxic wastes
Herfa-Neurode

The underground repository (UWR) at Herfa-Neurode is operated in combination with the adjacent Wintershall potash salt mine. The Wintershall mining claim, to which the underground repository for chemical toxic wastes belongs, is located in the salt deposit of the Werra basin. This salt deposit extends over an area of about 1100 km². Potassium salt is worked at a total of five mines (two are located in the old federal states, and three in the former German Democratic Republic.

The salt deposit is predominantly flat. The overall salt formation, which was deposited during the Zechstein some 240 Mio years ago, has a thickness of about 300 m and consists essentially of rock salt. Two potassium salt strata, each of which is 2.5 to 3 m thick, are intercalated in this salt formation. Only the potash strata are exploited at the Wintershall mine. The two potash strata are separated by about 60 m of middle Werra rock salt.

The salt formation is covered by alternating strata of clays and dolomite, which in turn is overlain by Buntsandstein with a thickness of 300 to 600 m. Four clay strata which belong to the interstratification, with a total thickness of about 100 m, seal the salt formation from the Buntsandstein aquifer. Consequently, the salt formation has persisted unaffected since its deposition some 240 000 000 years ago, with the exception of the edges. More than 30 000 t/d, that is, over 8 Mt/a of raw salt is currently being extracted at the Winterhall mine. Thus, a useful cavity volume of more than 3 000 000 m^3 is created annually; this space could be made available for the disposal of wastes.

The wastes delivered to the UWR are classified into material categories. Similar wastes within a given category are deposited together.

Wastes of different material categories are deposited in separate repository zones. The categories comprise the following:

a. cyanides, b. polychlorinated hydrocarbons, c. arsenic, d. mercury, e. electrolytic residues, f. chemical distillation residues, g. filtration and clarification residues, h. evaporation residues, i. dye and pigment residues, j. monochlorinated hydrocarbons, k. tars, l. wastes encapsulated in concrete, m. herbicides and pesticides, n. dry materials, o. capacitors, p. transformers, q. residues from incineration plants for problem wastes and household refuse.

At present, the annual capacity is about 120 000 t/a. The available capacity of the underground cavities is larger. The cavities currently approved by the state mining authority for waste disposal are sufficient for accommodating about 120 000 t/a for some twenty years. As a result of potash mining, a useful cavity volume of more than 3 000 000 m^3 is created annually; this space is suited for accepting at least 1 Mt of wastes.

A study has been conducted for appraising the long-term safety of the underground repository at Herfa-Neurode. In this study, the hazard potential has been considered from the standpoints of "rock mechanics", "hydrology", and "carbon dioxide"; any associated impairments of the repository concept have been ruled out.

Zielitz (Sachsen-Anhalt)

For the Zielitz potash mine, the regional planning procedure is currently in progress for the planned construction of an underground repository for problem wastes.

The underground repository at Zielitz belongs to Zielitzer Kali AG; the proprietor is Mitteldeutsche Kali AG. The planned underground repository is to be operated in conjunction with the mining of the potash deposit.

The mining claim is connected with the surface by the open shafts Zielitz I (806 m) and Zielitz II (740 m), as well as the ventilation shafts Zielitz III (425 m) and IV (429 m).

The Zielitz I shaft was excavated between 1968 and 1970; it is employed as hoisting shaft. The Zielitz II shaft was excavated between 1966 and 1969; it is employed for man haulage and material handling as well as for upcast ventilation. The hauling installation consists of a wide frame with a useful area of 15 m^2. The Zielitz III and IV shafts are designed exclusively for the purpose of ventilation and can be employed for man haulage only in emergencies.

The bedding horizon consists of sylvinite with layer thicknesses from 0 to 20 m; the average layer thickness is 7.3 m.

The mine structure selected for waste disposal purposes has a cavity volume of about 4 600 000 m^3. It was worked in a depth interval between 316 and 424 m during the period from 1976 to 1984. The waste disposal area can be isolated from the other fields.

Springen (Thüringen)

The Springen potash mine is located in the Werra potash district to the southwest of Eisenach in Thüringen near the border with Hessen. For the site at Springen the regional planning procedure for the construction of an underground repository for chemical toxic wastes has already been concluded. The initiation of the project evaluation procedure is currently in preparation. The owner of the planned final repository is likewise Mitteldeutsche Kali AG. The Springen potash mine (formerly Heiligenroda) is a relatively old mine; potash extraction was already in progress in 1914.

2.4 R&D Transfer

2.4.1 Selected projects of the GSF

Together with partners from industry, universities, and governmental authorities, the GSF-Institut für Tieflagerung has executed or begun a wide variety of projects for the final disposal of radioactive wastes. The results of these projects may be useful in connection with the underground disposal of chemical toxic wastes.

The titles of selected R&D projects are as follows:

- Rock-mechanical and geophysical investigations for exploring and monitoring final repositories in salt formations
- Hydrogeological investigations and long-term observations in the area of the Asse ridge
- Disposal and consolidation of weakly and moderately radioactive wastes in underground cavities
- Investigation of the stability of a final repository in salt formations
- Investigation of appropriate backfilling materials and development of techniques for filling cavities
- Dam construction in salt formation - experimental dam
- Filling and plugging of boreholes, drifts, and shafts in a final repository
- Geochemical investigations of the occurrence and behaviour of water and salt solutions in formations for final disposal
- Geochemical investigations for the case of "water and brine invasion"
- Long-term safety analysis for final repositories in geological formations

The Netherlands

2.1 Legal stipulations

2.1.1 Legal aspects of waste disposal underground

One of these days the political discussion has to end on the question if it is desirable to use the underground for waste disposal. Also is circulating for advise an extension of the minerules of 1964. This extension is formulated by the Ministries of Economic Affairs and The Environment. Till now it is only permitted to bring materials underground in a mine if they are needed in relation to the exploitation of the mine, or materials extracted together with the minerals e.g. formation water, rock.

The introduction of other materials underground is also necessary to use salt caverns as storage facilities for mineral oil and natural gas. Also for this reason the mine rules have to be extended. Only after publication in the State-Journal (Staatscourant) the rules have legal properties, until that time changes and amendments are possible.

In principle the new rules indicate that bringing down other materials (oil, gas, wastes) can be done only by the owner of the mine. His actions have to be in accordance with the minelaws and rules regarding the safety of the mine, properties at the landsurface above the mine (environment), and the working conditions of the miners.

This means that the mine owner has to set conditions for acceptability of the wastes. Also the Minister of Economic Affairs has to accept the waste for disposal with the consent of his colleage of The Environment.

Harmonization between the viewpoints of both ministries regarding the new mine rules has not yet been attained.

2.2 Characterization of wastes

2.2.1 Data collection and classification of chemical toxic wastes

2.2.1.1 Introduction

The registration of chemical wastes is limited to those materials of owners or producers that are in one of the classes mentioned in the law as

chemical waste and are to be handed over for treatment and/or disposal. The action of handing over to another party (a processor, collector or disposer) has to be declared to an institute on behalf of the government. As long as materials from production processes are stored on-site of the plant they are not registrated as wastes. In most cases they are known to exist. Reasons for this on-site storage are lack of disposal sites, not suitable forms for disposal, or are under study for recovery processes. In practice there is a reasonable accurate knowledge about the amounts of chemical wastes present and wastes to be produced in the near future. The increase in registration recently is mostly from small producers. An overview of chemical waste registration in the years 1988-1990 has been published in December 1991 (Basisdocument Chemisch Afval 188-1990). The comparison of the registrations during these three years gives also the possibility to comment the trends in waste production and the reliability of the data collected.

The classification of chemical wastes is based on the toxicity to the environment. The first step in law making -the chemical waste act 1976, decree 1977- was based on concentrations of toxic elements and compounds present in the waste materials. Also a number of processes are cited known to result in chemical wastes.

2.2.1.2 Chemical Waste Classification for Disposal

Actually three classes of wastes are in use abbreviated C-1, C-2, and C-3 according to the toxicity of the wastes to the environment. Originally the wastes were considered as final wastes after treatment for recovery of valuables or to produce an acceptable waste form for disposal (neutralization, solidification, non-reactive, etc.). Under pressure of environmental groups the disposals have to be considered as storage until newer and better techniques are available to recycle the wastes. This means storage at land surface with control, maintenance, and remedial action if necessary. According to the environmentalist view a non-retrievable underground disposal is not allowed.

For the actual situation it makes no difference: there is no underground facility available. Under the guidance of the Ministry of the Environment a public discussion is going on the theme "Is the deep underground suitable for waste disposal and is it desirable". Next to the ethical argument in the discussion is the growing pressure of the steady accumulation of waste.

The waste classes C-1, C-2, and C-3 contain typical the wastes also suitable for disposal underground in a saltmine. The yearly production amounts to about 200.000 tons. To be added are possibly the "historical" wastes originating from contaminated soils and stored wastes from older production processes. The collection of wastes for storage (disposal) has to go on until space in a saltmine becomes available for disposal.

In the Netherlands there is no saltmine in operation to the complete procedure to obtain the concession (ownership) for exploitation has to be started according to the minelaw of 1810.

2.3 Concepts

2.3.1 The total amount of waste available for disposal

The annual volume of waste to be disposed of then depends on two important parameters:

- Start of the mining project, i.e. the construction of the shafts
- Start of the disposal operations.

The construction of the shafts is considered the start of the mining project. The duration of the preceding legal procedures can not be estimated very precisely since part of the necessary legislation is not yet available.

The procedures are expected to take at least five to ten years. During this period exploration of the specific location considered for the repository may begin. Legislation will also influence the components and duration of the exploratory phase of the project. It is assumed that shaft construction may start in the year 2000.

With the available annual amounts of waste to be considered after 1990, it is clear that the amount of waste to be stored at surface in interim storage linearly increases. Every year of delay results in a larger volume of stored waste at the start of the project. Once construction of shafts and development of the mine has started it will take about 6 years at least before salt production may begin. Because of the operational separation between mining and disposal operations, a certain amount of cavities has to be created before disposal can begin. In this study, it is assumed that disposal of the waste in drums will begin 8 years and the bulk volume waste 10 years after the beginning of the project.

The cumulative amount of waste to be disposed of in an interim storage facility at surface is a result of the start of underground disposal and the lenght of the disposal period. It is clear that start of disposal in year 15 or 20 of the project necessitates more surface interim storage facilities. The annual production and disposal capacity of the disposal mines is also a result of the start of the mining project and subsequently the start and duration of the disposal operations.

2.3.2 Mining and disposal operations

The waste drums are collected in the El-containers of the subsequent waste category at surface. They are transported to the disposal level through the waste transport shaft. At the disposal level the containers are transported to the specific disposal gallery by trackless equipment.

The bulk waste is disposed of in large cavities, i.e. rooms. There are five successive phases in mining and disposal operations:

1. Room preparation for production
2. Production of salt
3. Room preparation for waste disposal
4. Waste disposal
5. Sealing of remaining openings

A general planning for a mine based on the expected amounts of waste in the Netherlands will be developed to demonstrate the magnitude of the operations to be performed. In the planning of the different disposal mines, the mining and disposal activities will be contemplated in more detail.

2.3.3 Consequences of disposal operations on the mine lay-out

The combined production of salt and disposal of toxic wastes asks for a suitable infrastructure underground.

Shaft capacity should be used efficiently. It is proposed that skip transport is planned in the exhaust air shaft and waste transport through the fresh air shaft. The latter asks for strict monitoring of the wastes for transport to prevent contamination of the ingoing air stream.

Waste and salt transport, as well as mining and disposal should be strictly separated from each other. This not only affects the mining ventilation system but also the underground routing of material streams. For the mining ventilation a suitable monitoring system is necessary along the transport routes and in the exhaust air ways and galleries. This, and separation of material routing may lead to extended infrastructure. This extension should be balanced against its purposes and use since the development is generally a cost intensive part of a mining project.

2.4 R&D Transfer

2.4.1 Introduction

The experience and lessons learned from the disposal of radioactive low and intermediate level wastes can be of profit for the management of toxic chemical wastes. Both types of wastes were disposed of in the earlier days in the way of shallow land burial or landfill. In both cases the isolation from the environment proved to be insufficient. Radwaste considered most dangerous, received the attention as the first one. Studies were started at laboratory scale to investigate the behaviour of radionuclides in soil. In a later stage the large scale natural systems - analogs - were taken for study subject. It proved to be not so easy to connect the short duration experiments with the very long term processes in nature. The scientific knowledge on very long term behaviour became more important with the decision in most countries to dispose in principle all radioactive waste deep underground. Safety studies seemed to be necessary until the last radionuclide has decayed. Since this proved to be no practical viewpoint the idea of an cut-off time was introduced. This means that the long-term is limited for most of the safety related processes to 10^4 or 10^5 years.

Beyond that time it has to be shown that no real dangerous situations will develop, but no detailed study is needed. But even this time to the cut-off is so long that short-term laboratory studies have less importance compared with the results from thermodynamic data on minerals. In nearly all cases wastes are produced and conditioned under conditions different from those in the environment of the final disposal place. This means that a rearrangement to a new stable situation will occur on the long time scale.

2.4.2 Long term Safety

At least twenty years have been devoted to study the predictability of a nuclear waste repository in a salt formation. Due to a better geologic knowledge the problems of diapirism and suberosion of a salt formation vanished from the timescale for serious effects on the slow decaying waste (cut-off time). The main danger to the formation is still the intrusion of water due to some voids inside the salt formation and an imperfect layer leaking groundwater in. To minimize the effect no more excavations are made than strictly necessary and at the end of the operational lifetime all space is backfilled, and dams and barriers constructed up to ground level.

The radiation doses to individuals calculated according to this scenario are smaller than the levels accepted nowadays.

In principle the same can be carried out for a salt production mine, but keeping in mind that the space to be filled or backfilled is orders of magnitude larger compared with the nuclear facility, the formulation of a scenario of events in the toxic chemical waste is much more complicated than in the nuclear waste. Chemically speaking the nuclear waste consists of only concrete and iron. The reactions with brine are predictable. Toxic-chemical waste is a complex collection still to be defined. Reactions and solubilities in brines have to be determined before the next scenario step can be performed: expulsion of the contaminated brine into the surroundings of the salt formation. The transfer through aquifers to the biosphere and the effects there are in analogy to the well developed programmes for radioactive waste.

Very long-term processes have to be assessed in another way. There is ample time for mineralisation of the wastes buried. Based on the chemical composition of the wastes the stable end products have to be calculated thermodynamically. According to recent views on salt-dome formation it is most probable that diapirism starts again due to a tectonic pulse in relation to crustal rearrangements, mountain building, etc.

List of publications

Mühlenweg,U., Brasser,Th.: Abfallentsorgung auf dem Hintergrund der Rechtsbereiche Atomrecht und Abfallrecht.- AbfallwirtschaftsJournal, Vol. 4 (4), pp. 315 - 328 (1992).

Title	:	Use of methods and programmes developed in nuclear field for treatment and disposal of toxic and hazardous waste
Contractor	:	NUCLECO S.P.A., SNIA Tech.
Contract	:	FI2W-CT91-0110
Duration of contract	:	from 01/01/1992 to 30/06/1993
Period covered	:	from 01/01/1992 to 31/12/1992
Project leader	:	F. Lo Giudice (NUCLECO S.P.A. - co-ordinator) V. Pellecchia (SNIA Tech.)

A. OBJECTIVES AND SCOPE

Aim of the research is to make a general overview on the industrial wastes (by the technical and regulation point of view) in order to identify toxic and hazardous wastes (THW) subjectable to be processed with methods or techniques up to now adopted only for low and intermediate level radioactive wastes.

B. WORK PROGRAMME

B.1. To select and evaluate THW groups, featured by an environmental impact involving particularly restrictive management rules similar to low activity radwastes.

B.2. To select the radwastes treatment and disposal techniques already tested and used.

B.3. To analyze the feasibility of converting specific kinds of THW into an inert form, with reduced volume and hazard, allowing a landfill disposal.

B.4. To develop the basic design of a pilot plant performing a selected process for THW treatment.

B.5. To study for the process : costs/benefits analysis, environmental impact, future experimental campaign with the pilot plant, interventions in-situ.

C. PROGRESS OF WORK AND OBTAINED RESULTS

This research has identified refuses containing asbestos (RCA) as the wastes more suitable for the compaction and immobilisation process, widely considered a good balance between technical and economical features for low activity radwaste management. In the second half of the year, an experimental campaign, pointed to verify the feasibility of the above mentioned process for RCA has been started and is still in process. In fact this activity has been shifted three months for reasons due to the availability of NUCLECO facilities, engaged for nuclear waste treatment. Results of the experimental tests will be used to set up the definitive input data for the RCA treatment, whose basic design and benefits/costs evaluation are the main targets of the present research contract.

State of advancement

For what concerns the above mentioned 2.2.1 and 2.2.2 points, the relevant activities have been performed, while experimental tests as per point 2.2.3, in real scale have started and will be completed at beginning of 1993. We must underline that these tests will interfere with normal utilisation of the nuclear facility; any time we must satisfy two main conditions: the availability of plant between, two nuclear campaign, and adequate decontamination of shredding and compacting confinement areas according to Health Physics which state adequate monitoring either for nuclear reasons as well as for asbestos free floating fibers counting.

Progress and results

Industrial (but not only) wastes are defined toxic and hazardous if the concentration of pollutant elements is higher than a value defined as limit concentration (LC). To follow this definition it is necessary at first to define correctly which are the pollutant elements and which are the sources of their production that means the identification of the industrial production processes by the chemical-physical point of view.

More precisely, this means that the residues of some particular production processes are suspected to be toxic hazardous wastes depending by the overcoming of the LC value.

The classification, according to the regulation, is very useful because allows to group the wastes produced in the European Countries in order to evaluate the total volume produced each year, the trend of production and the different capabilities to dispose the wastes.

Asbestos (as dust and free fibers) is one of the groups in which are divided the toxic hazardous wastes, and maybe this group represents one of the most consistent by the quantitative point of view.

Wastes containing asbestos can be produced by various kind of sources.

Generally these wastes can be divided in wastes coming from mining and milling activities, from manufacturing of materials containing asbestos, from the maintenance of a lot of industrial plants in which asbestos was used due to its behaviour in terms of thermal insulation or chemical resistance, from the demolition of structures (buildings, ships, railway carriages etc.) and finally from the consumption of a lot of products of domestic or industrial use.

Mining activities and the cement industry are the most relevant sources of wastes by the quantitative point of view.

In the light of the above mentioned concepts the first activity performed is related to the evaluation of entity of RCA produced and stored waiting for final treatment and/or disposal.

In Italy, for instance, this first step of work has identified a production of RCA ranging in the field of some tenths of thousands of tons per year, excluding refuses coming from mining activities which up to now have been collected in an amount of millions of tons.

These numbers give a significant idea of the problem relevant to RCA treatment and disposal, and justify the interest pointed to minimise the environmental impact and disposal costs.

To do that, the compaction and cement embedding of solid radwaste process has been considered the most promising for RCA treatment and successive disposal.

As consequence of above statements, it has been established a test programme in order to verify the feasibility of the process, in full scale by means of real RCA gathered from the decommissioning of obsolete plants where asbestos has been removed.

RCA collected in plastic bags and delivered to NUCLECO facility in metal drums, have been previously shredded and then compacted using two different pressing equipment available in the plant:

1 - vertical four columns heavy load press (1500 tons maximum);
2 - horizontally mounted double stroke press (80 tons).

First results show that the only shredding reduces the volume of RCA by a factor 2, while the following compaction step, depending on the pressing load, provides a further reduction by a factor 3÷5, so attaining a total Volume Reduction Factor (VRF) ranging between 6÷10 and a corresponding increase of the volumetric mass (initial = 0.2 kg/dmc, 0.4 kg/dmc after shredding up to an average value of 1.2 kg/dmc after pressing).

This result is quite positive overriding the corresponding results obtained by compacting other categories of solid wastes, where normal values of VRF are in the range of 3÷5.

On the other hand the negative result obtained is the very low consistency of compacted RCA, which makes in fact quite impossible to handle the pressed material for the following overpacking operations.

Many tests have been carried out by increasing load pressures and varying the RCA packing before pressing.

After these process steps the compacted material has been transferred in concrete overpacks and then embedded in a mortar matrix with the same recipe as duly qualified for radwaste embedding.

During the above process steps, done in nuclear containment conditions, have been taken air samples in order to evaluate the contamination due to asbestos free fibers. The results of the analysis gave very high values of contamination justifying the choice to perform all the operations inside containment rooms (tent or containment box).

Also the final step of embedding has been carried out using such containment criterion.

The final result, in terms of volume reduction, shows a total VRF about 3, in spite of the handling difficulties a/m which have produced a not negligible increase of volume after compaction partly due to the spring-back effect and partly due to the collapse of pressed material during the overpacking.

The next step, after a 28 days curing period will be the cutting of the final manufacts, in order to check the embedding effectiveness to retain asbestos fibers, which is the most important parameter to characterise the final product for disposal towards a less restrictive dump category.

It is foreseen to get the complete data set within the first

quarter of 1993. The analysis of these results will allow to set up the input data for the final choices to implement the basic design of the plant.

Anyway, the data already gathered during experimental campaign show that it is very difficult to attain at the same time the best performance in terms of volume reduction and quality of embedded material (according to the preliminary concepts already developed at basic design level without experimental check). This means that after completion of cost/benefits preliminary analysis, it would be necessary to make a choice between two different paths:

1 - embedding RCA in an inert matrix, declassifying it, in order to dispose the waste in low category dumps (less expensive and with less environmental impact too), in spite of an increase of the volume and weight of the manufacts due to the embedding.

2 - only high volume reduction in order to minimise the disposal costs (based on the waste volume) in higher category dumps.

Title :	Study of a communication strategy aimed at achieving a possible better understanding of the consequence of radioactive waste management in a well defined group of public
Contractor :	ONDRAF/NIRAS, Belgium
Contract N° :	FI2W-CT90-0036
Duration of contract :	24 months : from April 1991 to March 1993
Period covered :	January - December 1992
Project leader :	V. Vanhove

A. OBJECTIVES AND SCOPE

Starting from the hypothesis that the information of the public on radioactive waste management is confronted with prejudice and ignorance, the study tries to establish whether it is possible, by working out and disseminating an argumentation that is well adjusted to a specific target group, to reduce obstacles to information and to induce the public to understand and accept the approach of ONDRAF/NIRAS.

The study consists of two phases :

1. Identify the target : determine the orgin and state of the knowledge of the target group on the subject concerned; work out documentation and arguments by following the general argumentation of ONDRAF/NIRAS and by adapting it to the target group;

2. Apply this argumentation to the target group and register the resulting modifications of public opinion.

B. WORK PROGRAMME

The following planning has been worked out :

1. definition scope project

2. determination communication model and plan

3. development prototype pedagogical package

4. definition concept and content information centre.

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

During the period considered, the results of the opinion poll conducted in the autumn of 1991 were used to define the scope of the project and to determine the communication model and plan that will serve as a basis for the further development of the project.
The first steps were taken to develop a pedagogical package, the structure, form and content of which have been determined.
Preparations were also made to define the concept and the content of an information centre tuned to the pedagogical package and, like the other information, intended to inform 15-to-18 year old students.

Progress and results

1. The determination of the communication model

The results of the first phase of the study, i.e. the qualitative attitude survey conducted on a representative sample of the target group (15-to-18 year old students) completed with individual interviews with teachers from various disciplines, were used to construct a communication model that will serve as a basis for the further development of the project.

Main results of the opinionpoll

1. The survey and the discussions have revealed that there is no real demand for information on the issue. The lack of interest requires an organized and structured framework within which the issue can be dealt with. Schools can provide this framework.

2. Owing to the lack of interest and specific expectation, interest must be stirred. School management and organizing authorities should be contacted for this purpose.

3. It appears from the survey that the content of the information should cover the following five aspects : technical-economic, humanitarian, political, technical and deontological aspects.

4. The public targeted by this study should be as broad as possible, this means that the communication strategy must not only be focused on the elite of the future scientists. Other education levels and disciplines should have access to the information. The actual goal is indeed to provide youngsters with keys to a better understanding of the issue, with a view to changing their opinion and attitude.
   Information should be provided by experts who are confronted daily with the issue.
   The project must therefore be organized jointly by pedagogical experts (teachers), experts (authorities, scientists and ONDRAF/NIRAS in its capacity as expert in the field of radioactive waste management).

5. Direct confrontation with or visual and on-site immersion in the daily reality of the issue is considered to be the best experience.

6. Dissemination of information should be as wide as possible. The study should be used at national level.

7. Information on the various aspects of the issue (technical-economic, humanitarian, political, technical and deontological) is essential.

8. The objective is to bring about positive change in the students' opinion and attitude towards radioactive waste management.

Global framework

1. It was found that producing documents only is considered inadequate. Youngsters have a need for participating in the experience of experts who are confronted daily with the reality of radioactive waste management. The intervention of an expert lends credibility to the information.

2. Immersion in the daily reality of management lends more value to the information. Visiting a specially designed information centre and the processing facilities is of immense importance from the point of view of insight and conviction (immersion in daily reality).

3. The scope of the project is determined by the budgetary, functional and human framework.

Communication plan

Starting from the structured and organized framework provided by the school environment, the communication plan is executed on four levels.

1. school management and organizing authorities
2. teaching staff
3. students
4. students and teachers

2. Form of the project

The project developed within the scope of this study consists of a pedagogical package, composed of documents and audiovisual material. The project is focused on visual and on-site immersion in the daily reality of radioactive waste management.
For this purpose, an information centre is being equipped on the site of BELGOPROCESS, the industrial subsidiary of ONDRAF/NIRAS.
The initiative was taken by ONDRAF/NIRAS, in its capacity as expert in the field of radioactive waste management. The actual project is being developed in cooperation and in consultation with various experts, i.e. teachers for the pedagogical aspect and scientists/authorities for the scientific and technical matters of no immediate interest to ONDRAF/NIRAS.

The pedagogical package will be composed of:

- an introductory document intended to arouse the interest of the school management and the organizing authorities;
- a pedagogical manual for the teachers;
- an introductory videotape placing the topic in its social context;
- an introductory document for the students, to be used in school;
- visual and on-site immersion in the information centre in Dessel where visitors will be directly confronted with the management of radioactive waste;
- reference files for the students;
- a feedback file for ONDRAF/NIRAS (optional).

2.1. Description of the pedagogical package

a. File for organizing authorities

Owing to the lack of interest in the issue and the absence of particular expectations with regard to the information's content, attention and interest must be aroused, in the first place on the part of the school management and the organizing authorities.

b. Pedagogical manual

A manual will be provided to the teachers telling them how to use and apply the pedagogical package, and dealing with the various aspects of the issue.
The manual will provide the teacher with additional information and possibly also exercices which he will be free to incorporate in his teaching package.

c. Introduction of the issue

In order to introduce the issue to the students, the pedagogical package will contain a videotape of 15 minutes and an introductory document "Handling radioactivity", which will prepare the students for a visit to the information centre and the processing facilities of BELGOPROCESS.

Introductory videotape

This videotape is intended to introduce the issue to the students, to raise questions, to draw their attention and to give them food for thought. It raises questions, but does not answer them.

Introductory students file "Handling radioactivity"

This file is introduced at school, to prepare the students for their visit to the information centre in Mol-Dessel and the processing facilities of BELGOPROCESS, where radioactive waste management is explained in more detail.
The objective is to familiarize the students with the phenomenon of radioactivity and with its daily applications, i.e. to demystify the phenomenon by providing the keys for a better understanding.

d. Reference students files

After visiting the information centre in Mol-Dessel, where experts will explain radioactive waste management in an interactive and visual manner, the students will receive two reference files summarizing in a comprehensible manner the information provided during the visit.

Students file II "Managing radioactive waste"

This file gives a brief description of what is currently being done in Belgium with the radioactive waste produced, more particularly with regard to processing/conditioning and storage.
The file goes more deeply into the management cycle of radioactive waste.

Students file III "Disposal of radioactive waste"

This file, which is also a reference file as a reminder of the visit, sketches in broad outlines the ongoing research and development activities as well as the envisaged solutions.

e. Feedback file

Through an optional "assignment" which could be carried out in class after visiting the information centre, the youngsters are incited to voice their opinion on the issue. This file comprises a limited survey to gauge whether the visit has changed the youngsters' attitude towards the issue.
There is a possibility of using role-playing in which the youngsters would play specific parts.

2.2. Information centre

An information centre, specially equipped to familiarize the youngsters with the management of radioactive waste and to achieve understanding of the issue, is being realized in Mol-Dessel on the industrial site of BELGOPROCESS, where the processing and storage facilities for conditioned waste are located.

This information centre, which will be developed in an existing building on the BELGOPROCESS site (in the former cafetaria of the EUROCHEMIC reprocessing plant), is the epicentre of the project.
Visual and on-site immersion in the daily reality of radioactive waste management will benefit the credibility of the information and help to retain the students' attention and interest.

Concept of the information centre

The concept was chosen on the basis of the communication plan. This means that the information centre is developed around three modules.

Module I : Handling radioactivity
Module II : Managing radioactive waste
Module III : Disposal of radioactive waste (future solutions)

During the period considered, a limited invitation to tender was sent out to eight Belgian design offices.
Finally, a design office from Ghent, Bailleul, has been entrusted with the design and the realization of the modules for a total amount of 8.900.000 BEF (excl. a large cloud chamber, estimated at 1.950.000 BEF). This office has been chosen because the concept proposed links up well with the global project and is expected to yield the anticipated results.

The concept has just been decided on.

Priority target groups

The information centre is in the first place intended to familiarize 15-to-18 year old students with the management of radioactive waste with a view to changing their attitude and opinion towards the issue. Another priority target group is the local population, living in the vicinity of the industrial processing facilities of Belgoprocess. And of course, the information centre will also open its doors to all persons interested in this matter.

Accessibility

The information centre will only be accessible on written request.

Visit

a. Objective

The target figure is two groups of 100 people per day. This comes down to four visits of 50 students (1 bus) per day or two visits every half day.

b. Programme

. welcome (20 minutes), consisting of :

a videotape of 15 minutes to bring all visitors on the same level of understanding for an optimum proceeding of the visit;

division of the whole group in three smaller groups (max. 15 persons), each accompanied by a guide to shepherd them through the visit;

. one hour of interactive work on the student files II and III;

. limited visit, per bus, to the processing facilities on the BELGOPROCESS site (half hour);

. debriefing and conclusion of the visit (max. 15 minutes).

c. Organization

To improve its efficiency, the visit will be conceived as a guided explorative trip through the management cycle of radioactive waste. The groups will be limited so that individual questions and interests can be dealt with to the greatest extent possible.
This approach emphasizes the interaction between guides and visitors and ensures that the message gets across.

To retain the youngsters' attention and interest, very distinct atmospheres have been chosen for the development of the various modules, and the design and use of the various materials. Moreover, the modules will be strictly separated from each other.

Title : Information of the public in the field of decommissioning waste
Study of strategies and means for specific information

Contractor : CEA Saclay - Direction du Cycle du Combustible (DCC)
Contract N° : F12W-CT90-0043
Duration of contract : June 91 - May 94
Period covered : January - December 92
Project leader : Mrs. Danièle Gerster

A OBJECTIVES AND SCOPE

DCC/UDIN is the nuclear dismantling installations unit of CEA and manages most of its waste. The nature and importance of the waste justifies public information. UDIN is in a good position to transpose and transmit technical and economical information.

The first step of the work aims at : searching and defining a good media dissertation and realizing a pilot operation of communication.

The results expected will form a practical contribution to solve sociological problems issued by waste management, whether they be hazardous or not.

The economical benefits expected from this information will be tied to human analysis, positive and intelligent, in solving conflicts related to waste management in the European Community.

To answer public needs for information, several partners were selected :

- University of Paris-Orsay to translate technical information into common ("popular") language
- A group of sociologists explore and explain the fears and hopes of the public.
- A movie maker skilled in technical, didactic and TV films.

B WORK PROGRAMME

The programme of the study is approximately structured according to the following steps :

B1: Selection of partners, define basis of discourse and iconographic data ; evaluation of application to actual dismantling plants (e.g. : G2-G3, Rapsodie)

B2: Analysis of similar actions evolving in other fields ; investigation of results, definition of the basis of the discourse.

B3: Investigation of different fields ; selection of targeted public ; acceptance of such a public ; approach and motivation of (media) "atypique" persons and evaluation of their reactions to the proposal discourse.

B4: Methodology of pilot operation : study of original communication charter ; meetings with support producers.; contacts with media.

B5: Development of adaptation operations and validation of the elaborated processes.

B6: Final Report with global recommendations. Drafting of Annexes according to the discourse and transposable actions.

C. PROGRESS OF WORK AND OBTAINED RESULTS

STATE OF ADVANCEMENT

A large part of 1992 was devoted to analyzing the context of the study. An attempt was made to draw conclusions from the controversy in France concerning radioactive waste, to describe the viewpoints of those people involved at the local and national level, and to come to a preliminary opinion and thoughts on the mechanisms determining this opinion in a conflictual situation. The role of communication in risk management has also been studied, the goal being to know why, over and above information, communication is necessary when, beyond the technical (knowledge), legal (regulations) and economic (the market) approaches, politics becomes an issue? And if, when risk is the question, is it really a question of risk (and not of some large-scale debate on society)? Lastly, a preliminary study was made with a view towards laying down wording concepts for information documents.

PROGRESS AND RESULTS

1 - Bibliographical study in various countries

According to the literature, no special information programs dealing with dismantling wastes seem to exist.

77 people were questioned (outside of France), all specialists in nuclear communication or dismantling in Europe, Canada, USA and Japan (50% of them answered). Twenty five answers deal explicitely with communication. Several brochures, magazines and journals were attached. It seems that this material is directed more at elected officials, journalists or political authorities than the general public. The actions mentioned are conventional: conferences in associations, local meetings, press meetings, television and video programs, toll-free telephone number, ... The comments received bring out three major lines : dismantling is essentially a problem of waste ; the economic factors may be important locally (loss of jobs, of revenue) ; communicating with the public through structured groups, local representatives, the media, is unavoidable.

2 - Analysis of the controversy

The controversy concerning six radioactive waste disposal sites in France has been analyzed.The analysis was made based mainly on the local press which rather faithfully describes everything that happens in the communities involved.

For the four underground laboratory sites, the controversy was triggered by the announcement that it was possible that the region be chosen for an underground laboratory, and then for the installation of a high activity radioactive waste disposal. To reach its goals, the "disposal" industry must convince or appeal to the largest number of key people who may be considered neutral at the start of the action. These authorities are those with whom discussion, or even negociation, is possible. They are mainly elected officials, industrials, craftsmen, business people, as well as salaried employees, (all of whom may be represented by unions), media, other authorities who may play an important role as a relay of public opinion through their reputation or their position as doctors, teachers, lawyers, religious representatives, etc. All environmental defense associations are anti-nuclear. Questioning the choice of nuclear and its industrialization are part of their dogma. Therefore, from the very start of the action, they must be considered a major opponent with which negociation will prove very hard if not impossible.

In the prevailing controversy, the assertions exchanged essentially involve:

- technical criteria: what are the risks involved? what technical solutions are feasible to avoid these risks? can the waste continue to be stored on production sites? what are the alternatives if any? etc...
- economic criteria: what economic impact will the project have on the communities or the region? will the positive impact outweigh the negative impact? ...
- political-institutional criteria: are the fundamental principles of democracy respected? is the information provided unbiased? can a governmental agency be trusted? shouldn't the role of those at the origin of waste production be reconsidered? ...

But for any of the parties to change their opinions, these arguments may play only a secondary role. The adversaries will also bring in the range of symbols and values. Emotion and gut feelings will be appealed to. The adversaries will either be valorized or discredited, the problem of waste will either be dramatized or played down. The risks perceived and the credibility of the main protagonists then appear as the major stakes in a controversy, the result of which may depend more on psycho-sociological factors than on the technical reliability of the information or the arguments presented. Nuclear waste provides the opportunity to overthrow the powers that be and, co-relatively, the policies and solution that were only the expression of a modus vivendi and not of a public consensus. What role does information have in such a debate if it does not benefit from communication networks?

3 - Interviews of dismantling authorities

The points of view of the different dismantling authorities have been gathered and analysed through an inquiry made in Marcoule, a pilot region for dismantling in France, after consulting with some nationally reknowned nuclear authorities. Those people interviewed were mainly representatives of associations, teachers, local elected officials, union leaders, industrialists (including nuclear plant operators), and representatives of the administration.

Marcoule is the dismantling site for two graphite-gas reactors, G2/G3, used in the production of nuclear electricity and materials for defense programs. A very slightly contaminated scrap metal melting furnace has been installed inside the very G3 reactor containment. The controversy concerning this operation results from the planned re-use of very low radioactive ingots thus produced. Detailed analysis of the answers received brings out some predominant ideas:

- information concerning large industrial projects is one of the facts of life in our highly industrialized democratic societies. It is considered an indispensable element of technological democracy, especially where potentially dangerous industries are concerned.
- dismantling nuclear facilities and the resulting low activity wastes is a particularly sensitive subject in the eyes of the public since, although it is indeed a question of very low radioactive wastes, they are nevertheless "nuclear". Without a doubt an information campaign on this subject is opportune, as the inquiry has shown. But before taking any action, it is important to examine not only the content of this information and the media used, but also those to whom the information is addressed as well as the vectors used.
- the data gathered clearly shows that, as a first step, the information should be directed not at the general public but rather to relays of opinion, often poorly informed, even among nuclear operators (even if they consider that the information has already been satisfactorily communicated and that some information must not be released outside the company such as whatever concerns exemption thresholds and more generally, regulations).

- to be credible, the information addressed to the "general public" must not come from a single source, especially if the operator is the source. Experience in other fields has proven that information coming from groups that represent diversified interests was perceived as being more reliable than that coming from a single source.

Any information campaign on the dismantling and waste theme will provide the advantage of presenting the issue in precise terms and bringing about a democratic debate.

4 - Analysis of particular documents

- The Le Déaut report

Mr. Jean-Yves Le Déaut, then President of the Parliamentary Office for the evaluation of scientific and technological choices, was, in 1990, put in charge by the National Assembly of a report on the management of very low radioactivity waste. The interest of the French public opinion (and consequently, their elected officials and political authorities) was aroused in 1990 by a local press campaign against the rehabilitation of a storage site for very low radioactivity wastes and residues coming from a uranium ore processing facility dismantled between 1970 and 1979. The writer interviewed, most often during public meetings, more than 70 people from different Ministries (environment, health, labor, equipment, industry, ...), CEA, COGEMA, ANDRA, labor unions, "anti-nuclear" associations, European Communities, etc. He came to several conclusions:

- no exact definition exists, as yet, of the notion of "noxious radioactivity" and it is difficult to communicate on orders of magnitude for the assessment of this radioactivity;
- current French legislation is abundant and confused (613 pages in the Journal Officiel), rife with successive addenda. Furthermore, the operators do not apply this legislation, they "self-censure";
- an exemption threshold must be set up (2 Bq/g in alpha) and two additional types of specialized disposals must be created (one for waste from 10 to 100 Bq/g in beta/gamma, the other for radium-bearing wastes);
- epidemiological studies on the effect of low doses must be developed.

It may be mentioned that, on all these subjects, the issues of information and communication are both of paramount importance... and extremely difficult!

- The French Press

We have not analyzed the very many press campaigns that have been launched in France on low activity wastes and their disposal. Those cases that have been dealt with only rarely explicitely refer to dismantling (debris coming from the demolition of laboratories or plants and used as filler for roads for example). The other controversies regarding dismantling passed on by the Press concern the re-use, once considered unrestricted, of scrap iron and other very low activity metals or materials.

In mid-September, CEA organized a trip to Marcoule for the Press on the theme of dismantling and of the future of the resulting materials, taking the example of the G2/G3 reactors mentioned earlier. A moratorium in fact was set up: no more very low activity material will come out of CEA centers, even for controlled disposal. As soon as it is no longer a question of reusing very low activity materials, the dismantling operations are better understood on the technical level, and even on the social level since it does not imply a site shutdown and the subsequent loss of jobs. The re-use of surfaces thus released for the construction of future nuclear facilities is even, in some cases, presented as obvious, preventing the nuclearization of new sites.

The dismantling shown in situ remote from any crisis context, "cold bloodedly", as an operation concerned with the safety of workers and the environment based on proven techniques, manageable amounts of waste and acceptable costs, benefited from an overall positive image.

5 - State of Opinion

A national inquiry on nuclear was made in France in March 1992. The results of specific questions on waste and dismantling issues are analyzed here, as are the answers concerning nuclear information and communication.

Waste is the second argument against nuclear, ranking just after Chernobyl. Among the subjects regarding environment of most concern to the French, nuclear waste ranks second after the ozone layer but ahead of chemical waste, deforestation and nuclear power stations (5th place).

The disposal of radioactive waste ranks 5th in French interest in nuclear, after measures in case of accident, risks involved in power plants, impact of radioactivity on man and effects of the facilities on the environment.

To the question "whom do you trust in the issue of radioactive waste?", ecologists rank first, followed by "nobody", and the Ministry of Environment (Brice Lalonde, the previous French Minister of Environment was a former anti-nuclear militant from way back. He was replaced by Mrs S. Royal whose reputation comes from her local opposition to underground laboratories involved in the study of radioactive waste disposal). ANDRA and CEA come next. Industrials take the very last place. To the question "should we re-use the metals from nuclear facilities that are dismantled?": 35.6% answered "do not agree", 18.6% "agree", 18.2% "maybe" and 27.6% gave no opinion. To the question "when radioactivity is very low, it is not dangerous": 31.6% answered "do not agree",34.9% answered "agree", 22.8% answered "maybe" and 10.8% gave no opinion. Lastly, when French people were asked which sources of information tell the truth about nuclear, the ecologists come in first, followed by consumer associations, doctors and the CNRS. At the top of the least credible sources came politicians followed by unions and journalists.

6 - Communication and risk management

In collaboration with CNRS research scientists and the "Commissariat Général au Plan", this theme is under preliminary study. It is shown why the discussions on risk can be understood only if they are placed back successively in the context of the debate on energy choices (here, nuclear), and then of broader debates that shake society.

An attempt has been made to describe the social process whereby, at a given time, a risk takes on importance. The risk that may threaten populations (or future generations) constitutes, for the citizen-individual not directly concerned by the activity generating the problem, a means to communicate with others on subjects having only a remote relation with the risk involved, but with which he is deeply concerned (his children's future for instance). To be able to hope to sort this out, through the messages delivered, progress must be made in the way how to question the public and how to answer to this public. What does the public really want when it declares unbearable a residual risk deemed reasonable by experts?

For nuclear, the simultaneous analysis of the risk and the activity generating the risk leads to this conclusion: the risk declared to be perceived, insofar as it expresses the opinion held concerning the activity, cannot be dealt with as a request addressed only to the safety system. It must be placed back in the framework of a wider social play where the advantages of the potentially dangerous activity may counterbalance the disadvantages.

7 - Working out wording concepts

A study was made with a view towards working out the contents of public information on the dismantling of nuclear facilities and the resulting wastes, without prejudicing the media used to disseminate this information.

A first step drew up an inventory of the possible elements that could be used, based on the information provided by dismantling specialists. The areas covered are: the facilities to be dismantled, general dismantling regulations, a comparison of the different strategies, possible re-use of the site, solutions for packaging and storing waste, the inventory of the facility's radioactivity, available technologies, surveillance and maintenance measures, the future of the materials. These elements have been structured: the technical, economic and social stakes have been brought out. It was made evident that dismantling resulted from an organized strategy and not from the pressure of events. If there is one fundamental notion to be put forward in communication with the public (which so often shows an irrational fear regarding nuclear), it is that those people responsible for dismantling have a rational conduct (which is expressed particularly through strategies).

The second step consisted in determining, in the light of sociological and bibliographical studies, the place and treatment that will have to be reserved for each element defined in the first step so as to organize them into a coherent discourse. The amount of information is such that it is necessary to sort it out, especially with respect to what is known of the target-public demands. However, we must not neglect to provide information on essential points the implications of which may not have spontaneously perceived by the public. But there is not only one public and first of all the goals targeted must be defined when addressing each one of these publics and, for each one, work out a specific content, choose the best adapted media and find the most efficient way to disseminate this information.

8 - Continuation of the program

To continue the program, the study will be developed in two directions:

- the role of in-house communication and of the personnel,
- the use of the image as information media.

The first information vector, especially locally, is the personnel of a facility. It is indispensable that this personnel have a minimum of knowledge about the strategy applied in his/her field of activity, the techniques used up and downstream of his/her own work, and the stakes involved by the communication in the sector under consideration... and that he/she have the appropriate supports to transmit this information.

For this purpose, an in-house inquiry is necessary. An attempt will be made to draw out a methodology for training personnel in outside communication, which may be transposed to sectors other than that of dismantling waste.

At a time of image and television supremacy, the video media is unavoidable. A concrete example (a video production) will be given.

In parallel, the preparation of a written reference document at several levels of technicality on dismantling and its wastes will be pursued.

Title	The evolution and implementation of a public information strategy on radioactive waste management
Contractors	GCI London
Contract n°	FI2W/CT90/0074
Duration of contract	From July 1991 to June 1993
Period covered	January 1992 - December 1992
Project leader	Michael McAvoy

A. OBJECTIVES AND SCOPE

The Radwaste Plan of Action, now extended to 1999, requires that the public has to be informed of developments in radioactive waste management in the European Community. Member states and the European Commission should provide the public with regular information regarding radioactive waste management and storage.

Aims & Objectives

The aims of the CEC radioactive waste information programme are :

- To provide a firm basis for the evolution of Community policy on the public information aspects of radioactive waste disposal.
- To enable the communications lessons learned by individual Member Country authorities to be shared across the Community.
- To provide a resource base of independent and authoritative communications materials to be used in the communications programmes of Member countries.

Cooperation with other contractors

A key element of the radwaste programme is to enable the lessons learnt by those responsible for public information to be shared amongst the national agencies to enable the development of "best practice". A seminar was organised in Brussels in June 1992, at which radwaste communicators from the national agencies described their public information strategies and experiences.
Participants included : ONDRAF/NIRAS, ENRESA, Nirex, BNFL, NAGRA, Swedish Nuclear Fuel and Waste Management Co.

B. WORK PROGRAMME

1. A review of European Community public information policy

2. Information exchange between national agencies to encourage best practice.

3. Development and production of authoritative information materials.

C. PROGRESS OF WORK AND OBTAINED RESULTS

1. A review of European Community Public Information Policy

Since the introduction of the Radwaste Plan of Action in 1992, the foundations for developing a firm Community policy on radwaste communications have been established.

An initial report by consultants explored the following :

- The extent and scope of current opinion research in the EC
- Strengths and weaknesses of the radwaste and nuclear industry's public information strategy
- Recommendations for a role for the CEC
- A review of young people's knowledge of and attitudes to radioactive waste agencies
- A survey of relevant information materials available for schools and teachers' use
- Suggestions for developing a flexible teaching package which could be incorporated in various EC syllabuses for the 14-16 age range

2. Exchange of Information between member agencies

In order to share the communication experiences of member country national agencies and encourage "best practice", a public information seminar was organised in June 1992. Representatives of national agencies outlined the range of activities employed in communicating about radwaste. A proceedings document of the event was produced and a questionnaire has since been compiled and sent to radwaste communicators to further assess communications activities.

3. Production of Authoritative Information Materials

In addition, a number of authoritative and credible information materials have been produced :

- A leaflet entitled "Managing Radioactive Waste", which provides background information about radioactivity and the management of radioactive waste in the European Community. The leaflet has now been produced in English, French, German and Dutch and has been distributed to all national agencies.

- A video entitled "Securing the Future" provides an overview of the work carried out by the Commission and member agencies in providing safe and secure storage and disposal of radioactive waste. The video examines the variety of storage and disposal facilities throughout the European Community and explores the sources and different categories of radioactive waste, both natural and man-made. The video has been distributed to national agencies for use in public information programmes.

- A detailed report entitled "Managing Radioactive Waste in the European Community". This brochure provides background information about radioactive waste, including sources and categories, regulation and control, safety measures and R&D work, in addition to a detailed overview of the role of the Commission in European radioactive waste management. The brochure will be distributed to all important European and national opinion formers, specifically those with an interest in the environment and energy.

- Exhibition panels to be used at CEC radwaste events, which includes background information about radiation sources and the role of the Commission in ensuring that radioactive waste is managed to the highest standards.

A public information campaign to support a proposed national deep repository for low and intermediate level radioactive waste

Contractor: BNFL (UK) - Institut SYMLOG (F) University Surrey (UK)

Contract No: F12W/CT91/0105

Duration of contract: 1 November 1991 to 30 April 1995

Period covered: 1992

Project Leaders: B. Williams (BNFL - coordinator)
C. Mays (Institut Symlog)
P. Allen (University Surrey)

A. Objectives and Scope

The primary objective of the campaign is to gain support in Cumbria for a radioactive waste repository at Sellafield through the dissemination of factual information in various forms to the public.

Opinion polls will establish an initial baseline level of support which will represent an appropriate yardstick for evaluating the effectiveness of the campaign as it progresses. Analysis and comparison of data gathered from subsequent polls and interviews will enable change in support to be measured.

A second objective is to generate information in a suitable form for detailed consideration by other European Community Member States by assisting them to produce similar programmes of their own. The comparison of the baseline opinion data in the United Kingdom and France will be the principal method for fulfilling this objective.

B. Work Programme

This involves opinion surveys, the development and production of appropriate publications and videos, the development of exhibition material and display facilities and informing the public of this new material. The main components of the campaign are:-

i. Opinion Research

a. The University of Surrey Robens Institute would conduct detailed research work, obtain baseline measures of public understanding and reactions to the siting of the Repository at Sellafield and identify particular concerns by conducting a survey in Cumbria.

b. The Institute would evaluate the various publicity media available for the BNFL information campaign and advise on the most effective methods to communicate to the public.

c. The Institute would also conduct follow up surveys to assess the effectiveness of the campaign in terms of changes in the knowledge and attitudes of the Cumbrian people.

ii. International Comparisons

a. The Institut SYMLOG de France would carry out detailed research work involving comparisons of Cumbrian public opinion data and French public opinion data concerning the siting of a radioactive waste repository.

b. The Institut would compare the public opinion data with the interview data from appropriate officials concerned with radioactive waste management in France and the UK.

c. The Institut would also compare institutional approaches and the extent to which their policies are appropriate, given public views.

iii. Publications

Two brochures would be produced aiming to provide the Cumbrian public with background information on the need for and purpose of, a radioactive waste repository.

The first one, produced early in the campaign, would generally describe the nature of the waste, the proposed area selected and the impact it would have on the community.

The second one would be produced nearer the time of the public planning inquiry and explain the findings of the investigation, the proposals and forthcoming steps.

iv. Videos

Two videos would be produced and made freely available to the public. The first will cover geological investigation and be used to the end of 1993. The second would run during the public planning inquiry and explain the findings of the investigation, the proposals and forthcoming steps.

v. Exhibition Material

The main exhibition material would be situated in the Sellafield Visitors Centre which is now well known as a major tourist attraction.

a. Interactive Video

This will be a principal element of the programme designed as a system to promote an informed attitude towards nuclear waste management. Most of the general public would use the product unattended, irrespective of age or educational ability. It will be necessary to refurbish part of the Sellafield Visitors Centre to incorporate the interactive video.

b. Portable Display

A portable display will also be produced comprising a lightweight scissor unit housed in a tube. The face of the display will measure about two square metres when expanded. This will be used at public meetings.

c. Borehole Exhibition

A small exhibition would be located in a Portacabin at the central borehole site and will be designed to make it suitable for VIP visitors.

vi. Informing the Public of New Material

Regular public information notices will be placed in local and regional newspapers to advise the general public where information on the repository can be obtained.

C. Progress of Work and Obtained Results

1. REPORT BY UNIVERSITY OF SURREY ROBENS INSTITUTE

a. Tasks

The tasks allocated to the University of Surrey Robens Institute, and carried out during the period, were to design and develop a questionnaire, commission a survey using this questionnaire to obtain baseline measures of knowledge, attitudes and beliefs with respect to the proposed Repository, and analyse the results with the aim of providing a background to the information campaign.

The questionnaire also had the aim of identifying any particular concerns of the population and was to be designed to permit direct comparisons between the situation found in West Cumbria and that of French people, as revealed by national opinion polls.

Five main criteria were used to form the basis of the questionnaire. The first concerned the affiliations of the population in terms of geographical area, commitment to residence in that area, employment in the nuclear industry and/or membership of ecological groups. The second concerned information in terms of self-attributed knowledge, use of information sources and information needs. The third was to gauge support for the Repository. The fourth was to measure levels of perceived confidence and trust in the main institutions concerned with the development and the fifth was to examine confidence in the decision procedure.

b. Implementation

French survey results were obtained in the Spring 1992 and the Cumbrian questionnaire was produced. The survey was conducted in July and August 1992 and comparisons between its findings and those from French surveys have subsequently been conducted by Institute SYMLOG de France. Consequently some information on the questionnaire responses can be found in the SYMLOG report.

The survey area was divided into three zones. The first closest to Sellafield and the third furthest away. Zone 1 comprised the West coast, from Maryport to Millom, including Cockermouth. Zone 2 comprised Barrow and Lakeland whilst Zone 3 was the M6 corridor including Carlisle and Penrith. The survey was weighted in favour of the coastal zone (Zone 1); twice as many respondents were sought in this zone compared with the others. The sample was representative of the population as a whole with respect to age and sex composition.

c. Summary of Results

One very important and unusual characteristic of the population proves specific to this area, namely the considerable proportion of people who are employed in the

nuclear industry; most of them for British Nuclear Fuels. Having some employment connection with the industry, either directly or through some other family member, is obviously likely to be a major factor affecting beliefs, knowledge and attitudes towards a development like the proposed Repository. The survey found that a total of 31 per cent of the sample had some employment connection with the industry through one or more family member.

Since there is a stronger concentration of employees in the areas closest to Sellafield the sample found few employees in the outer zones. These latter areas therefore constitute a useful 'control' element for the effects of employment in the industry.

The survey also found systematic differences in the stability of the population. The analysis was based on questions about the length of time people had resided in their area and about their intentions with respect to moving from the area. A large majority had been resident for fifteen or more years and this proportion was greatest in the coastal zone. The people living closest to the proposed development have, on the average, been in the area the longest whilst there appears to have been rather more recent migration into the rural and Lakeland areas of Cumbria some distance from the Sellafield site. Those in the coastal area were also significantly more committed to their location than those in the outer zones.

Awareness and knowledge about the Repository was variable. In effect awareness reduced with increasing distance from the site. It also depended on the employment connection. However, even in the immediate area of Sellafield nearly 12 per cent had not yet heard of the Repository. Amongst those who had heard the overall level of knowledge that people attributed to themselves was very low. Analysis confirmed that both employment connection to the nuclear industry and geographical location had an effect on the level of self-attributed knowledge about the Repository.

To provide a baseline for the enquiry, respondents were asked to give their opinion of the proposal. The figures show a considerable level of antipathy towards the Repository with the majority view being opposition (47 per cent). However those who did not know or who were generally unsure also comprise a large group, 41 per cent, whilst only 12 per cent welcomed the proposal.

Several factors were found to have some effect on the measured attitudes. These were age, sex, qualifications, zone, employment status with respect to the industry and the level of self attributed knowledge about the proposal. A further analysis was conducted to discover which of these factors appeared to have the most influence in determining or predicting support. It was found that three variables; zone, employment status and sex were the most significant contributors. Of these, employment status and zone had similar large effects, with sex having about half the influence. Combined together these three pieces of information accounted for nearly three-quarters of the variation, which demonstrates their considerable power in

accounting for response.

Analysis shows that two-thirds of those opposed to the Repository claimed to know very little about it, or were unsure that they knew enough. Amongst those who were undecided about the development 86 per cent claimed to know little or nothing. In contrast, amongst those welcoming the proposal over a third claimed to know quite a lot or be well informed.

However, whilst it could be said that a large majority of those who were opposed to the Repository claimed to know little or nothing about it, it does not follow that those who support the Repository are well informed. The majority of such supporters also claimed little or insufficient knowledge. Of even more importance is the finding that about as many who opposed the development as supported it claimed to be well informed. Thus the likely impact of information cannot be assumed to produce change in the one direction of greater support.

Similar strong effects for area of residence and employment affiliation with the industry were found in the case of trust for BNFL and other nuclear industry organisations. As noted above those people living in the areas farthest away from Sellafield were least like those living near the site and least trusting of the industry. Their responses probably reflect the views of the national population of UK.

Finally, the views of the sample with respect to the decision procedure are worthy of remark. The overall response when asked if they thought that their views would be taken into account was negative, two-thirds thought that their views would be ignored. The level of confidence in the correctness of any decision taken was also equivocal; 40 per cent had at least some confidence in the decision but a nearly equal number were less than confident. Clearly both the process and its likely outcome are currently viewed with suspicion, although these findings were also dependent on where people lived with those nearest the site having a little more faith in the process.

2. REPORT BY THE INSTITUT SYMLOG DE FRANCE

Institut SYMLOG de France, a research organisation concerned with risk analysis and communication, carried out two levels of international comparison. Persons active in informing the public on radioactive waste management issues in France and the UK were interviewed. A more detailed report was produced in December 1992 comparing Cumbrian and French national opinion survey data.

a. Tendencies

This analysis pointed first to apparent acceptance of siting a repository in the Sellafield area, based on a professed lack of concern for the radwaste problem in comparison to other environmental problems. Cumbrian data showed, however, a great diversity of view underlying this average result.

The implication for the risk communicator would be that a

unified audience does not exist. A standardised information approach may not achieve satisfaction. Such data as these might best be exploited to identify target populations within which specific information needs may be better met.

b. Data

West Cumbrians described themselves as less likely than the French to take personal resistive action in response to a repository. This comparatively passive attitude seemed to be based on pragmatic reasoning as to the costs associated with resistive action such as moving away. The expectation by these residents that their own neighbours would be more likely to take action (joining protest groups or signing petitions, etc) coupled with the large range of negative images given in free responses, indicated however that de facto acceptance was underlain by anxiety. The rejecting feelings were apparently not finding outlet for expression.

Questions pertaining to perceived competence and credibility of officials in the Sellafield repository siting process showed relatively high levels of confidence and trust compared to the French, indicating that many of these officials have become familiar to the local community. A degree of suspicion and pessimism dominated, however, in the highly negative responses to questions as to whether enough information was given and whether the views of the people would be taken into account.

c. Acceptance as a multi-dimensional concept

These data imply for risk communicators the necessity of approaching "acceptance" as a multi-dimensional concept. The brand of acceptance revealed here by survey seemed composed of pragmatic inertia, underlain by reticence, suspicion, frustration and pessimism.

Ignoring such dimensions of "acceptance" would not only handicap information efforts, but could lead to residents lending (passive) support to any extreme position tending to express the negative feelings which up to then have not found constructive outlet, or positions tending to "get the problem out of the way".

d. Implications for community management risks

This "uneasy acceptance" state is suggested to threaten the community's ability to resolve complex problems. The radwaste management problem combines technological, economic, environmental, and social aspects. It is not the only issue before the public to do so today. More and more, communities will be confronted by urgent problems affecting the environment (eg toxic waste) and in today's social and political context, there will be less willingness to "just let the experts go about their business". It is thus equally urgent for communities to learn the skills necessary for negotiating such issues, to explore mutually agreeable compromises, to build reciprocal trust among the officials and the publics faced with waste management.

Successful community risk management is threatened by a situation in which persons feel underinformed, underempowered

and resistant. Thus all institutional officials have an interest in developing responses to this situation. Information is a big part of this response. However, the main issue here would not appear to be "packaging technical information in an easy-to-understand form". The challenge is rather to develop a range of forums for information and exchange as diverse as the persons and concerns present in the community.

The Sellafield Repository Project Information Unit, structured to remain close to community concerns and interests, is seen as apt to be particularly well adapted to favour such exchange.

e. Special status of environmental concerns

The Cumbrian survey also pointed to highest marks given to environmentalists - both militants and members of the establishment - for competence and credibility. The opportunities afforded by these groups for expressing persons' apparent desire to "save" the environment are of value to the community. The low rate of militant group membership among the Cumbrian sample indicates however that such groups do not correspond fully to residents' concerns or personal convictions. All officials in the waste management process might do well to explore what "protecting the environment" means in the idiosyncratic views of the public, in order to favour active participation by residents in the diverse efforts possible to improve environmental conditions.

f. Conclusions

De facto acceptance was revealed in this survey analysis to combine recognition of the complexity of the waste management problem, a large range of negative but underexpressed sentiment, and a feeling of powerlessness. The challenge to risk communicators is thus not solely to package desired technical information in easily understandable form, but to creative interactive forums for exchange of information. These communication opportunities should allow residents to express their current reaction to the situation, develop a fuller grasp of the complex socio-economic and technical problem of waste management, and become active in identifying solutions.

Such interactive communication forums may be proposed by any number of groups within the community in order to maximise the range of expression and gathering of elements toward better management of the radwaste problem. These forums can also serve as training for the community to handle other complex problems affecting their social, economic and environmental status.

g. Proposals

In order to test the generalisation of these action conclusions, and permit their transfer to other Community Member States as well as to other waste management issues, Institut SYMLOG would suggest:

i. Similarly detailed site-specific public opinion research

in a French community pre-selected to receive a repository or laboratory.
ii. Communication policy-building seminars for decision makers on the basis of comparative data.
iii. Design of background material aids for creating recommended interactive community risk management forums.

3. REPORT BY BRITISH NUCLEAR FUELS plc (BNFL)

a. Introduction

The main responsibility of BNFL in this campaign is the co-ordination of a comprehensive information service to the general public in Cumbria on the proposed radioactive waste repository at Sellafield. Established in late 1991 the Sellafield Repository Project (SRP) Information Unit has coordinated the public relations functions associated with the Repository. It is based at Sellafield and includes personnel seconded from UK Nirex Ltd.

The publicity work covered in 1992 including brochures, exhibitions, video production and public information notices is detailed below and has involved close liaison with UK Nirex Ltd.

b. Publications

A brochure "Sellafield Repository Project - A site-specific concept for public consultation" had been produced in December 1991. This outlined the investigations to be carried out in the Sellafield area and detailed the preferred design for the repository via spiral tunnels or drifts. It welcomed comments from the local population. This booklet was widely distributed in the Cumbrian area and was reprinted in June 1992.

Following the results of local opinion surveys by Copeland Borough and Cumbria County Councils in 1992 it was evident that further information was required on the plan to bring forward the development of an underground Rock Characterisation Facility (RCF). This Laboratory Facility would provide detailed information to allow a better assessment of long-term safety and on the final location, design and orientation of the repository. A report was prepared on the RCF in the form of a 27-page consultative document and this has been distributed to interested parties in the UK and to the general public particularly in the Cumbrian area. This is a comprehensive publication covering the RCF and its geological and environmental implications.

The Repository is also featured in schools materials produced by educational consultants which help in filling the requirements of the national curriculum and its attainment standards for children studying subjects such as geography, the sciences and social studies.

The Sellafield Repository Project has also been included in a number of UK Nirex Ltd and BNFL publications, including both organisations' annual reports which have had wide distribution to the general public.

c. Videos

Three videos were produced at the end of 1991 - "Alien Beans" which consisted of animation sequences and was made for young people; "Tunnel in Time" which was aimed at GCSE level students and the other for more general adult audiences "Design for Disposal". The latter is a 12 minute production and outlines the types of nuclear waste and the conceptual design for the repository and the transport, safety and environmental aspects considered in the selection of Sellafield as the proposed site. This video has been distributed freely throughout 1992 from the Whitehaven Information Office and shown at public meetings and mobile exhibitions throughout Cumbria.

A 10 minute video has just been completed showing the progress of the geological investigations being carried out at Sellafield. Whilst it will be of principal interest to specialised audiences it will be suitable for the general public.

A major new video on the Sellafield geological investigations is planned for production in 1993. This will take account of the results of opinion research carried out during 1992.

d. Exhibition Material

i. Interactive Video

It was established that the benefits of an interactive video system describing the Repository Project and providing answers to people's concerns would greatly enhance the campaign. It was envisaged that five information stations could be purchased three located at the Sellafield Visitors Centre, one at the refurbished Whitehaven Office and one fitted to an existing mobile exhibition. This would involve sophisticated hardware consisting of touch screen television, a laser disc player and a computer with an interface board allowing both computer generated and video images to be shown on the screen separately, or simultaneously. The equipment would be contained in an attractively designed and constructed console. It is a proven technique with high reliability and good quality of presentation.

It is planned to go ahead with the interactive video in 1993 and the feedback from all opinion research carried out in 1992 will be invaluable when production takes place. A major refurbishing of the Sellafield Visitors Centre will shortly take place and the interactive video and associated information panels on radioactive waste will be incorporated.

ii. Portable Display

A portable display within a tube has been produced and used comprehensively in support of speakers at schools and other public venues in Cumbria.

iii. Borehole Exhibition

The initial plans for the campaign included a portacabin exhibition at the central borehole site. This was rejected as it exposed the public to unnecessary dangers and the optimum

position to receive visitors lay within a neighbouring town. Whitehaven, twelve miles north of Sellafield was selected partly as a BNFL Information office already existed there. The refurbishment took place in mid-1992 incorporating an information desk, information panels and models and has proved successful. The overall philosophy of deep disposal and the geological investigations in a wider context can be discussed in attractive surroundings. However from early feedback it was found that people living adjacent to Sellafield were interested in the more detailed investigations and there is a need to meet them at the portacabin on site. Some refurbishing will consequently take place there in early 1993.

iv. Informing the Public

In January and February 1992 and from July 1992 to the end of the year comprehensive announcement notices were placed in the local Cumbrian newspapers. This was in part inviting the public to come and see a touring mobile exhibition at various venues including local agricultural shows and also advising people if they wanted more information on the Repository to either visit or phone the Whitehaven Information Office.

Another method of supplying information is by a series of SRP newsletters prepared at approximately monthly intervals. These are distributed to Regulatory Authorities, the media, local councillors and as handouts at the Sellafield Visitors Centre.

v. Future Publicity Proposals

It is intended to apply for planning permission to build the RCF laboratory in mid-1993 subject to satisfactory results following further hydro-geological borehole investigations. The precise timescale for the production of a new brochure and new video will depend to some extent on the outcome of these surveys.

The interactive video will be produced in 1993 for incorporation in the Whitehaven Information Office as well as a refurbished Sellafield Visitors Centre which will also include new panels on radioactive waste. There will also be some refurbishing at the borehole site.

The coming year will be a most important one for the Sellafield Repository Project and the associated publicity materials to be produced will play a major role in achieving public acceptability. The main focal point for information on the repository will continue to be the Whitehaven Information Office.

Title:	Transmutation of long–lived radionuclides by advanced converters
Contractor:	Siemens AG Power Generation Group (KWU)
Contract No:	FI2W–CT91–0103 Task 1
Duration of contract:	October 1st 1991 to September 30th 1993
Period covered:	01.01.1992 to 31.12.1992
Project Leader:	Dr U. Wehmann

A Objectives and Scope

The study will analyse the possibilities, limits and technological development steps needed for transmutation of actinides and long–lived fission products in unconventional advanced reactors and other advanced transmutation devices. The notion "unconventional advanced reactor" means a fast reactor with unconventional fuel or a coupled system of fast and superfast zones or a small unit, which mainly will be constructed for transmutation. The other advanced transmutation devices are special accelerators, spallation machines and fusion reactors.

This study is one part of a coordinated partitioning–transmutation study of a group of organisations: CEA, ECN Petten, SIEMENS.

B Work Programme

1. Large fast reactor with MOX– and metal fuel, fast zones and high axial leakage.
2. Fast reactors, small units
3. Spallation machines
4. Fusion reactors

C Progress of Work and Obtained Results

C1 State of Advancement

Referring to programme items 1 and 2, reference cores with MOX fuel and sodium coolant have been defined and investigated. Mainly the following physical aspects have been studied:

- Minor Actinide (MA) transmutation efficiency in dependence of core geometry
- Pu^{238} build up in MA transmuters, Pu–burning potential
- Transmutation efficiency of MA being irradiated in special peripheral S/A.
- Influence of MA admixture on operational and safety parameters of the core

The study for the MOX cores is now complete and calculations for metal fuel cores are under way.

Regarding item 3, various publications about accelerator driven transmutation devices have been studied and a preliminary judgement on the potential of these concepts has been given.

C2 Progress and Results

C2.1 Fast Reactors with MOX fuel (item 1 + 2)

Four different core layouts have been considered: 3 layouts which are EFR–like (core radius $\approx$ 2 m), but varying in core height (100 cm, 70 cm and 50 cm) which corresponds to reactor powers of 3600 MW_{th}, 2600 MW_{th} and 2000 MW_{th} and one layout with a small core (70 cm core height, 450 MW_{th}). The boundary conditions for the neutronphysics calculations (including some typical EFR–type operational parameters) are given in Table 1. MA content in the heavy metal has been assumed to be 0, 5 and 15 %, where the case without MA is taken as reference. The following topics have been studied:

Influence of core size on performance parameters of the reference cores

- The sodium void effect (SVE) is strongly decreasing with decreasing core volume (from 6$ for core 1 to 2.5 $ for core 4 at EOEC (= end of equilibrium cycle)).
- The Doppler constant is reduced in case of core size reduction.
- The absorber worth is increased, but the reactivity loss per cycle is also increased in case of core size reduction.

Influence of MA admixture on performance parameters

The main results are given in Table 2 for the EOEC state

- The SVE increases by about 0.13 $ per % MA admixture, thus the negative effect of a moderate MA admixture on the SVE could be easily compensated by a relatively small core size reduction.
- The Doppler constant is reduced in case of MA admixture: for moderate MA contents the Doppler constant is reduced by 5 % for 1 % MA admixture. In order to keep inherent self–stabilizing properties of a fast reactor, a large MA content seems undesirable.

- The reactivity loss per year is strongly reduced in case of MA introduction. On the other hand the decrease of the shutdown worth of the rods is only small so that as a whole MA introduction is beneficial for shutdown worth requirements.

Influence of core size on MA transmutation efficiency

In order to compare the transmutation capabilities of the various cores, one may take a look at the relative transmutation rate per year (or cycle). This can be transformed into effective transmutation half times (THT) which is the period after which the content of the MA is reduced by a factor of 2, assuming continous full power irradiation including normal shutdown periods. Typical THT values are between 6 and 10 years as can be seen in Figure 1, where the mean Pu enrichment was taken as the parameter characterizing the core size. Due to their high flux level, the large cores show a very good transmutation efficiency. A large MA content is beneficial for the THT.

MA transmutation efficiency in peripheral zones

The transmutation capabilities of the axial and radial blanket zones for a large core (EFR–like) have also been investigated. Generally, due to the low flux level in these peripheral zones, the transmutation efficiency is considerably less favourable than in the core zones. Also, a large relative Pu^{238} build up in these zones is expected.

Plutonium burning capabilities

The Pu burning capabilities mainly depend on the mean Pu enrichment: a high Pu enrichment is beneficial for Pu burning. A reasonable upper limit is a mean Pu content of about 30 %, both for fuel solubility and for a large Doppler constant. Unfortunately, as can be seen in Fig. 1, such a high Pu enrichment deteriorates the MA transmutation efficiency.

Pu^{238} build–up

The generation of Pu^{238} is inevitable when transmuting MA (Np^{237} capture). This is an undesirable feature of MA transmutation because Pu^{238} has a high radioactivity and heat-generation which is unfavourable for reprocessing and fuel fabrication. At the moment a Pu^{238} content of 5 % relative to total Pu is considered as a reasonable upper limit, although this is not a technological limit. If this limit is to be respected, the MA content at BOL has to be restricted to 3 %.

Conclusion

If a MOX–fuelled fast reactor is taken as a MA transmutation device, the best solution would probably be a large core but with reduced core height (e.g. as our core no. 2). If a Pu^{238} limit of 5 % is to be respected, such a core could allow the introduction of about 900 kg MA. It could transmute about 65 kg MA per year which is the yearly production of about 2–3 LWR's. A "normal" EFR type reactor with 1 m core height could transmute the MA waste of 4 LWR's.

C2.3 Spallation machines (item 3)

Two concepts of accelerator based transmutation devices have been studied in detail:

- *The PHOENIX concept*

  In this concept which has been developed at BNL, emphasis is on the transmutation of the MA and I^{129}. The MA are transmuted in a fast neutron spectrum. The proton beam of the accelerator hits by aid of a beam expander up to eight target modules. Each module is similar to the core of the Fast Flux Test Facility (FFTF). Apart from the fuel composition, the technology is much the same as FFTF, including sodium as coolant. PHOENIX is designed to operate at a k_{eff}–level of 0.9. In a device with eight target modules 2.6 t MA and 300 kg I can be transmuted per year which corresponds to the yearly production of LWR's of about 75 GW_e. A disadvantage of this concept is the large Pu buildup, most of it being Pu^{238}.

- *The Los Alamos ATW concept*

  In this concept all actinides including Pu are transmuted and as a fission product mainly Tc^{99} is transmuted. Contrary to the PHOENIX concept, the transmutation processes take place in a D_2O–moderated environment with a high thermal flux (> 10^{15} $cm^{-2}s^{-1}$). The proton beam in ATW supports 4 target/blanket modules. The target is surrounded by an annulus of technetium in D_2O, an actinide slurry region and a D_2O reflector. The actinide slurry is contained in double walled pressure tubes. The design is mainly based on the CANDU technology. A new feature is the continuous processing of actinides and technetium in separate loops. ATW operates with a k_{eff} of 0.95. It transmutes the waste of LWR's of about 7.5 GW_e.

Conclusion

Compared to the PHOENIX concept, ATW seems to be very advanced and ambitious, whereas the PHOENIX concept is more realistic in the extension of a proven technology. Keeping in mind that for both concepts the operational k_{eff} is between 0.9 and 0.95 and that therefore much care has to be taken regarding criticality safety and that integral powers and power densities are similar to commercial power reactors, it seems questionable wether one can take considerable credit of the subcriticality of these systems regarding simpler licensing or better public acceptance, compared to conventional power reactors.

C3 List of publications

1.) U.K. Wehmann
Some Physics Aspects of Minor Actinide Recycling in Fast Reactors IAEA Specialists Meeting on Use of Fast Breeder Reactors for Actinide Transmutation, Obninsk, September 1992

2.) U.K. Wehmann, W. Löhr, A. Stojadinovic
Design Studies on LMFBR Cores with Reduced Sodium Void Effect and Minor Actinide Burning
Proc. Int. Conf. on "Design and Safety of Advanced Nuclear Power Plants"
(ANP '92) October 25–29 1992, Tokyo

- Maximum burnup of 20 %
- Maximum linear rating limits:
  520 W/cm at BOL, 410 W/cm at EOL
- 1 year cycle length with 5–batch refuelling
- Fresh LWR plutonium (40 MWd/kg HM):

Pu^{238}	:	Pu^{239}	:	Pu^{240}	:	Pu^{241}	:	Pu^{242}	:	Am^{241}
2	:	54	:	26	:	10	:	8	:	2

- Minor actinide composition:

Np^{237}	:	Am^{241}	:	Am^{243}	:	Cm^{244}
49	:	37	:	11	:	3

- Minor actinide contents in the HM:
  0(ref.), 5 %, 15 %
- Plutonium contents were adapted so that k_{eff} is about 1.01 at EOC with rods out
- Homogeneous recycling of minor actinides

Table 1 : Boundary conditions for neutronphysics calculations

parameter	*MA–content*	*core 1*	*core 2*	*core 4*
fissile SVE	0 %	5.9	4.4	2.5
	5 %	6.5	5.1	3.1
[$]	15 %	7.5	6.3	4.8
Doppler constant	0 %	– 1.7	– 1.6	– 1.1
	5 %	– 1.3	– 1.2	– 0.8
[$]	15 %	– 0.7	– 0.6	– 0.5
Δϱ per	0 %	– 8.9	– 10.4	– 12.3
full power year	5 %	– 4.6	– 6.7	– 8.9
[$]	15 %	+ 1.6	– 1.5	– 4.9
control rod worth	0 %	25	23	31
	5 %	24	21	30
[$]	15 %	20	17	27

Table 2 : Performance parameters of cores with different MA contents (EOEC)

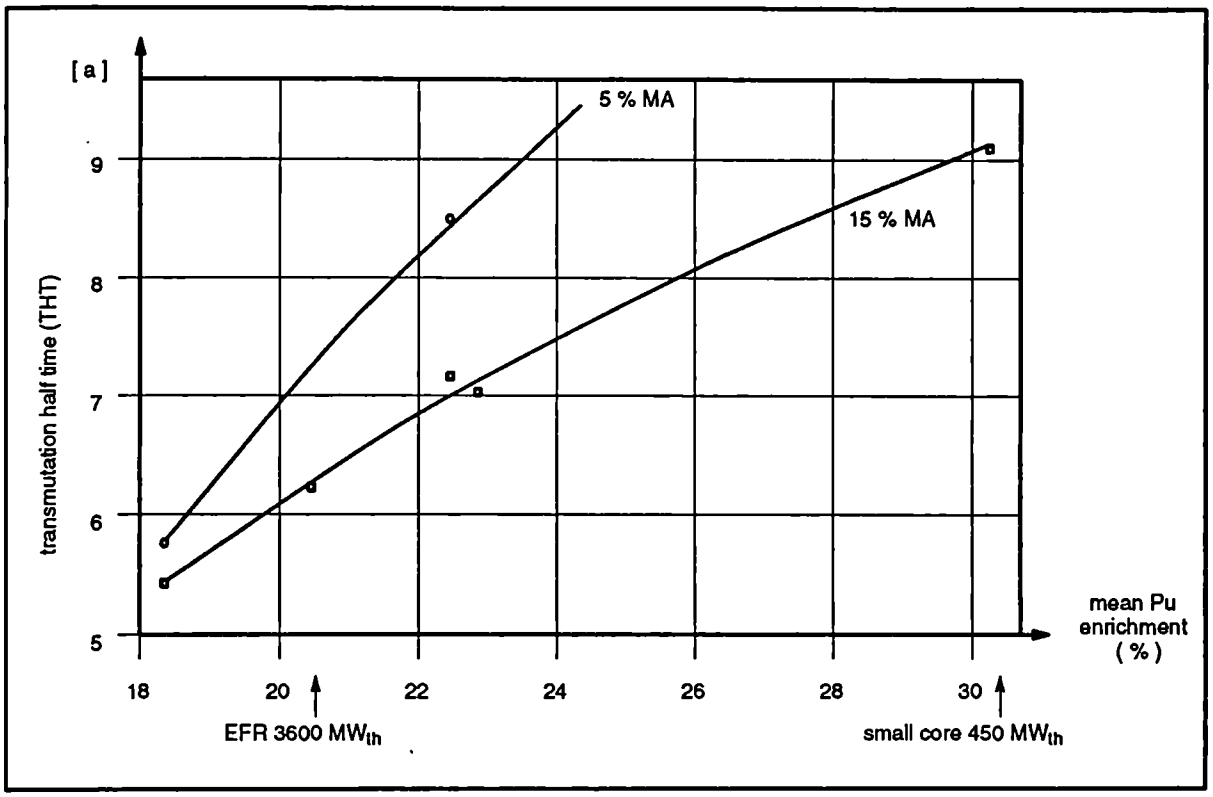

Fig. 1 : MA transmutation efficiency in core regions

Title: Participation in a CEC strategy study on nuclear waste transmutation
Contractor: Stichting Energieonderzoek Centrum Nederland-ECN
Contract No: F12W-CT91-0104
Duration of contract: from 1 November 1991 to 31 October 1993
Period covered: from 1 January 1992 to 31 December 1992
Project Leader: K. Abrahams

A. OBJECTIVES AND SCOPE

This contract "Participation in a CEC strategy study on nuclear waste transmutation" has first of all as an objective the improvement of the nuclear data base needed for strategy study on nuclear waste transmutation, including inventory calculations. A second objective is the presentation of a contribution to the CEC strategy study, in the form of a paper on transmutation of long-lived fission products. Both objectives fit into the "Integral Research Program 1991-1994 for the study of Recycling Actinides and Fission Products" of the Dutch national centre ECN [1], which has the intention to give a contribution to an international effort to evaluate the recycling option of the nuclear waste problem. Besides strategy and scenario studies, reactor physics research, and an effort towards small scale demonstrations of transmutation possibilities, the integral program is focused on the nuclear parameters, relevant for transmutation.

Although the Netherlands Energy Research Foundation ECN, acted as the sole contractor for this contract, there has been a close collaboration in related strategy studies, such as the ones of CEA and Siemens.

B. WORK PROGRAMME

2.1 Preparation of a nuclear data base for actinides and fission products, which is needed for the experimental verification of technological aspects of transmutation

2.2 Preparation of derived data in order to asses the ORIGEN nuclear data library for transmutation studies.

2.3 Performing sample burn-up calculations for several scenarios with the updated ORIGEN nuclear data library.

2.4 Investigation of possibilities of transmutation of long-lived fission products.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In coordination with CEA and Siemens the work on three Community contracts is being harmonized. These three contracts regard studies on possibilities to reduce the long-term radio-toxicity of nuclear waste, and the ECN work is of vital interest, as far as it aims towards common data sets and standardized libraries for relevant cross sections, and the ECN work on long-lived fission products is considered to be an important contribution to the joint studies.

As a first step the Petten group now has adapted codes and libraries (ORIGEN and FISPACT, and especially working libraries of cross sections, nuclear decay constants, and risk data) for reactor physics and burnup calculations. With respect to the work on codes and libraries the ECN data set has been used as a basis. Next the most recent JEF-2 library has been inspected on quality and completeness. As the JEF-1 library is readily available in processed data, it has been used as a back up. Especially for nuclear data on actinides and long-lived fission products this data set could be improved, but in general the improvements for inventory calculations are not large. Therefore it can be expected that a number of earlier conclusions, which have been based on the previous data set, are still valid. Substantial progress was reached in the study of fission product transmutation (work programme 2.4 is almost completed by now). It has been shown that the partitioning and transmutation, e.g. by means of accelerator techniques, would enable the reduction of the dose risk from the long-lived and geo-chemically mobile fission products Tc-99 and I-129.

Progress and results:

Chapter 1. Work programme 2.1 and 2.2: Common data sets

Regarding the nuclear data programme it can be mentioned that this work mainly relates to nuclear data on actinides and long-lived fission products. Existing codes and libraries (based upon JEF-2) have been evaluated. Apart from this contract, ECN will make an effort towards small-scale demonstrations of transmutation possibilities by using the Petten High Flux Reactor (HFR) [2], which is an ideal test reactor for thermal transmutation. This effort in itself is not subject to the present contract, but it is strongly related and relevant information will be used to be included in the report for this contract. For example: In order to support these demonstrations, some nuclear data are required: capture cross sections of Tc-98,99 of Ru-100, I-128, 129, Xe-130 and also for elements in carrier materials and elements in cladding. Further the (n,2n) cross sections for Tc-99, Ru-100, I-129, and Xe-130 are needed. Most of these data have been extracted from the available libraries. For reactor physics and burnup calculations, the codes ORIGEN and FISPACT are being adapted together with their working libraries of cross sections, risk data, yields and decay constants.

Limitations and formats of the data sets to be used were defined in agreement with work of the partners in these CEC strategy studies. These definitions have been coordinated on quarterly meetings, and concern the following work:

- Standardized libraries based upon JEF-2 will be used. ECN has checked the JEF-2

files for completeness and delivered improved I-129 and Tc-99 compilations. A I-129 evaluation has already been finished and forwarded to CEA-Cadarache. An update of the Tc-99 evaluation has been prepared.

- At Petten the relevant JEF-2 data have been processed by means of the NJOY code into 172 group constants (XMAS structure).

- The laboratories engaged in the present study averaged the data over standard spectra (PWR N4 en FBR Super PHENIX), which were exchanged. Resulting one group data (for infinite dilution) have been compared for the most important actinides .

- For PHENIX moderated blankets, a standard LWR and for the Petten HFR the fission product transmutation capabilities have been compared [3].

For the most important actinides table 1 gives an image of the present state of the evaluation. Part of the differences between JEF-2 and ORIGEN-S is due to corrections for self shielding, which are made in ORIGEN-S only.

		Fission cross section in LWR spectrum			Capture cross section in LWR spectrum		
Nuclide Symbol	Nuclide Z/A	JEF1.1 (barn)	JEF2.2 (barn)	ORIGEN-S (barn)	JEF1.1 (barn)	JEF2.2 (barn)	ORIGEN-S (barn)
U	92234	$5.3801\ 10^{-01}$	$5.3801\ 10^{-01}$	$6.9247\ 10^{-01}$	$2.0943\ 10^{+01}$	$2.0943\ 10^{+01}$	$3.4832\ 10^{+01}$
U	92235	$3.8723\ 10^{+01}$	$3.8801\ 10^{+01}$	$4.0620\ 10^{+01}$	9.0179	8.7055	$1.1396\ 10^{+01}$
U	92236	$3.1407\ 10^{-01}$	$3.1407\ 10^{-01}$	$5.8125\ 10^{-01}$	8.1003	8.1003	9.6135
U	92238	$1.0882\ 10^{-01}$	$1.0526\ 10^{-01}$	$1.0728\ 10^{-01}$	5.0454	5.0334	1.0358
Np	93237	$5.3365\ 10^{-01}$	$5.2256\ 10^{-01}$	$4.3883\ 10^{-01}$	$3.2235\ 10^{+01}$	$3.2668\ 10^{+01}$	$4.3179\ 10^{+01}$
Pu	94238	2.3662	2.3500	2.1138	$2.7682\ 10^{+01}$	$2.7697\ 10^{+01}$	$3.5493\ 10^{+01}$
Pu	94239	$1.0260\ 10^{+02}$	$1.0245\ 10^{+02}$	$1.0102\ 10^{+02}$	$5.7968\ 10^{+01}$	$5.8711\ 10^{+01}$	$4.2231\ 10^{+01}$
Pu	94240	$6.4856\ 10^{-01}$	$6.4856\ 10^{-01}$	$4.4132\ 10^{-01}$	$2.1977\ 10^{+02}$	$2.1977\ 10^{+02}$	$1.0939\ 10^{+02}$
Pu	94241	$1.0508\ 10^{+02}$	$1.0505\ 10^{+02}$	$1.0917\ 10^{+02}$	$3.5503\ 10^{+01}$	$3.5627\ 10^{+01}$	$3.7895\ 10^{+01}$
Pu	94242	$4.6587\ 10^{-01}$	$4.6587\ 10^{-01}$	$2.8498\ 10^{-02}$	$2.8188\ 10^{+01}$	$2.8188\ 10^{+01}$	$5.7553\ 10^{+01}$
Am	95243	$4.5740\ 10^{-01}$	$4.4080\ 10^{-01}$	$9.2180\ 10^{-02}$	$4.9408\ 10^{+01}$	$4.8930\ 10^{+01}$	$7.2257\ 10^{+01}$

		Fission cross section in LMFBR spectrum			Capture cross section in LMFBR spectrum		
Nuclide Symbol	Nuclide Z/A	JEF1.1 (barn)	JEF2.2 (barn)	ORIGEN-S (barn)	JEF1.1 (barn)	JEF2.2 (barn)	ORIGEN-S (barn)
U	92234	$3.2897\ 10^{-01}$	$3.2897\ 10^{-01}$	$5.1000\ 10^{-01}$	$6.4103\ 10^{-01}$	$6.4103\ 10^{-01}$	$4.5000\ 10^{-01}$
U	92235	1.9759	1.9810	2.0300	$6.0230\ 10^{-01}$	$5.7121\ 10^{-01}$	$5.6600\ 10^{-01}$
U	92236	$1.0513\ 10^{-01}$	$1.0513\ 10^{-01}$	$1.1600\ 10^{-01}$	$5.8226\ 10^{-01}$	$5.8226\ 10^{-01}$	$6.6300\ 10^{-01}$
U	92238	$4.5675\ 10^{-02}$	$4.4147\ 10^{-02}$	$4.2800\ 10^{-02}$	$3.5302\ 10^{-01}$	$3.5188\ 10^{-01}$	$2.9600\ 10^{-01}$
Np	93237	$3.2318\ 10^{-01}$	$3.1677\ 10^{-01}$	$3.6000\ 10^{-01}$	1.7546	1.6615	$7.6500\ 10^{-01}$
Pu	94238	1.1271	1.1196	1.3800	$7.2837\ 10^{-01}$	$5.8452\ 10^{-01}$	$2.2400\ 10^{-01}$
Pu	94239	1.8883	1.8633	1.8500	$5.7136\ 10^{-01}$	$5.6425\ 10^{-01}$	$5.0300\ 10^{-01}$
Pu	94240	$3.8218\ 10^{-01}$	$3.8218\ 10^{-01}$	$3.5400\ 10^{-01}$	$6.0807\ 10^{-01}$	$6.0806\ 10^{-01}$	$4.1500\ 10^{-01}$
Pu	94241	2.6361	2.6150	2.4900	$5.2310\ 10^{-01}$	$5.6724\ 10^{-01}$	$4.3200\ 10^{-01}$
Pu	94242	$2.6239\ 10^{-01}$	$2.6239\ 10^{-01}$	$2.7800\ 10^{-01}$	$5.1623\ 10^{-01}$	$5.1622\ 10^{-01}$	$3.4200\ 10^{-01}$
Am	95243	$1.9974\ 10^{-01}$	$2.0654\ 10^{-01}$	$2.3700\ 10^{-01}$	1.6634	1.8023	$5.5500\ 10^{-01}$

Table 1: One group cross sections for the most important actinides averaged over some standard PWR N4 and Super PHENIX spectra (JEF data only for infinite dilution).

Chapter 2. Work programme 2.3 : Sample burn-up calculations

There are some results available from calculations on LWR's and LMFBR's with an old one group data set taken from literature. Although final conclusions can only be made when these calculations have been repeated with the new library, a summary of preliminary conclusions showed to be a good preparation for further work. Because it has been shown that the old JEF-1 and the new JEF-2 files do not lead to important discrepancies for the major components of nuclear waste, these preliminary conclusions will not change significantly. Calculations were made for an (unrealistic) scenario in which all transuranium nuclides were recycled until equilibrium was reached. For an LWR as well as for an LMFBR, the actinide radio-toxicity increases after recycling, and eventually reaches an equilibrium value, which depends on the scenario and especially on the cooling time. After an equilibrium has been reached the total toxicity (waste plus fuel) hardly changes, and most of the waste which is generated will be due to losses in reprocessing. Scenario studies e.g. performed at ECN Petten [4] show how one may reduce the production of actinide activity by repeatedly recycling in power reactors.
Whereas light water reactors in such an unrealistic scenario would reach a relatively high equilibrium alpha-activity (PWR-EQ in fig.1) after many recycling steps, fast reactors would reach their equilibrium (FBR-EQ) relatively soon. Our studies indicate that there are certainly possibilities to reduce the overall source term of radioactive waste by means of reactor based incineration systems. Because the value of the equilibrium toxicity is about an order of magnitude higher than that of LWR "once through" spent fuel, and the assumed losses were of the order of 1%, a total reduction of the waste toxicity of roughly a factor ten might be reached. This however would imply that the cycle continues indefinitely unless the last reactor loading is disposed of safely in some other way. A main difference between LWR and LMFBR scenario's is the time it takes to reach equilibrium, which ranges from 50 years up to hundreds of years. Of course this equilibration period could be shortened, for instance if one could load an LWR with artificial equilibrium fuel.

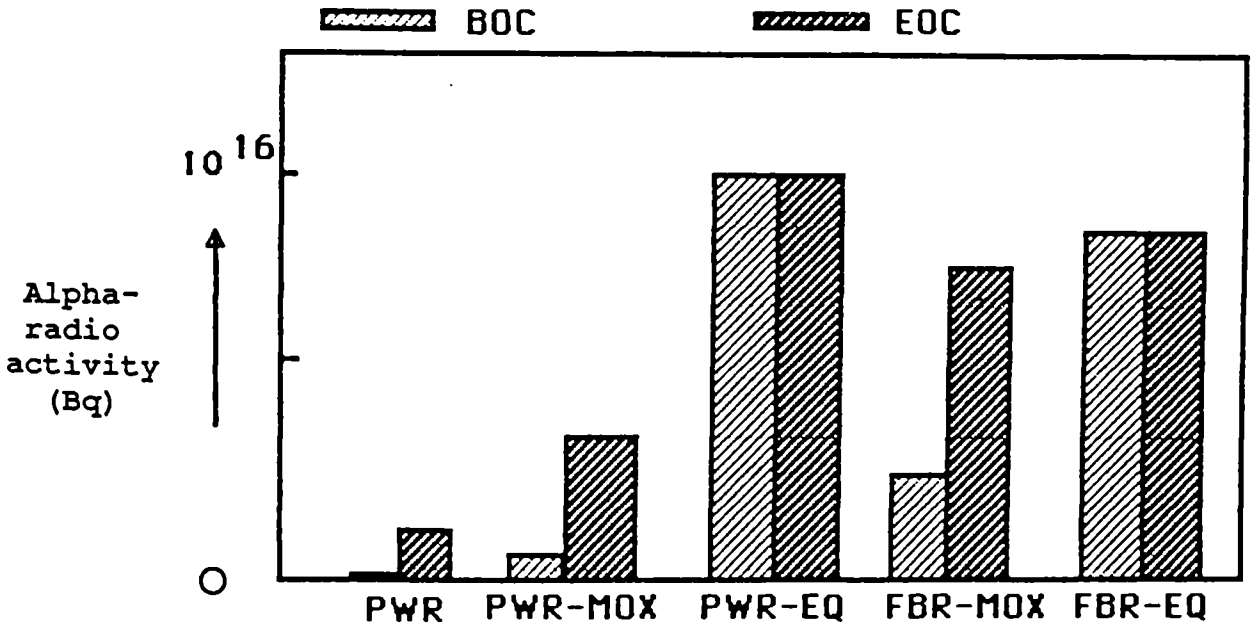

Figure 1: Alpha radio activity in PWR and FBR reactors [11]. Here BOC stands for "beginning of cycle" and EOC for "end of cycle", EQ stands for the equilibrium situation after recycling many times.

It is much too early to draw conclusions from these preliminary calculations, as more advanced transmutation schemes (including partitioning) are possible. Actinide recycling-scenarios will reduce risks for future generations, but also may impose new risks for the present generation. It would seem that a net reduction could be reached in collective radiation dose for the present generation because less mining would be needed per unit of produced energy. If one however would recycle the uranium, this reduction in collective radiation dose will be offset, at least partially, by the build up of U-232 and U-234 during the irradiation. These uranium isotopes cannot easily be transmuted and may act for a long term as a source of Tl-208 and Ra-226 background in the uranium tailings. It is not yet clear whether the integrated radiation dose for the population would decrease by actinide incineration in normal power reactors, and further study is necessary. Important arguments to continue research may first of all based upon the wish to reduce the source term of radioactive waste and, correspondingly, to reduce the number of repositories. Secondly one may wish to destroy and peacefully use weapons material or limit the need for safeguarding in case of retrievable storage of actinide waste.

Chapter 3. Work programme 2.4: Study of possibilities of transmutation of fission products by means of thermal neutrons

It should be investigated whether transmutation of fission products could be helpful in further reducing the long-term radiation dose. It seems obvious that this would be so if one could transmute Tc-99 and I-129 by neutron capture to harmless Ru-100 and Xe-130. Some first considerations on this study are given below. Under coordination with the partners a full discussion paper on this subject will be given, which may serve as a basis for a final report on fission product transmutation.

3.1. Introduction on motivation for partitioning and transmutation of fission products.

There are geo-chemically mobile components, which after a very long period of time may leak out of deep repositories towards the surface. A few long-lived (up to millions of years) waste elements give a high contribution to the long-term dose-rate. Considerations on the risk of waste disposal will depend on scenarios for leaching out waste from imposed barriers. If these scenarios would also involve leaching out by water, after human intrusion of the disposal site, the high mobility amplifies the risk of Tc-99, I-129 and Np-237. Although toxicity of fresh spent fuel is hardly determined by Tc-99 or by I-129, the long half life and the high yield in the fission process and the geo-chemical mobility are such that the risk for these two radio-nuclides will be amplified to a value, which already may be dominant after expiration of a thousand years period. Methods are being searched to diminish the technetium solubility by reducing agents such as metallic iron, tin, copper, manganese and vanadium, as well as the compound stannous chloride. At the moment experimental verifications are being made [5]. If such an immobilisation cannot be trusted over very long periods, one should consider as special candidates for transmutation of fission products the following isotopes: technetium (Tc-99), iodine (I-129), and cesium (Cs-135), as well as geo-chemically mobile actinides such as neptunium (Np-237) and its precursors. Therefore experiments on transmutation of these isotopes are being performed. In general Table 2 (refs. 4,6) shows, for a hypothetical set of unperturbed granite repositories the surface dose-rate, due to leakage of the stored amount of nuclear waste from an assumed EC total nuclear production over the next 100 years (relative to natural rates).

TABLE 2: RELATIVE GLOBAL DOSE RATE DUE TO LEAKAGE OF STORED SPENT FUEL FROM A 120 GW(e) LWR PARK OPERATING FOR 100 YEARS (such a park could generate the electric power in the EC according to CEA)

Period :	0- One million years		0- Hundred million years	
Storage :	Vitrified	Direct storage	Vitrified	Direct storage
Nuclides :				
Tc-99	100 %	98 %	17 %	46 %
I -129	-	2 %	-	1 %
Cs-135	-	-	10 %	24 %
U -235	-	-	-	6 %
U -238	-	-	-	14 %
Np-237	-	-	71 %	5 %
Pu-239	-	-	-	4 %
Am-243	-	-	3 %	-
Relative dose rate	0.2 ppm	2 %	12 ppm	400 ppm

The last line in table 2 indicates the dose rate relative to the natural background. In the case of direct storage there is an expected average individual dose-rate of the order of a few percent of present natural dose rates. Proper vitrification and removal of Tc would reduce the collective dose rate to 0.01 man Sievert per year, and would lead to marginal individual dose rates. Contributions of U-235 and U-238 show that vitrification is beneficial even for uranium ore which never has seen a reactor! It could be concluded from this table that the surface dose-rates due to leakage, is negligible especially if one could properly vitrify and/or transmute mobile components.

It has to be noted that the results of this UK study [6] rely heavily on assumptions on the effectiveness of vitrification and on geological characteristics of the repository. They may not be quite representative for other repositories, as calculations are based upon site dependent geo-chemical characteristics. If the waste is not in contact with oxygen, the mobility of Tc will be strongly reduced. In clay repositories [7] or in rock salt [8] repositories the I-129 risk could dominate, especially if the spent fuel is stored directly. Although there are differences among the deep geological repositories, it nevertheless can be concluded that, if the repositories remain unperturbed, fission products will dominate the collective risk in case of direct storage of spent fuel for the first million years. As for example follows from [6], the removal of Tc and I from the waste, would reduce the collective one million year dose with more than five orders of magnitude.

In order to reduce the long-term risk, one may decide on transmuting Tc-99 and I-129 to stable Ru-100 and Xe-130 by means of low-energy neutron capture. An intense flux of thermal neutrons may be created with a spallation source, an accelerator-driven reactor, a fast reactor with a moderator flux trap, a thermal high flux reactor or any other high flux device, based on fission, fusion, spallation or a combination of these processes.

Possibilities to include transmutation of fission product waste in common fuel cycles are not available, and special burner scenarios should be studied. Fission products can be

transformed into less harmful or even valuable materials by neutrons, and some groups are working on this solution. Such work is proceeding within the OMEGA project in Japan and the ATW project in Los Alamos. Demonstration tests e.g. at the Petten High Flux Reactor and the PHENIX reactor (in a moderated irradiation facility) are prepared by the Dutch and the French organisations ECN and CEA respectively. In a recent study the possible transmutation rates and mass reductions have been estimated for experiments in the High Flux Reactor (HFR) located in Petten (the Netherlands) and in PHENIX (France). For small, but not too thin targets, the effective half lives are about a few years for Tc-99, I-129 and Cs-135 irradiation respectively in HFR or in an LMFBR moderated irradiation facility [3]. In fact it seems that transmutation rates in both facilities are comparable for similar sizes and loadings. It has been claimed [9] that accelerator based systems could transmute the annual production of Tc-99 and I-129 even more efficiently.

3.2. Studies on homogeneous recycling of fission products

Global scenario studies on light water power reactors show that in principle such reactors could consume their own technetium production by means of neutron capture only in case that some surplus of technetium is being situated in the core. If the Tc would be homogeneously mixed through the LWR fuel, the inventory of Tc (a few hundred kg) would probably be too high to be practical in present scenarios for reprocessing this fuel. For inhomogeneous combinations of waste and fuel, the inventory would have to be even higher, and in general it can be stated that problems with LWR based incineration are complicated whereas only marginal advantages are to be expected. Therefore incineration schedules have been studied, which use an inventory as low as possible, and which would involve a high flux thermal neutron field for example at accelerator-based reactor systems. Unfavourable for any incineration scheme, which uses neutrons generated in the fission process is that the very fission process yielding these neutrons, also yields fission product waste. Simple calculations show that for fission products such as Tc-99 (yield about 6 %) and I-129 (yield about 1 %), the amount of newly formed fission products competes significantly with the amount of transmuted fission products unless the concentration of Tc-99 and I-129 in the reactor is high. Environmental economy therefore may favour transmutation in an intense thermal neutron field in a special burner High Flux Reactor or in a flux produced by a spallation neutron source (in both options one should generate electricity for economic reasons).

3.3. Studies on heterogeneous recycling of fission products.

As it seems hardly practical to recycle the fission products homogeneously in the reactor fuel one might wonder whether a heterogeneous recycling method might be more efficient. This method might involve the use of special targets for example for iodine, or it might involve the application of technetium layers on the cladding and/or the fuel pellets. Especially the moderated sub-assemblies of LMFBR's might be of interest in this respect. Decisive in respect to the choice of the method will be the possibility and the effort needed to regenerate new targets after the old target has been used long enough (a burn up of more than 20 % in a heterogeneous target is probably a practical limit due to failure of the cladding and target material).

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Title : **Potentialities and costs of partition and transmutation of long-lived radionuclides.**

Contractor : CEA-Centre de Saclay; France
Contract n° : **FI2W-CT91-0106**
Duration of contract : October 1991 to September 1993
Period covered : January to December 1992
Project Leader : G. Baudin

A. OBJECTIVES AND SCOPE

The purpose of this conceptual study is to analyse the different strategies of waste management aiming at reducing contents of long lived radionuclides by partitionning and transmutation ; technical ways and costs will be evaluated.

In a first step reference scenario will be defined ie to draw up an inventory of long lived radionuclides produce by the European installed or foreseen reactors and estimate radiotoxicity of such nuclides.

In a second step will be estimated the expected decrease of radionuclides stockpile according to two mains scenarii : first one using presently known or available technologies, second one taking into account all foreseen innovative technologies.

B. WORK PROGRAM

The different items of this program are the following :

1.- References scenarios :
- . definition of involved reactors (number, type, ..)
- . evaluation of produced radionuclides (Am, Np ...)
- . potential radiotoxicities.

2.- Step one : available technologies :
- . separations :
  - . definition of processes
  - . evaluation of efficiencies and losses
  - . costs.
- . transmutation :
  - . in FBR
  - . in PWR

3.- Step two : foreseen technology :
- . same items as for 2

C. PROGRESS OF WORK AND RESULTS OBTAINED

1. Selected Scenarios

The evolution in material balances and radiotoxicity has been assessed for three reference scenarios: R_1, R_2, R_3 and two separation-incineration scenarios RP_1 and RP_2, namely:

R_1 - UOX-fueled N_4 type PWR reactor and direct storage of the irradiated fuel,
R_2 - UOX reactor, reprocessing and multirecycling of the Pu as MOX,
R_3 - idem R_2 but recycling of the Pu in a FBR of the EFR type, starting in 2020.

RP_1 - separation and transmutation with currently feasible technologies: $RP_1.1$ for transmutation in PWR and $RP_1.2$ for transmutation in FBRs.

RP_2 - separation and transmutation with advanced methods: incineration-dedicated reactors, accelerators, ...

1.a - Evolution in material balances for R_1, R_2, R_3.

The three scenarios have only a small impact on the evolution of the depleted uranium stockpile coming from reprocessing plants which will reach about 1,400,000 t in 2100, after a linear increase. The irradiated heavy metal stockpile increases linearly for R_1 and will reach 180,000 t in 2100. The stockpile stabilizes rapidly for R_2 at 7000 t (5-year cooling). For R_3, the UOX decreases from 7000 to 2500 t in 2100, whereas during the same time the MOX increases from 0 to 2000 tons.

By 2100, heavy metals and fission products increase linearly to reach the values given in the table below (in tons):

Scenarios	Np	Am	Cm	Cs	Tc	I
R1	120	148	15			
R2	100	420	65	700	200	52
R3	90	250	40	2500	200	55

1.b - Evolution in the radiotoxicity for the 3 scenarios R_1, R_2, R_3.

The radiotoxicities were inventoried:

- in the waste intended for final disposal. The radiotoxicity is always much lower than in scenario R1. R3 generates two times less radiotoxicity than R2,

- for the cycle that represents the total toxicity to be managed in the event of total nuclear shutdown in 2100.

2. Separation

2.a - Aqueous Processes

Radiotoxicity calculations have been made, estimating reprocessing losses at 0.3% for Uranium, 0.5% for Pu and 5% for the other long-lived elements.

The separation processes considered show that, although in-plant recovery of neptunium and technetium is possible on condition that some modifications are made to the process, the other elements must be separated from the fission product solutions from reprocessing.

The most highly developed processes use an actinide, lanthanide coextraction (TRUEX or DIAMEX)as a first step, subsequently followed by a separation between the two families (TALSPEAK, TRAMEX, diamides, ...).

Selective extraction processes are being developed.

Using the most advanced processes, it was possible to define a plant design based on the following assumptions:

- recovery of Np in the plant
- extraction of Ln + Am + Cm by DIAMEX
- separation of Ln-Am/Cm by the DIDPA,
- separation of Am-Cm by HDDIBMP.

After oxalic precipitation and calcination, NpO_2, AmO_2 and CmO_2 (or their mixture) are obtained and separated from fission products and lanthanides.

2.b - Non-Aqueous Processes

Two methods are examined:

. chlorides: at the present time, most of the research is being done in the USA under the IFR framework and in Japan which has actually transposed the IFR process for metallic fuels or oxides to the processing of fission product solutions;

. fluorides: abandoned today but was studied in the USA, in France and in the former USSR in the '60s and '70s.

These processes are not very far advanced and it is difficult as of yet to evaluate their losses.

3. Transmutation

Whatever type of reactor is used, the recycling can be done either as homogeneous fuels or as heterogeneous targets. The following must be studied for each option:

- the influence of actinides on the physical parameters of the core,
- the transmutation yield,
- the variations in mass and radiotoxicity of the minor actinides.

The studies were first carried out for FBRs.

In a homogeneous method, the maximum allowable enrichment of minor actinides is limited by:

- the consequences on the safety parameters (sodium voiding, Doppler),
- the increase in Pu 238 enrichment over the course of irradiation.

Enrichments of 2.5% by mass of heavy isotopes for a large core like EFR and of 5% for a smaller core such as PRISM appear reasonable. In order to recycle all of the minor actinides produced by a nuclear industry, it is necessary to supply approximately 20% of the total fast reactor power using EFR-type burners, or 15% if PRISM-type burners are used.

The potential radiotoxicity of the waste depends mainly on the performance of the process used in separating different isotopes during reprocessing. With a loss rate of 0.3% for Pu and 1% for minor actinides (Np, Am, Cm), we show that the radiotoxicity could be reduced by a factor of 7 to 30 depending on the time scale (from 100 to 10 million years) compared to the reference scenario corresponding to a closed fuel cycle.

Radiotoxicity reduction factors/reference

		10^3	10^4	10^5	10^6	$10^{7\text{years}}$
Losses	Targets					
0.3%Pu+	40%	14	6	8	33	25
1% (Np, Am, Cm)	100%	20	10	11	25	25

The size of the core and the nature of the fuel have little effect on these results.

Heterogeneous recycling presents the advantages of not modifying the standard fuel and of concentrating the wastes in specific targets.

In FBRs, the ability to "stockpile" these very important wastes could be attained (less than 2 EFRs to manage the minor actinides of the current French nuclear industry, with targets enriched to 100% in actinides placed in the outermost layer of the core).

However, other problems specific to the manufacture of the highly enriched targets and their maintenance under irradiation, particularly for AmO2, have been established involving fluctuations of the neutron flux shape and power variations in the targets which are very difficult to control. The use of targets with reduced concentrations (approximately 50%) appears more reasonable.

The initially attractive idea of a single recycling of the targets, i.e. burning the waste in a single irradiation, is not realistic. The levels of irradiation are insufficient to ensure the complete burning of the waste and, in addition, it is necessary to reprocess the targets to recycle the Cm and Pu produced.

With multirecycling, the fraction of FBRs necessary to recycle all the waste produced by a nuclear industry is 30% of the total power supply compared to 20% in the case of homogeneous recycling.

The radiotoxicity of the waste is also reduced by a factor 6 to 30 depending on the time scale.

So the reference scenario for homogeneous transmutation in FBR to be studied in EFR is a fuel with an initial concentration of 2.5% of minor actinides in heavy metal.

For heterogeneous transmutation in FBRs, the scenario is defined as a specific target NpO2-AmO2 embedded in an inert matrix (A12O3) with an enrichment in minor actinides of 40% of the total mass.

These specific S/As are placed in the outermost layer of the EFR core and irradiated three times more than standard fuel subassemblies.

For PWRs, a similar approach is made in homogeneous and heterogeneous mode to define the equivalent transmutation scenarios.

Consequences of incineration on the physical characteristics of the fuel:

Recycling the americium and neptunium in homogeneous form will modify the physical characteristics of the fuels after irradiation: activity, neutron emission, residual power.

- in PWRs

For a N4 fuel with a burnup of 47.5 GWd/t, adding 1% americium requires an initial enrichment of 4.75% in U 235 and of 5.06% for 1% of neptunium. Consequently, at the end of irradiation, the following results are obtained after 5 years of cooling:

Property	Standard Am recycling	Standard Np recycling
Total activity	2.3	1.5
ß, γ , activity	1.1	1.1
α activity	14.4	5.4
Neutron source	28.2	0.7
Total residual power	3.4	1.7

- in FBRs

Introducing 3% of Np and Am gives, in EFR, a burnup of 150 GWd/t of oxide without changing the initial plutonium content.

After 5 years of cooling, compared with a standard fuel:

- the activity of the heavy nuclei is increased by 10%,
- the neutron source is multiplied by 2 owing to the production of curium,
- the total residual power is multiplied by 1.7.

A2: WASTE TREATMENT

Task 2

"Treatment of Radioactive Waste"

Topic 1	:	Minimization of radioactive discharges
Topic 2	:	Reduction of waste volumes to be disposed of
Topic 3	:	Waste de-categorisation and actions at the source
Topic 4 *	:	Spent fuel conditioning for disposal
Topic 5	:	Potentialities of transmutation of long-lived radionuclides

* No activity running on this topic

Task 2

Topic 1 : Minimization of radioactive discharges

FI2W/0054 Improvement in the performance of the conventional treatment of liquid effuents by co-precipitation.

FI2W/0057 (Part of work programme carried out by LNETI = see topic 2)

Topic 2 : Reduction of waste volumes to be disposed of

FI2W/0052 Compaction of radioactive hulls by high-temperature melting in a cold crucible.

FI2W/0053 Wet oxidation of organic containing wastes.

FI2W/0057 Advanced processes for the treatment of low level liquid wastes at a pilot plant scale.

FI2W/0095 Process design and feasibility study for incineration under pressure, condensation and effluent treatment of radioactive waste.

FI2W/0100 Melting of incinerator ashes using a microwave furnace.

FI2W/0108 Treatment of radioactive solvent waste by catalytic oxidation.

FI2W/0118 Press compaction of LWR hulls.

Task 2

Topic 3 : Waste de-categorisation and actions at the source

FI2W/0062 New macrocyclic extractants for radioactive waste treatment : Ionizable crown ethers and functionalized calixarenes.

FI2W/0070 Decontamination of solid alpha, beta, gamma waste for de-categorisation purposes in terms of disposal route.

Topic 5 : Potentialities of transmutation of long-lived radionuclides

FI2W/0047 Partition of radioactive wastes.

FI2W/0112 High-level liquid waste partioning by means of completely incinerable extractants.

TASK Nr. 2 : TREATMENT OF RADIOACTIVE WASTE

A. Objectives

Improvement of radwaste management schemes by means of new treatment processes allowing :

* the minimization of radioactive discharges into the environment;
* the reduction of the waste volumes to be disposed of;
* the de-categorisation of waste packages in terms of disposal routes;
* the removal of long-lived radionuclides from high level waste for partitioning and/or transmutation purposes.

B. Research topics investigated within the programme 1985-1989

Investigations were carried out on volume reduction techniques for liquid waste from reactor operation, spent fuel reprocessing and from research centres. The work was focused on ultrafiltration techniques, electrochemical ion-exchange and chemical precipitation coupled with centrifugation.
Research work was devoted to the waste de-categorisation for making easier conditioning, transport and disposal operations of a number of alpha and MLW, particularly on :

- treatment flow-sheets relying on solvent extraction;
- chemical precipitation and inorganic ion-exchange techniques;
- exhaustive decontamination of solid alpha waste by leaching with electrogenerated Ag(II).

New immobilisation matrices (modified sulphur cement, ceramics and new cement formulations) have been investigated for various wastes like incinerator ashes, ion-exchange resins, sludges, dissolver residues.
Actions taken at the source of production (MOX fuel fabrication plant) for reducing alpha waste arisings also played an important part in this programme. Quality assurance schemes for waste products in conditioning facilities for cementation, drying and compaction were elaborated and critical parameters for disposal criteria selected.

C. The present programme 1990-1994

Presently Task 2 comprises 13 research contracts, four of them being multinational. They cover the following topics :

Topic 1 : minimization of radioactive discharges

- Setting up of a downstream treatment processes for low level liquid effluents at the La Hague reprocessing plant (CEA Cadarache).
- Radium recovery from uranium tailings (LNETI).

Topic 2 : Reduction of waste volumes to be disposed of

- Recovery of boron from PWR low level liquid waste by electrodialysis, reverse-osmosis, distillation, ion-exchange and electrochemical ion-exchange as alternative treatments (Laborelec, AEA Harwell and CEN/SCK).
- Volume reduction of alpha-bearing incinerator ashes by microwave furnace and melting processes for spent fuel zircaloy hulls in a cold crucible (CEA-Valhrô).
- Ion-exchange resins destruction by H_2O_2 (AEA-Winfrith) and by incineration with oxygen under pressure (Bertin, CEA-Cadarache and INITEC).

Topic 3 : Waste de-categorisation and actions at the source

- Evaluation of decontamination performances of leaching technique with nitric acid and electrogenerated Ag(II) on different solid alpha-bearing wastes (CEA-FAR).
- De-categorisation of medium-level reprocessing concentrates by using "tailor-made" macrocyclic extractants (calixarenes and crown-ethers). This multipartner project associates CEA-Cadarache with the Universities of Barcelona, Belfast, Mainz, Parma, Strasbourg and Twente.

Topic 4 : Conditioning of spent fuels in view of their direct disposal

There are no activities running on this topic.

Topic 5 : Potentialities of transmutation of long-lived radionuclides

- Development and testing of enhanced treatment scheme for separation of long-lived radionuclides from high level liquid waste. This co-ordinated research programme is being carried out by CEA-FAR and KfK.

Title :	Improvement in the performance of the conventional Treatment of Liquid Effluents by Co-Precipitation
Contractor :	CEA-DCC
Contract N° :	FI2W/CT90/0054 TASK 2
Duration of Contract :	From May 1st 1991 to April 30th 1995
Period Covered :	January-December 1992
Projet Leader :	FROMONT Michel

A. OBJECTIVES AND SCOPE

The capacity of treatment of the COGEMA irradiated fuel reprocessing plant at The Hague is to be progressively increased from 400 to 1600 tonnes a year. The regulations concerning the release of radioactive effluents into the sea remain unchanged, that is to say they authorize :

- 45000 Ci (1665.10^3 GBq) for all radioelements (except tritium) including 6000 Ci (222.10^3 GBq) for Sr90 and Cs137;
- 45 Ci (1700 GBq) for α emitters.

The efficiency of radioactive liquid effluent chemical treatment should therefore be improved.

At present, the Liquid Effluent Treatment Plant (so called STE3) implements a process involving a chemical co-precipitation for low activity (act.β<5 Ci/m^3) and medium activity (act.β<300 Ci/m^3) radioactive effluents and a neutralization, followed by filtering for any effluents suspected of the slightest radioactivity (act.α<10^{-4} Ci/m^3, act.β<10^{-2} Ci/m^3).

In association with the treatment plant (STE3) operators who are to supply actual radioactive effluents, we propose to implement complementary treatments in a hot laboratory, using for example mineral exchangers, organic extractants and chemical precipitation, the application of which, in the STE3 plant at The Hague, should entail only minor modifications to the existing process.

B. WORK PROGRAMME

The work programme consists of :

10/91 to 10/92

- the characterization of the chemical forms of the radioelements to be removed,
- the insolubilization of these radioelements by means of mineral exchangers in powder form (oxydes, sulfates, phosphates, ...), of supported organic extractants (active carbon, silica) and of precipitation treatments.

10/92 to 10/93

- the study of the separation of the insolubilized activity by means of the most appropriate processes : tangential filtering, centrifugation or columns used singly or in series.

10/93 to 10/94

- the carrying out of tests on a radioactive pilot mock-up (1/60 scale).

C. PROGRESS OF WORK AND OBTAINED RESULTS

- State of advancement

The evolution of the radioactive liquid effluents discharged into the channel by the STE/La Hague shows a reduction of 30% of the active effluents and of 50% of the suspect effluents (so called "V"), but the distribution stays almost unchanged : 27% of 90Sr, 23% of 127Sb, 17% of 106Ru and 3% of 137 Cs. To reduce the released activity, we focused therefore our attention to these radioemitters. Moreover, V effluents should be investigated as they account for 21% of the discharged alpha activity, although they represent only 6% of β activity. With complementary treatments implementation in view, our goal is to obtain a decontamination factor of the order of 10.

During the previous period (1991), the ionic form identification tests carried out by means of electrophoresis indicate that ruthenium is under molecular and anionic forms at the same time, that strontium is always under cationic form and that antimony is under anionic form at the pH of the effluent.

Considering these results, we studied the fixation of radioelements on organic resins, mineral exchangers and active carbons. Some products yield good results for strontium and antimony, but a compromise must be found for the pH of the treatment. On the other hand, results for ruthenium are disappointing with at best a decontamination factor of 3 with active carbon.

PROGRESS AND RESULTS

1. PERFORMANCE OF ORGANIC RESINS

Sr elimination can be achieved by means of a resin column. The best results are obtained with the iminodiacetic resin TP207 which proves to be more effective than the carboxylic resin CNP80. Figure 1 compares the efficiency between the two materials. Sr85 which is used for γ analysis is eluted from the resin CNP80 just after flushing the column by the effluent, whereas it appears in the eluted effluent after 700 volumes of resin bed for the resin TP207.

According to the analytical conditions, 600 m^3 of effluent can be purified per m^3 of resin TP207. Moreover, elution would require 8 m^3 of 1M nitric acid which would be recycled on a chemical treatment line.

2. USE OF MINERAL EXCHANGERS

Sb125 elimination is possible by using mineral exchangers. Four different exchangers giving the best results are selected to study the influence of the pH in the effluent range : Zirox (zirconium oxide), Manox (manganese oxide), Pertitanic (pertitanic acid) and Oxti (titanium oxide). As can be shown in figure 2, Zirox gives the higher decontamination factor (DF). Nevertheless a quantity of 5 kg/m^3 is required to obtain a decontamination factor higher than 50. As the present cost of this product is expensive (1500 FF per kg), the treatment can be considered as excessive.

3. TREATMENT BY USE OF TITANIUM OR ZIRCONIUM

According to the cost of the previous mineral exchangers, we are turning toward the use of materials containing titanium and zirconium. The products have to be produced at industrial scale. Their particularity is that they can be used either by precipitation in situ either as preformed precipitates or in powder.

Whatever the form of the product, tests give always the same results. Decontamination factors increase with the quantity as can be observed for titanium obtained by precipitation in situ in figures 3 and 4. Then, DF of Sb decreases as the pH increases, whereas the contrary is observed for Sr. With the objective to reduce Sr and Sb, a compromise must be adopted to emilinate in one step these radioactive products.

Metatitanic acid G3 which is a material containing TiO_2 seems to give attractive results for decontamination. With the consideration of price, it is less expensive than the other products and gives the highest volume concentration factors (produced sludges are reduced in volume).

4. ELIMINATION OF ALPHA EMITTERS AND CAESIUM

For alpha emitters, few tests carried out with active carbon and titanium or zirconium salts are good but they must be confirmed in the future. They seem to act as strontium in so far as elimination increases as pH becomes more basic.

As the quantity of caesium is not important in the effluents we received, some treatments give good result, but they are more attributed to floculation of traces of ferrocyanure-nickel preformed precipitate and not to the treatment itself.

LIST OF PUBLICATIONS

No publications other than progress reports dealing with the work under with contract.

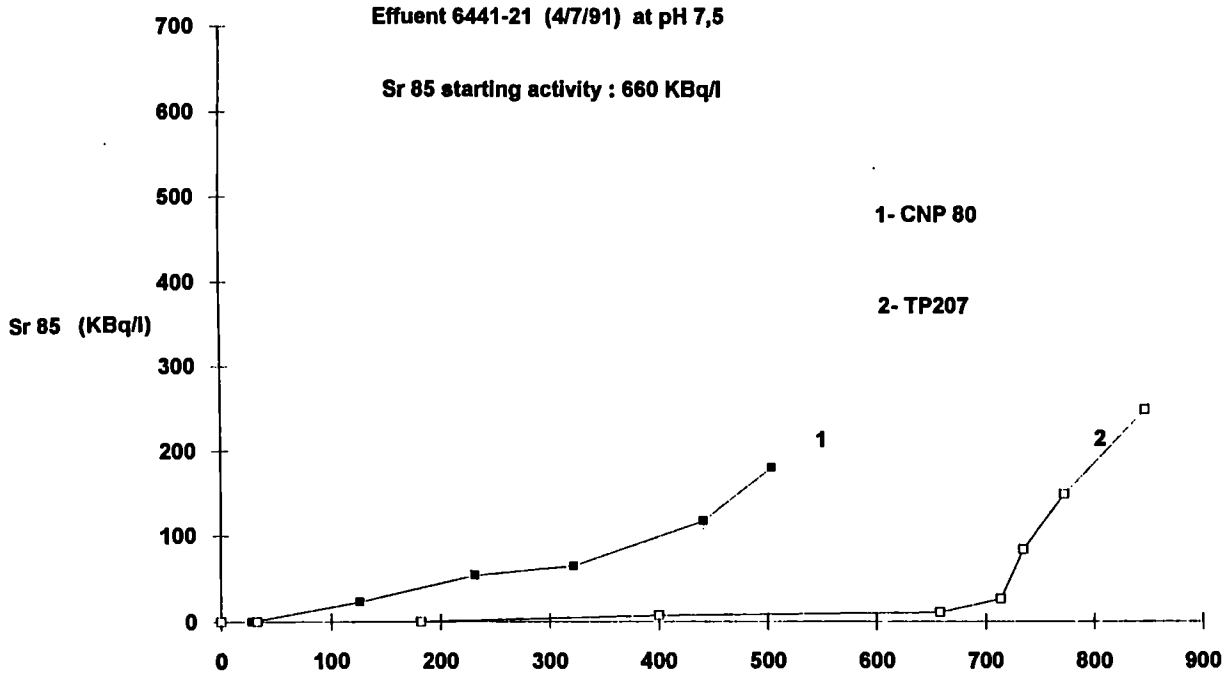

FIGURE 1 : Comparison between the two materials

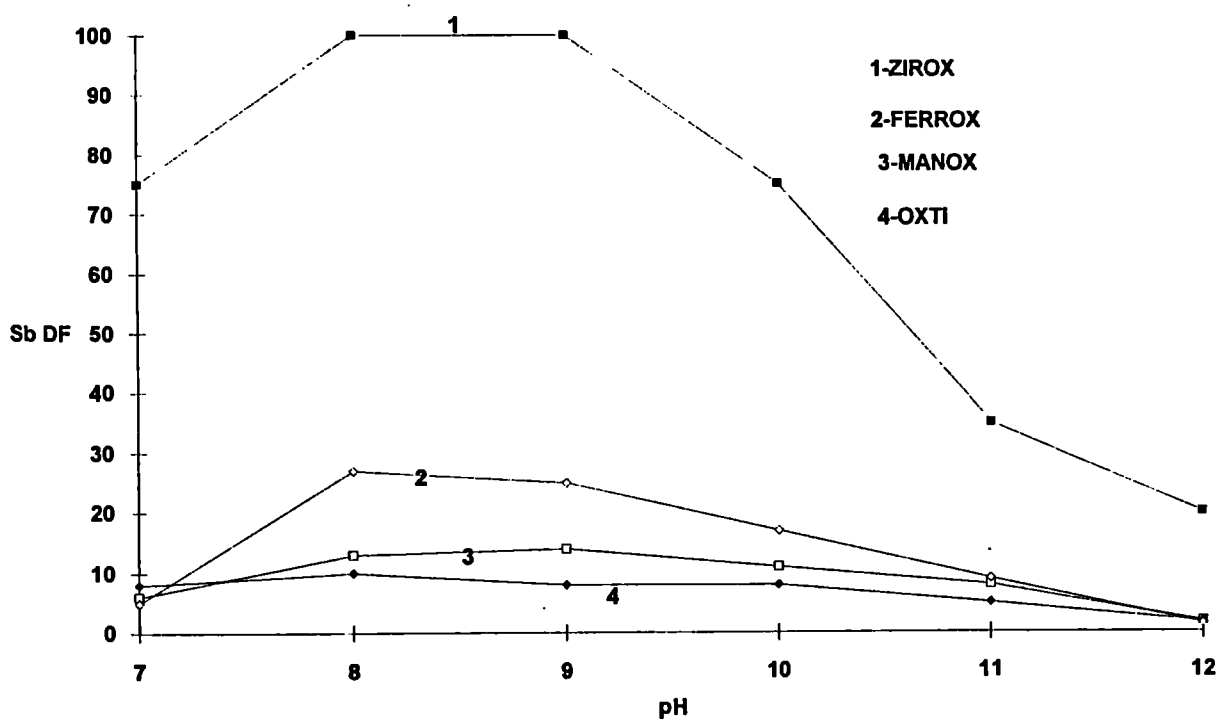

FIGURE 2 : FD Sb function of pH

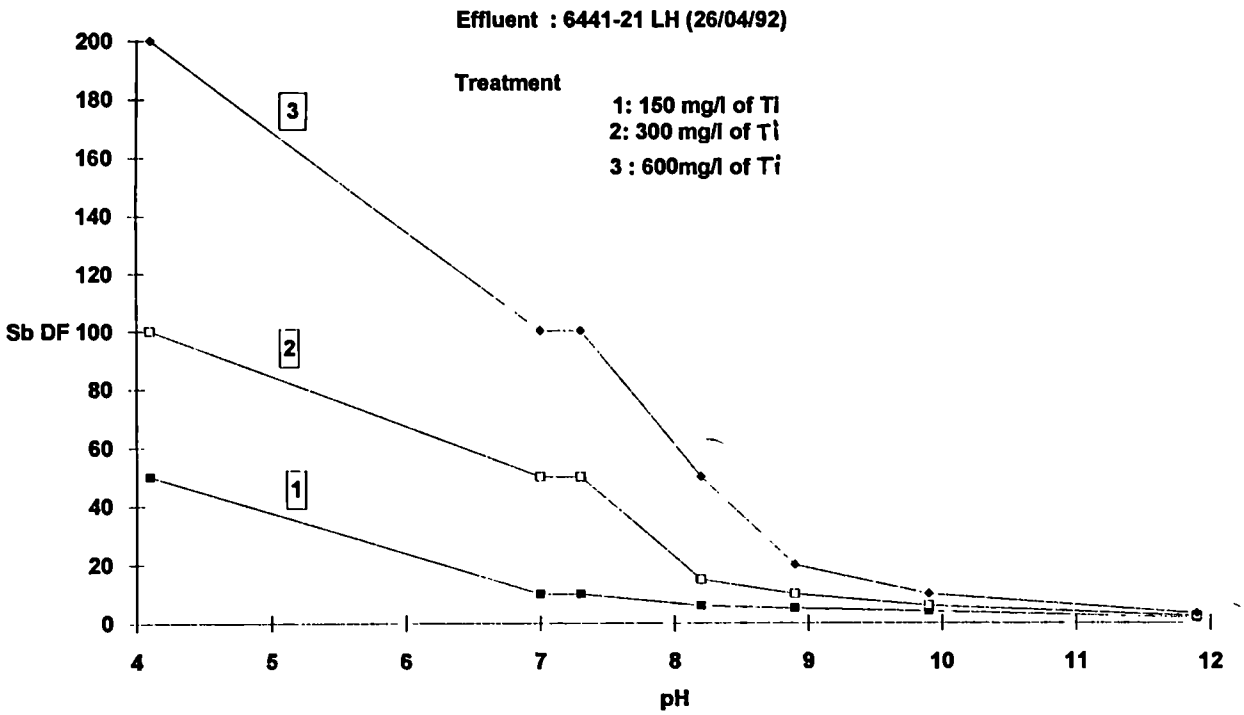

FIGURE 3 : Sb DF function of pH

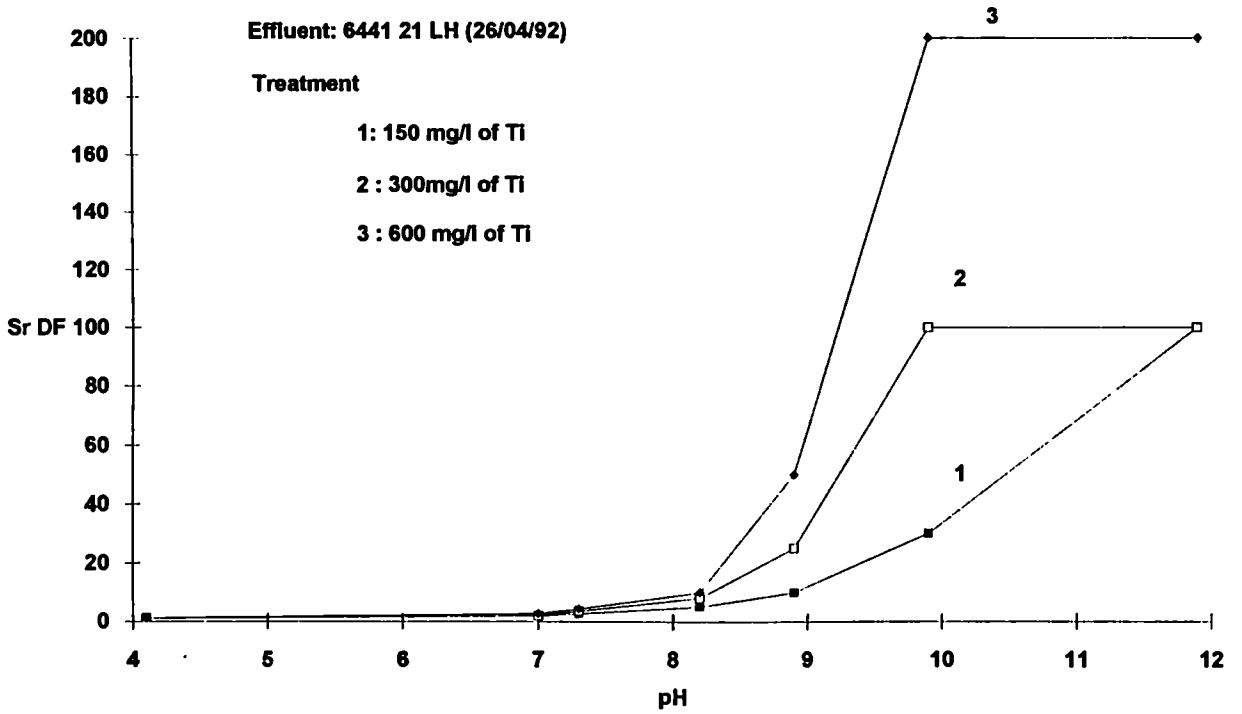

FIGURE 4 : Sr DF function of pH

COMPACTION OF RADIOACTIVE HULLS BY HIGH-TEMPERATURE MELTING IN A COLD CRUCIBLE

Contractor:	CEA - DCC - CEN Valrhô
Contract No:	FI 2W CT90 0052
Contract duration:	January 1991 to December 1992
Period covered:	January 1992 to December 1992
Project leader:	R. Piccinato

A. OBJECTIVE AND SCOPE

The cold-crucible high-temperature melting process for compaction of cladding hulls has been developed in France by the CEA at Marcoule since 1982 under inactive conditions in a full-scale industrial prototype, and since 1988 under active conditions in a laboratory facility (Cell 73). This method reduces the waste volume and exchange surface area, and eliminates any occluded radioactive gases. Its feasibility has been demonstrated for conditioning radioactive stainless steel hulls.

This research project involves compacting radioactive zircaloy cladding hulls in Cell 73. The programme objectives are:

- to produce zircaloy ingots from radioactive hulls;
- to characterize the ingots;
- to determine the volatility balances;
- to assess the decontamination factor obtained.

B. WORK PROGRAMME

B.1 Production of four radioactive ingots in Cell 73 with zircaloy hulls from the Obrigheim reactor.

B.2 Investigation of the activity partition between the flux and ingot.

B.3 Characterization of two ingots:
- Structural homogeneity
- Internal activity distribution
- Leaching resistance.

B.4 Determination of the process volatilization balance.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

The fourth ingot planned under this contract was produced in cell 73, with a composition identical to that of the three previous ingots. It was produced under the same conditions as the third ingot, but with a larger quantity of flux added from the beginning of the melt.

The structure, homogeneity and internal radioactivity distribution were investigated in two ingots, Zi-06 and Zi-07.

The current state of advancement is as follows:

B.1 All four active ingots have been produced: Zi-03, Zi-04 & Zi-06 in 1991, and Zi-07 in 1992.

B.2 The activity partition between the flux and ingots has been determined for all four ingots.

B.3 Characterization of ingots Zi-06 and Zi-07 is nearing completion. The examination of ingot structure and homogeneity has been terminated. Only the leach test of ingot Zi-07 in the CLOVIS cell is still in progress, after delays resulting from contamination problems while testing specimen Zi-06 in cell 73.

B.4 The process volatilization and off gas balance has been determined for all four ingots.

Progress and Results

1. Production of Ingot Zi-07 (B.1)

Ingot Zi-07 was produced from a mixture of 90% active zircaloy hulls[1] and 10% inactive stainless steel hulls; this composition was required after safety studies covering interactions between water and the molten metal. Fifty percent of the flux was melted from the beginning, and the total flux quantity represented 9.8 wt% of the active hulls.

No unmelted hulls were observed in the ingot.

The mass balance deficit was comparable to the results obtained for the first three ingots: about 1.05% for the metals and 5.78% for the flux.

2. Radionuclide Volatilization for Ingots Zi-06 and Zi-07 (B.4)

The volatilized α activity was very low.

The most volatile β-emitter was ^{137}Cs, which accounted for some 90% of the total β activity recovered from the off-gas. Small amounts of ^{134}Cs and ^{90}Sr were also found.

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[1] *Some Inconel or stainless steel fragments of springs or grids remained after manual sorting, however.*

Tritium released during melting was largely recovered as tritiated water after oxidation into the CuO furnace at the end of the off-gas treatment cycle, although the presence of oxygen in the circuit caused a small fraction to be converted to tritiated water after oxidation in the oxygen directly in the off-gas stream.

3. Slag Activity for Ingots Zi-06 and Zi-07 (B.2)

The α-emitter fraction trapped in the flux increased significantly between melts Zi-06 (61.86%) and Zi-07 (79.2%). This may be attributed to the use of a higher grade of CaF_2 flux in larger amounts from the beginning of melt Zi-07.

Most of the β activity in both melts (86.7% and 87.4%) was due to ^{90}Sr. Over 90% of the ^{90}Sr in the hulls was recovered in the slag.

4. Ingot Activity and Chemical Analysis (B.2)

Elemental analysis showed uniform metal chemical composition for all the samples.

The α and βγ activity was also uniformly distributed. The activation products (^{60}Co and ^{125}Sb) remained concentrated in the ingots. This homogeneity was confirmed by α and β autoradiography, although some local heterogeneities were observed.

A large fraction of the tritium was trapped in the ingot: about 14.8 $MBq \cdot g^{-1}$ (400 $\mu Ci \cdot g^{-1}$) in ingot Zi-06 and 9.62 $MBq \cdot g^{-1}$ (260 $\mu Ci \cdot g^{-1}$) in ingot Zi-07.

The activity distribution in the off-gas stream, the slag and the ingot is indicated in Table I (Zi-06) and Table II (Zi-07), together with the overall hull decontamination factors.

5. Metallographic Examination of Ingots Zi-06 and Zi-07 (B.3)

Density measurements, followed by optical and scanning electron microscopic observation and by α and βγ autoradiography showed overall microstructural and radioactive homogeneity in the ingots, despite local three-phase heterogeneities. Each ingot consisted principally of pure zircaloy, with two minor phases resulting from the zircaloy-stainless steel mixture. Most of the activity was concentrated in the zircaloy phase, which exhibited the greatest solubility for fission products.

6. Leach Testing (B.3)

Ingot Zi-06 was leached for 28 days in distilled water in cell 73. Two test specimens were leached: one from which all the outer surface was removed, and the second comprising a large fraction of the ingot exterior. However, contamination problems arising mainly during specimen handling operations corrupted the test results.

Fresh leaching equipment was installed in a clean cell, CLOVIS, and leach testing has recently begun on specimens from ingot Zi-07.

Table I.
Activity Distribution for Ingot Zi-06
Activity Percentages as of April 30, 1991

Nuclides	A Volatility (%)	B Slag (%)	C Ingot (%)	A + B Decontamination Efficiency (%)
^{90}(Sr+Y)	3.93	93.13	2.94	97.06
^{137}Cs	74.68	20.66	4.66	95.34
^{134}Cs	(68.56)	(18.69)	(12.75)	> 87.25
^{106}(Ru+Rh)	–	–	–	–
^{144}(Ce+Pr)	–	–	–	–
^{125}Sb	(0.28)	(0.29)	(99.43)	< 0.57
^{60}Co	0.01	0.10	99.89	0.11
^{54}Mn	–	–	–	–
^{154}Eu	(9.38)	(71.39)	(19.23)	> 80.77
Total β	16.31	34.36	49.33	50.67
$^{239\text{-}242}$Pu	0.57	11.32	88.11	11.89
^{238}Pu+^{241}Am	0.83	66.82	32.25	67.65
^{244}Cm	4.43	87.82	7.75	92.25
^{242}Cm	–	–	–	–
Total α	1.64	61.86	36.50	63.50

( ) The measured results only allow decontamination factors to be indicated as upper or lower limits.

– Values measured at detection limits with no statistical significance.

Table II.
Activity Distribution for Ingot Zi-07
Activity Percentages as of April 30, 1991

Nuclides	A Volatility (%)	B Slag (%)	C Ingot (%)	A + B Decontamination Efficiency (%)
^{90}(Sr+Y)	5.86	90.54	3.60	96.40
^{137}Cs	82.05	14.65	3.30	96.70
^{134}Cs	(54.42)	(9.17)	(36.41)	> 63.59
^{106}(Ru+Rh)	–	–	–	–
^{144}(Ce+Pr)	–	–	–	–
^{125}Sb	(1.32)	(0.59)	(98.09)	< 1.91
^{60}Co	0.001	0.14	99.86	0.14
^{54}Mn	–	–	–	–
^{154}Eu	(1.40)	(29.23)	(69.37)	> 30.63
Total β	16.15	23.91	59.94	40.06
$^{239\text{-}242}$Pu	9.40	64.65	25.95	74.05
^{238}Pu+^{241}Am	5.23	84.41	10.36	89.64
^{244}Cm	3.71	92.69	3.60	96.40
^{242}Cm	–	–	–	–
Total α	5.35	79.02	15.63	84.37

( ) The measured results only allow decontamination factors to be indicated as upper or lower limits.

– Values measured at detection limits with no statistical significance.

WET OXIDATION OF ORGANIC CONTAINING WASTES

Contractor:	AEA Decommissioning and Radwaste
Contract No:	F12W/CT90/0053 Task 2
Duration of contract:	from March 1991 to February 1995
Period covered:	January - December 1992
Project Leader:	Dr. N S Holt

A. OBJECTIVES AND SCOPE

A wet oxidation process for the destruction of organics from intermediate level radioactive wastes has been developed in parallel by AEA Technology (Decommissioning and Radwaste) for the treatment of reactor sludges from the Winfrith Steam Generating Heavy Water Reactor, and by Nuclear Electric for the treatment of spent organic ion exchange (IX) resins from their nuclear power stations.

The process, which is based on catalysed reaction with hydrogen peroxide, has already been subject to experimental investigations up to 10-50 kg inactive resin batch using pilot scale plant for the above applications.

The main objective of this programme is to demonstrate the feasibility of the wet oxidation technology on a range of real radioactive wastes by the design, construction and operation of a fully active mobile pilot plant (50-100 kg/day capacity).

The key organic wastes identified for investigation include:-

- IX resins from power reactor operation
- Decontamination liquors
- Mixed reactor sludges from WSGHWR
- Solvents and scintillants
- Cellulose containing soft wastes.

B. WORK PROGRAMME

The programme consists of the following tasks:-

Task 2.2	Analysis of literature data and assessment of candidate waste in UK and EC context.
Task 2.3	Evaluation of previous experimental results outside this CEC contract.
Task 2.4	Completion of wet oxidation experiments at small scale for both inactive and active conditions.
Task 2.5	Appraisal of alternative plant concepts.
Task 2.6	Evaluation of complete treatment schemes.
Task 2.7	Design, construction and operation of a mobile active wet oxidation pilot plant.
Task 2.8	Drawing-up of flow sheets
Task 2.9	Analysis of safety and economic aspects

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

In the first year of the project (1991), the published world-wide experience of wet oxidation techniques for radwaste treatment was reviewed, and the results of previous studies by AEA and the UK nuclear industry evaluated comparatively. After assessment of current and planned future organic radwaste streams in the UK, several waste types were identified as candidates for wet oxidation treatment. Amongst these, ion exchange resin waste classified as intermediate level (ILW) was the major target group. Laboratory studies confirmed the feasibility of treatment for three important IX resin types, and established the optimum reaction conditions for each using a batch reaction mode. At this point sufficient information was available to initiate the design of the mobile active pilot plant. The first step of the design stage was to examine all possible reaction concepts, ranging from a simple batch tank reaction system to a fully continuous process, and to select the most appropriate for a mobile treatment facility. A semi-continuous reaction concept was chosen as the lead option, which combines the relative simplicity of a batch reactor with the enhanced throughput of continuous processes.

In the year covered by this report (Jan-Dec 1992), the design for the mobile active pilot plant has been completed. This procedure has included a two-level Hazard and Operability (HAZOP) study on the preliminary design and subsequent scheme design. The final detailed design produced was subjected to a rigorous safety review procedure before authorisation for plant construction was granted. The completed wet oxidation plant will be available for commissioning trials in February 1993.

The assessment of data from previous experimental programmes undertaken by AEA and Nuclear Electric has been completed and a report issued.

Further experimentation at laboratory scale with inactive waste simulants has demonstrated that efficient organic removal from mixed organic/inorganic IX material, non-foaming and foaming decontamination liquors (including a chelating agent), cellulosic material (paper/cloth) and scintillation cocktail residue are achievable using a batch reaction. Semi-continuous experiments using cationic IX resin and also with WSGHWR reactor sludge have shown that significantly less hydrogen peroxide is required for this reaction mode relative to the equivalent batch reaction. Samples of spent radioactive IX resin stored at the Trawsfynydd Magnox power station have been obtained for future laboratory scale experimentation.

Progress and Results

Task 2.2 - Analysis of Literature Data

This task has been completed, with the production of a comprehensive literature survey, and an assessment of UK candidate wastes. Considerable information regarding candidate waste for wet oxidation treatment in an EC context has also been gathered.

Task 2.3 - Evaluation of Previous Experimental Results

Both AEA and Nuclear Electric had performed extensive research and development work on the wet oxidation process prior to the commencement of this programme. A review of this earlier experience has been carried out /1/. The review covers experimental studies undertaken by AEA at up to 250kg batch scale using non-radioactive WSGHWR reactor sludge simulant, and supporting small scale active experiments. Nuclear Electric's parallel studies on a range of organic IX resins at up to 10kg resin batch scale, and product conditioning using a wiped film evaporator are also discussed.

Task 2.4 - Completion of Wet Oxidation Experiments

The susceptibility of several candidate wastes to treatment by wet oxidation was examined at laboratory scale with non-radioactive material. The following waste types were studied:

Mixed inorganic / organic ion exchangers
Soft cellulosic waste
Chemical decontamination liquor components
Foaming decontamination mixture
Scintillation cocktail residue

In addition to the above, which were studied using a batch reaction mode, the possibility of treating mixed reactor sludges from the WSGHWR and Lewatit DN IX resin by a semi-continuous reaction scheme was considered experimentally. These latter experiments were carried out to support the decision, from the plant concepts study, to proceed with the semi-continuous process design for the mobile plant.

a) Inorganic / Organic Cationic Exchanger Mixtures

Both organic Lewatit DN, a phenol-formaldehyde based resin, and the inorganic zeolites AW500 and Decalso Y have been used by the UK nuclear industry for ^{137}Cs removal from fuel storage pond water. In some cases, mixtures of Lewatit DN with one or other of the zeolites are present in waste storage facilities. The efficiency of the wet oxidation of Lewatit DN alone was compared with that of Lewatit DN / zeolite mixtures.

It was found that for laboratory scale batch reaction, the presence of either zeolite reduced the efficiency of organic removal from the Lewatit DN component, especially with regard to the initial oxidation and resultant dissolution of the resin. This effect may be attributable to competitive binding of catalyst cations by the zeolites, and results in an increased hydrogen peroxide requirement for treatment of such mixtures. However, the volume reduction achieved in each case by removal of the Lewatit DN component was unchanged by the presence of zeolite components.

b) Soft Cellulosic Waste

A mixture of tissue paper and cotton cloth was successfully treated, with 95% of the original organic content removed. When dried, the treated residue represented 24% of the initial waste mass, and

consisted mainly of catalyst salts. Higher mass reduction is anticipated if a semi-continuous reaction scheme were used. The key application for this treatment is for plutonium and transuranic contaminated cellulosic material.

c) Chemical Decontamination Liquor Components

Typical components of chemical decontamination mixtures were individually subjected to wet oxidation treatment. These comprised citric acid, formic acid and EDTA. For each substance, over 99% removal of organic carbon was demonstrated using an initial 10g l^{-1} solution of organics.

d) Foaming Decontamination Mixture

The mixture used for testing consisted of a solution of surfactants and a secondary alcohol in dilute sulphuric acid. When aerated it produces a foam of finite lifetime before returning to liquid form. It was found that during batch wet oxidation, each organic component of the mixture was oxidised. In these initial trials, 85-90% of the original organic carbon present was removed. Near complete removal of organic carbon is considered likely if the more recent semi-continuous reaction system were employed.

e) Scintillation Cocktail Residue

Efficient oxidation of a typical scintillation cocktail has been shown, both with and without the presence of the xylene base solvent. Over 95% reduction in organic carbon was achieved, with the option of preliminary xylene recovery and recycle.

f) Semi-Continuous Reactions

In this modification to the batch wet oxidation reaction, successive batches of organic feed are added throughout an extended reaction period. This maintains a large excess of organic substrate at all times and hence tends to increase overall reaction efficiency. The reaction is terminated when an upper limit for solid inorganic salt products from the oxidation is reached.

It was found that the efficiency of reaction was enhanced for both cases studied relative to the equivalent batch reaction. For WSGHWR sludge, an increase in hydrogen peroxide utilisation efficiency from 45% for batch reaction to 86% for semi-continuous reaction was achieved. A smaller but significant increase from 42% to 60% was measured in the treatment of Lewatit DN resin. Thus the semi-continuous process may potentially halve the hydrogen peroxide requirement for IX resin treatment relative to single batch reaction.

Task 2.5 Appraisal of Alternative Plant Concepts

The study has concluded that the semi-continuous process i.e. partially continuous waste feed with batch discharge was the preferred option and offers advantages of high throughput for a given reactor size, increased efficiency of hydrogen peroxide use, and improved control of product conditioning and discharge/2/,/3/.

Task 2.7 Design, Construction and Operation of a Mobile Active Pilot Plant

Following from the appraisal of plant concepts and plant options studies, an overall scheme design and subsequent detailed design of the plant has been produced. A HAZOP 2 has been carried out on the scheme design and its recommendations incorporated into the detailed design. A pre-construction safety assessment of the risks associated with plant construction, commissioning and operation has been completed and approved /4/. Construction and assembly of the plant is near completion, with initial commissioning trials scheduled for February 1993.

The pilot plant is housed within a standard ISO transport container, and as such is readily mobile. It is based around a 160 l glass lined reaction vessel, and has an anticipated throughput of up to 100l per day for IX resin. The only external facilities required are 415 V electricity supply, water supply and hydrogen peroxide storage tank. For routine conditions, the plant is capable of fully automatic operation, via a sequenced control and data acquisition (SCADA) system.

External or internal radiation shielding may be fitted as required and the plant may be operated at a remote control desk to further reduce radiological dose to personnel.

List of Publications

/1/ WILKS, J.P., HEBDITCH, D.J., "A Summary of Experience in the Application of Wet Oxidation to Radioactive Waste Streams", AEA D&R Report CPDD(91)P763 (1992)

/2/ AEA D&R Report CPDD(92)P753 (1992)

/3/ HOLT, N.S., FINLAYSON, F., "Wet Oxidation Mobile Plant Options Study and Process Selection", AEA D&R Report AEA-D&R-0359

/4/ TWISSELL, M.A., WILKS, J.P., HOLT, N.S., "Preliminary Safety Report / Pre-construction Safety Report - Mobile Wet Oxidation Pilot Plant", AEA D&R Report CPDD(92)P829 (1992)

/5/ TWISSELL, M.A., WILKS, J.P., HOLT, N.S., "Wet Oxidation of Organic Wastes - Second Semestrial Report", AEA D&R Report CPDD(91)P798 (1992)

/6/ TWISSELL, M.A., "Wet Oxidation of Organic Wastes - Third Semestrial Report", AEA D&R Report CPDD(92)P906 (1992)

Title : Advanced processes for the treatment of low level liquid wastes at a pilot plant scale

Contractors : LABORELEC (B) - SKC-MOL (B) - AEA-Harwell (UK) - LNETI (P)
Contract n° : FI2W - CT90 - 0057 (DTEE)
Duration of contract : from April 1/1991 to 31/12/1994
Period covered : 1992
Project leader : Coordinator R. ROOFTHOOFT
SCK P. DE REGGE
AEA A. TURNER
LNETI J.P. GALVAO

A. OBJECTIVES AND SCOPE

The objectives of the programme are :

a) Eliminate boron from low level liquid waste of PWR plants.
Five processes will be evaluated (electrodialysis, reverse osmosis, distillation, ion-exchange and electrochemical ion-exchange).

b) Demonstrate the capabilities, reliability and cost-effectiveness of these processes for the treatment of real PWR wastes over realistic time scales at representative throughputs.
As a part of this, it is a key goal to achieve low activity discharge levels (< 2 MBq/m^3) and high waste volume reduction factors (> 500) in a cost-effective way.
An additional goal will be to obtain purified boric acid with less than 1 ppm Cl^- and a B-recovery of more than 75 %.

c) Evaluate electrochemical ion-exchange (EIx) on wastes from a nuclear research center (Harwell) in comparison with the flocculation/sand filtration process currently used for the removal of Cs, Co and α-emitters.

d) Evaluate electrochemical ion-exchange and reserve osmosis for the removal of Ra and other heavy metals from uranium mine tailing wastes in comparison with flocculation.

B. WORK PROGRAMME

First the composition of the waste streams will be identified. To select the optimal equipment batch experiments are carried out on simulant wastes. On the basis of these, bench-top experiments will be realized, firstly with simulant and then with genuine waste.

On basis of the obtained information one or more pilot plants will be designed and built. They will be used for testing on real waste :
- at Doel or Tihange PWR-stations
- at Harwell research laboratories
- on the Portuguese site Sacavem for uranium mine tailing wastes

The processes which will be evaluated are
1) electrodialysis
2) reverse osmosis
3) distillation
4) ion exchange
5) electrochemical ion exchange

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

For PWR-low level waste, both simulant and genuine waste treatments have been performed with different techniques. Reverse osmosis does not seem to allow boron recoveries in excess of 75 %.

Electrodialysis and electrochemical ion exchange seem the most promising techniques. Evaporation under pressure can also give a high boron recovery but is a more expensive and less desired technique.

Conventional ion exchange is not selective enough or gives low regeneration efficiencies. Reverse osmosis and electrochemical ion exchange have been tested on simulant and genuine uranium mine tailings.

For the treatment of Harwell LLW the design of a pilot plant has been completed.

Further investigations on electrode manufacturing and chlorine evolutions have been performed. This results in the production of electrode materials at much lower price and with reduced chlorine production.

Progress and results

1. Membrane techniques on simulated PWR-waste

1.1 Electrodialysis

It has been demonstrated in a first step (without EDTA) that B-losses increase with pH.

The removal of activity has been efficient under all conditions but adsorption of mainly Co on the membrane surfaces occurs.

With EDTA in the solution, similar conclusions have been found i.e. B-losses increasing with pH.

EDTA has also an effect of desorption of Co which had been accumulated previously on the membranes.

The removal of EDTA itself is good.

The loss of B becomes significant at pH 8 (10 - 15%) and important at pH 9.

Figure 1 summarizes the influence of pH and EDTA on boron losses of simulated waste treated by electrodialysis.

1.2 Reverse osmosis

1.2.1 Membranes in cellulose acetate

The amount of B which passes through the membrane is a function of pH. When the pH increases the B is more and more present as a borate ion which does not pass through the membrane.

The retention becomes significant at pH > 6 and is important at pH 9 (85 %).

Figure 2 summarizes the influence of pH.

The influence of EDTA was not examined on this type of membranes.

1.2.2 Thin film composite membranes

In thin film composite membranes (Film-Tech) the tests have been performed in presence of EDTA.

The boron recovery in the permeate is too low. At its best only about 50 % of the B is passing the membrane (to be compared to a goal of 75 % recovery).

2. Membrane techniques on real PWR-waste

All tests have been performed on an electrodialysis bench-top installation in the waste building of the Doel nuclear power stations.

The equipment contains three vessels of 1,5 l each and a stack of 30 membranes. The flow rate (recirculation) is 200 l/h. The vessels contain respectively the product, the brine and the electrode rinsing solution. The composition of the waste to be treated is given in table I. It has been shown that the activity and the polluting salts are removed in a short treatment time (10 to 15 min). In a second series of tests primary waste (higher B-content) was used.

The number of treatments without replacing the concentration has progressively been increased. As the boron is not lossed to the concentrate, only activity and conductivity are increasing in this concentrate. Up to 35 batches have been treated without major problems.

During this test the pH in the product water varied between 4,2 and 4,8.

The conductivity in the brine (concentrate) increased continuously to approximately 800 µs/cm starting from 50 µs/cm in the initial solution. The product water shows conductivity from 3,7 to 8 µs/cm. In all cases the activity in the product water remained below 1,8 MBq/m^3. In the brine it increased to 40 LMBq/m^3.

3. Distillation on simulated PWR-waste

The results of distillation of boron trimethylester, already performed in 1991, have been confirmed and succesfully concluded. Tests on steam distillation of boric acid have been realised in 1992. As the volatility is due to undissociated boric acid, the efficiency decreases at high pH. At 100°C the distribution coefficient of B is 0,005 to 0,01. It increases with the temperature.

Distribution coefficients have been measured in the range 5 to 10 bar.

A test at 5,9 bar with a simulated solution of 2580 ppm of H_3BO_3 (437,1 ppm B) gives a condensing vapour with a content of H_3BO_3 between 2000 and 3000 ppm giving a distribution coefficient of 0,02.

The pollution by Cl^-, PO_4^{3-}, Cs and Co in the condensate is very low.

At 10 bar the distribution coefficient for H_3BO_3 is 0,03.

At 8,75 bar a distribution coefficient of 0,032 has been obtained.

4. Ion-exchange on simulated PWR-waste

Amberlite IRA-743, an ion exchange resin from Rohm and Haas is considered as specific for borate and boric acid.

The theoretical capacity is 5,7 mg B/ml resin. At low boron concentrations however, the operating capacity varies between 1 mg/l (at 10 ppm B) and 3 mg/l (at 100 ppm).

The regeneration of the resin is rather low i.e. the boron concentration during elution remains low. Recovering small concentrations of boron is a problem.

5. Electrochemical ion exchange on simulated PWR-waste

Different types of electrodes and combinations of electrodes have been tested at several flow rates in order to assess Cl^- and Na^+ concentrations in effluent from continuous units.

The best performance was obtained by a combined continuous unit using IRC84 and IRA910 as cation and anion materials respectively (first tests).

Other types of ion exchangers have been tested afterwards. All results indicate that the rate of removal of Cl^-, Na^+, Cs^+ and PO_4^{3-} is higher at low pHs. The removal of B is also lower at low pH as the dissociation of boric acid is suppressed.

At high pH sodium and borate ions are removed from the stream as the majority ionic species. The rate of removal of trace species decrease accordingly.

When EDTA is added to the solution 50 % of the cobalt is found in the anion concentrate, indicating that the addition of EDTA produces an anionic cobalt species. The removal of caesium or sodium is not affected by EDTA.

Finally a combination IRA910/CG120 was selected for tests on genuine waste at Doel nuclear power plant.

In addition a cell was developed for the concentration of boric acid as an alternative to evaporation. The best conditions for this concentration process are :

- high current density
- right balance of feed flow rate / concentrate flow rate
- pH between 9 and 10

6. Electrochemical ion exchange on real PWR-waste

The tests have been performed on the same solution as the electrodialysis.

In all cases low activities (< 1,5 MBq/m³) have been obtained.

Analysis of the results are continuing.

7. Electrochemical ion exchange on Harwell LLW

The design of the pilot plant has been completed. This unit comprises two large scale modular continuous cells using Ir/Ta coated Ti-electrodes.

Due to the presence of particulate activity, better results are obtained with prefiltered solutions (5 µ filters) but the decontamination factors remain better for conductivity than for activity. This may be due to the presence of colloidal activity not removed by the coarse filter.

8. Electrode manufacture

Inexpensive current feeders are being developed. The most stable electrode materials have been runnning for over 20 months. The materials used cost approximately 100 £/m², almost a 10 fold improvement over the equivalent cost of platinised titanium.

9. Chlorine evolution

During continuous EIX processing of PWR-LLW the concentration of Cl^- in the anode concentrate compartment is approximately 700 ppm which can be oxidized to chlorine. This evolution of chlorine gas causes three problems :

- corrosion of outlet pipes
- potential degradation of anion exchange material and binder
- potential health risks associated with toxic gases.

Materials which could reduce the rate of oxidation have been tested. It has been found that manganese oxide coated substrates offer a surface that produces less than one sixth of the chlorine of a platinised titanium electrode under identical anodic conditions.

10. Treatment of uranium mine tailings

10.1 Lab-tests with reverse osmosis

These tests were done on flat membranes from Amafilters to assess sulphate and chloride retention. The membranes which were tested were cellulose acetate and polyamide composite.

At 40 bar operational pressure retentions for $SO_4^=$, are 96,9 % on polyamide and 98,7 % on cellulose acetate. For Cl^- these values are respectively 93,9 and 66 %.

10.2 Bench-top RO tests

All tests were carried out on a polyamide spiral wound membrane of 0,3 m^2 of area. For concentrations of 2300 ppm $SO_4^=$ in the influent values of < 2 to 5 ppm have been found in the permeate. Most elements are rejected more than 99,5 %. Only Na^+ and Cl^- show somewhat lower results (96 and 83,3 % respectively).

On genuine waste similar or even better results have been obtained (passage of Cl^- 5 %). Volume reduction factors of 6 could be achieved and approximately 80 % of permeate could be recovered. However calcium sulphate precipitation occurs.

10.3 EIX

A system combining EIX and internal precipitation has been tested on streams containing only radium and a simulant waste. In the radium only stream DFs of 100 were obtained at low flow rates. During the treatment of simulant stream DFs of > 5 have been obtained.

Table I : Characteristics of waste solution

	Before filtration	After filtration (5 µ)
Total γ	63,7	15,1
^{58}Co	27	
^{134}Cs	3,8	
^{137}Cs	2,7	
^{95}Nb	1,4	
^{54}Mn	0,9	
^{60}Co	15,2	
B ppm		19
Conductivity µS/cm		202
pH		6,74

Fig 1 Electrodialysis B-loss as a function of pH

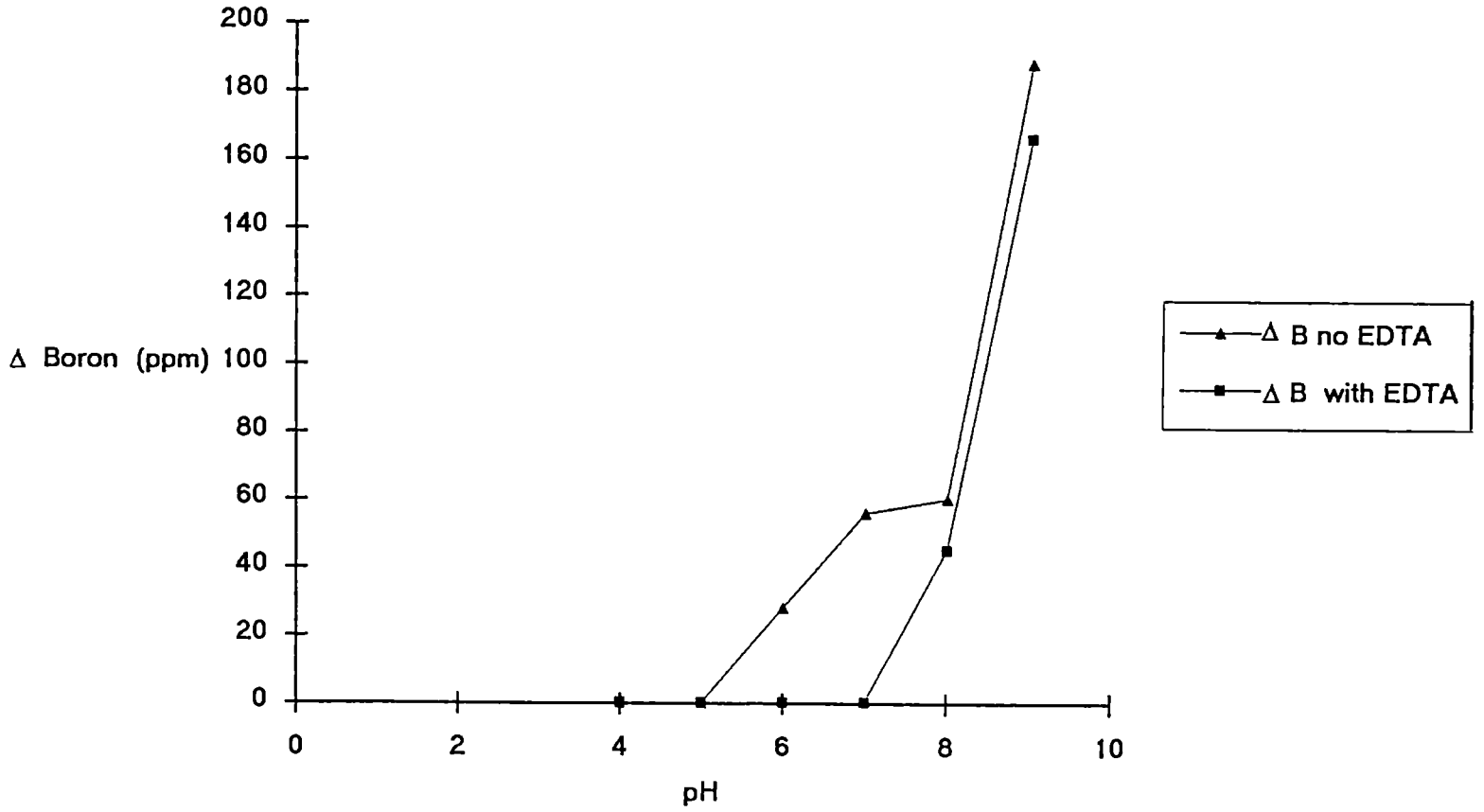
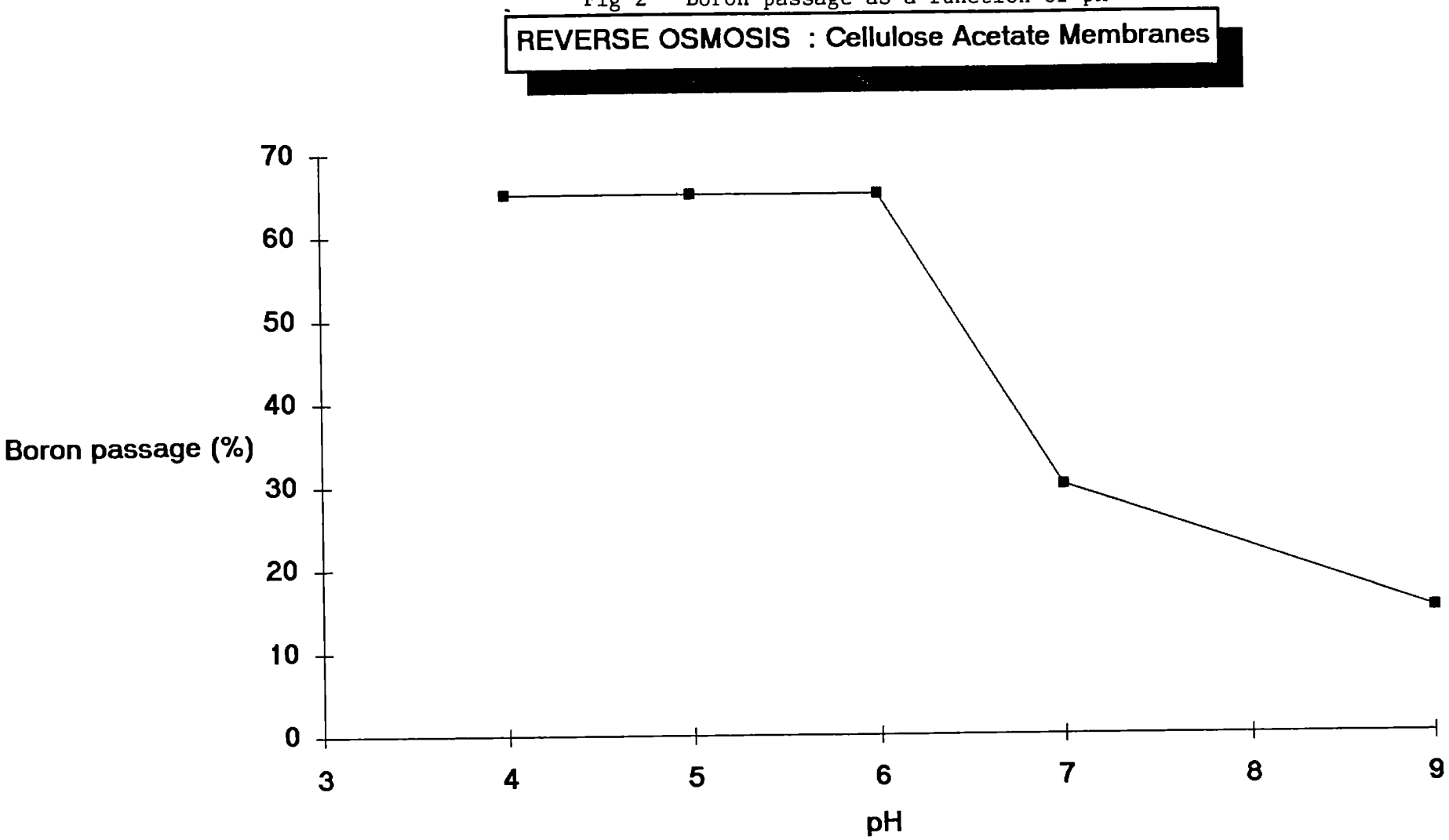


Fig 2 Boron passage as a function of pH



Title	Process design and feasibility study for incineration under pressure, condensation and effluent treatment of radioactive waste	
Contractors	BERTIN & Cie (F), CEA-Cadarache (F) and INITEC (SP)	
Contract N°	F12W-CT91-0095	
Duration of contract	July 1991 - December 1993	
Period covered	January 1992 - December 1992	
Project leader	C. LEONARD	BERTIN & Cie, Coordinator
	G. NAUD	CEA
	S. ALAMO	INITEC

A. OBJECTIVES AND SCOPE

The main objective of this research is the evaluation of the technical feasibility as well as economical and safety implications of the combustion of a range of organic wastes containing radioactive elements, by means of oxygen under pressure, using a new type of incinerator relying on the recent technical developments achieved within the MESMA (Autonomous Energy Module) project.
In particular, the study will have to demonstrate that this new type of incinerator enables a quantitative destruction of organic wastes while only giving rise to the release of inactive-gases (in terms of radioactivity and chemical toxicity).
The work to be performed is mainly focused on the study of the adaptation of a closed loop for combustion under pressure operating at 60 bar - including the setting-up of a suitable off-gas treatment - to incineration of at least four types of typical organic containing radioactive wastes (spent ion-exchange resins/sludges according to French and UK formulations, spent solvent used in the Eurex plant, decontamination liquors).
BERTIN has to adapt the process, developed for the MESMA project, to the case of waste incineration. The CEA will make a review of the possible waste to be processed, and will perform some laboratory trials in order to check the behaviour of waste samples under conditions of incineration. INITEC will design the main components of a plant, based on a 10 kg/hour throughput, and will make an evaluation of the process safety.

B. WORK PROGRAMME

The work programme comprises eight distinct steps :

1. Identification of radioactive waste : different organic wastes will be analysed. The choice will take into account the incineration characteristics as well as the interest in

removing organic elements from the waste (amount produced, existing solution of removal, ...)

2. Drawing-up of process flow-sheets : for several selected wastes, the best process and its main operating parameters will be defined
3. Design of the main plant components : relying on before mentioned flow-sheets, all the components of a 10 kg/hour throughput the pilot plant will be designed
4. Treatment and conditioning of secondary waste : ashes, dust, liquids and gases (uncondensable gases and the release of storage tanks under pressure)
5. Process safety : an analysis of risks will define control and safety procedures necessary for the plant
6. Bench-scale tests : some tests will confirm the hypothesis made upon the waste gasification and flue gases amount
7. Technico-economical evaluation : they will be done for a full scale incineration plant, around 50 to 100 kg/hour throughput
8. Radiological impact : assessment will be made by following the belgatom's methodology for instance or another tried method.

C. PROGRESS OF WORK AND OBTAINED RESULTS

1. State of advancement

Work carried out over the last year has made it possible to :

- study and partially characterize the thermal degradation of various types of waste (resins, TBP, citric acid) in air and nitrogen and at various temperature levels
- complete the process study by establishing new flowsheets for three configurations. The comparative analysis of these three configurations, together with the initial pyrolysis test results, have led to retain different solutions which depend on the type of waste.

After having asked the European Commission's advice, it has been established that the treatment of resins should be considered as the prime objective. So, a modification to the technical programme is at present being looked into in order to conceive and erect a testing bench devoted to characterizing the incineration under pressure of resins and the nature of the secondary waste generated during the incineration (pollutants and radioelements).

2. Progress and results

2.1. Drawing of process flowsheets

2.1.1. The three process configurations considered (see figure 1)

In configuration No. 1, cooling of the furnace and of combustion gases at the outlet of the furnace is performed by recirculation of cold gases. Ashes are collected in a cyclone filter. At the exhaust of the cyclone, the combustion gases are cooled, then treated with ozone (oxidation of NO to obtain NO_2) before being cleaned (SO_2, NO_2) in a scrubber. If a process pressure of 60 bar is chosen, the CO_2 condenses at around 10°C. The exhaust system enables the uncondensable gases (Ar, N_2) to be evacuated, and the process pressure to be maintained constant.
Radioelements are captured first in the cyclone filter, then in the water condensed in the cooler, next in the scrubber, and finally in the CO_2 condenser (if P = 60 bar). A T.H.E. filter could be placed in the exhaust system if necessary.

In configuration No. 2, the furnace is cooled by water.
Injection of water into the furnace enables the exhaust gas temperature to be controlled at around 900 to 1 000°C. These gases are then quenched with water.

Most of the ashes (and radioelements) are captured during this phase.
The waterlogged gases are next cooled in the H_2O condenser, then treated with ozone (oxidation of NO to obtain NO_2) before being cleaned in a scrubber. If a process pressure of 60 bar is chosen, the CO_2 condenses at around 10°C. The exhaust system enables the uncondensed gases to be evacuated.
Radioelements are captured first in the quench disposal, next in the H_2O condenser, then in the scrubber, and finally in the CO_2 condenser (if P = 60 bar). A T.H.E. filter could be placed in the exhaust system if necessary.

Unlike configurations No. 1 and No. 2, configuration No. 3 is based on the pyrolysis/post-combustion principle. Gas treatment processes at the outlet of the post-combustion chamber are the same as in configuration No. 1 (configuration No. 3A) or configuration No. 2 (configuration No. 3B).
The technology of the pyrolysis chamber needs to be defined according to the type of waste (liquid or solid). This chamber is kept at a constant temperature (500°C to 600°C) by means of electrical resistances.

2.1.2. Comparison between the different configurations

Comparison between configuration No. 3 and configuration No.1 or 2

The three main advantages of configuration No. 3 are :

- controlled thermal decomposition (pyrolysis) of the waste, particularly in the case of resins the oxidation reaction of which (process 1 or 2) could be difficult to control (violent reaction)
- significant decrease in the quantity of dust, and therefore radioelements, in the combustion gases. This point is to be confirmed by elementary tests.
- reduced quantity of polluting elements (S, P, N) in the pyrolysis gases, whence a simplification of the gas processing systems and a decrease in the gas and liquid flow-rates (also to be confirmed by elementary tests), and a predictable decrease in corrosion problems.

However, complete destruction of waste is not achieved because of the fixed carbon contained in the waste, which is not oxidised.

Comparison between configurations 1 and 2

The choice between configurations 1 and 2 essentially depends on the type of waste, and particularly on its sulphur, nitrogen and phosphorus content.

- Case of TBP

  Since TBP neither contains sulphur nor nitrogen, the analysis of flowsheets shows that configuration 1 enables a significant decrease in the flow-rates of "secondary waste" to be processed : 11 to 34 kg/h in the liquid phase for configuration 1, as opposed to 100 to 110 kg/h for configuration 2, the gas phase flow-rates being equivalent in both cases.
  However, process 2 is simpler from the technological point of view (no cyclone, and therefore no output of solid matter, small sized gas scrubber, no recirculation), and is therefore more compact.
  If the factor of 3 to 10 on the flow-rate of liquid to be processed is not an excessively constraining factor in the case of configuration 2, this process is the one that should be retained.
  Furthermore, configuration 2 overcomes the problem supplying the hearth with a solid neutraliser ($Ca(COOH)_2$) and the risk of fouling the cooler.

Finally, on the basis of the hypothesis that it would be necessary to inject a neutraliser ($Ca(COOH)_2$) into the hearth, it could be introduced with all or part of the water injected into the hearth without any need to modify the principle of the process.

- Case of resin mixture
  Unlike TBP, resins contain sulphur and nitrogen which reappear in the form of oxides in the combustion gases. It is therefore necessary to scrub the gases for both processes. In the case of configuration 2, for a comparable exhaust gas flow-rate, the flow-rate of the liquid to be processed ("secondary" waste) is reduced by a factor of 5, whilst retaining the main advantages mentioned for TBP (no cyclone or recirculation system) : furthermore, the gas scrubbing system of the process (bubble scrubber) will be very compact.
- Case of other types of waste (decontamination liquor, WINFRITH and EUREX solvent)
  The phosphorus, sulphur and nitrogen content of other types of waste is closer to that of resins than to that of TBP. Therefore, for the reasons stated earlier, configuration 2 will be preferable.
- Conclusion
  If one wishes to retain a simple process for all types of waste, configuration 2 is the obvious choice.

2.2. Treatment and conditioning of secondary waste

Two types of treatment are currently under consideration, and should be confirmed during the subsequent part of the study.

2.2.1. Liquid phase treatment

In the case of configuration 2, the liquid effluent from the quench, the condenser and the gas scrubber contains dust, salts and radioelements. After precipitation of the radioelements (at pH 7 for U, Pu, Ru in the case of TBP ; at pH 9 for 60Co and in the presence of barium for 90Sr, case of resins), filtering is to be carried out.

2.2.2. Gas phase processing

At the output of the process, only RuO_4 for TBP and traces of 137Cs are present in the gas. A T.H.E. filter is to be included in order to filter these radioelements
The filter residues (salts, ash, radioelements) and the pyrolysis residue (case of anionic resin with configuration 3) can be embedded.

2.3. Bench scale tests

In order to conceive the behaviour of wastes during their incineration initial experiments on a thermobalance have been performed. So, the work focused on thermal analyses - mass spectrometry experiments - in order to understand the thermal degradation of some compounds and identify the nature of the volatile products. The thermal decomposition of TBP, cationic and anionic IER and citric acid was studied by thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) techniques using a NETZSCH STA 409 thermal analyser system coupled with a mass spectrometer.
Samples weighing approximately 90 mg, placed uniformly in an alumina crucible, were heated from 20°C to 1 000°C at a $10°C.min^{-1}$ rate under air or nitrogen. The gas flowed at a rate of 50 $ml.min^{-1}$. The reference crucible was empty.

Main results are presented table I to IV.

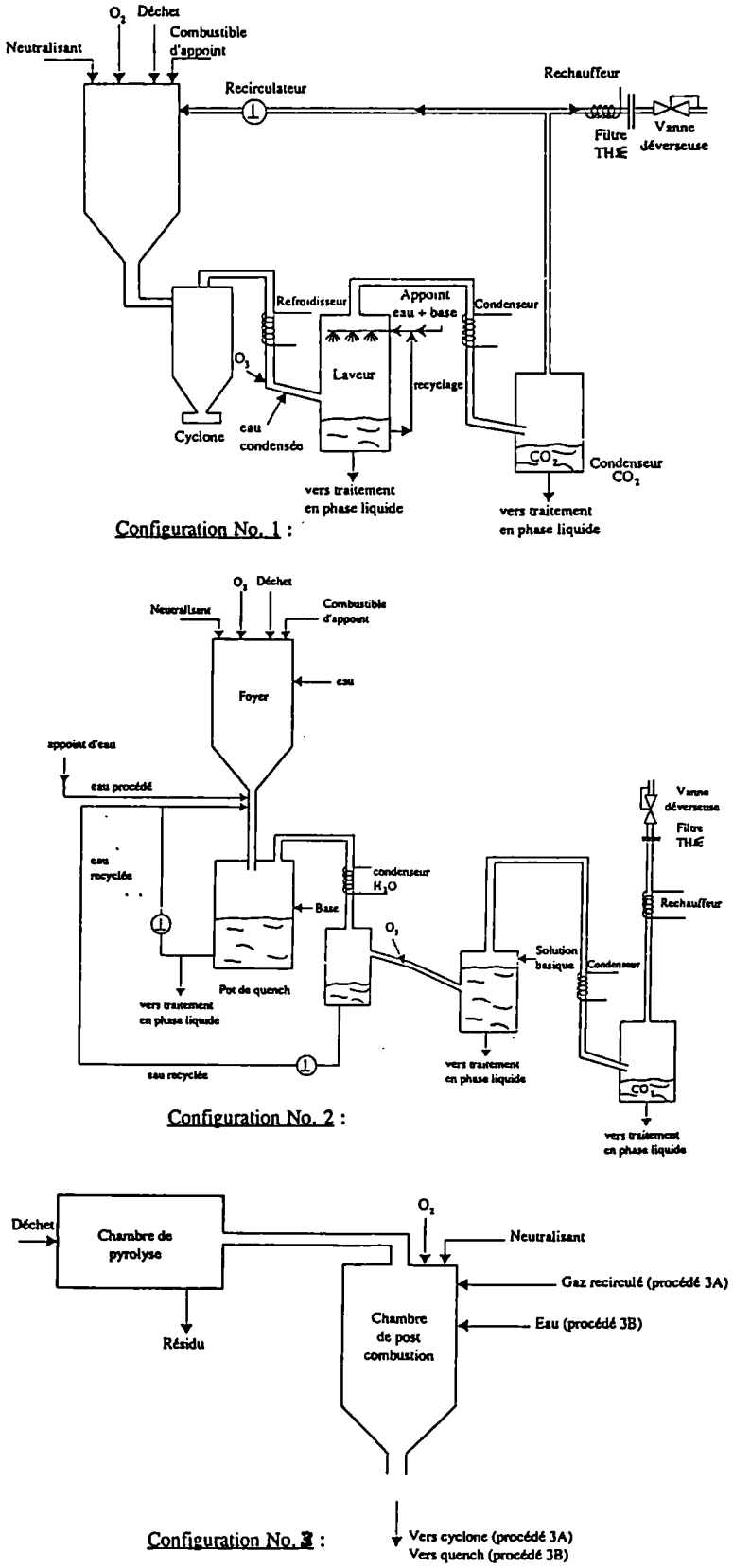


Figure 1 - The 3 considered process configurations

Temperature	Air	Nitrogen	Comments
200 - 230°C	TG : Δm = 86 %	TG : Δm = 96 %	degradation of TBP
	DTA : endothermic peak at 320°C	DTA : endothermic peak at 283°C	boiling
320 - 600°C	TG : Δm = 7 %		oxidation
	DTA : exothermic "massif"		
	$(\Delta m)_{total}$ = 93 %	$(\Delta m)_{total}$ = 96 %	

Table I - Characteristics of the thermal degradation of Tributylphosphate

Temperature	Air	Nitrogen	Comments
0 - 100°C	DTA : endothermic peak at 70°C		loss of H_2O
163°C	DTA : endothermic peak		melting
140 - 260°C	TG : Δm = - 90 %	TG : Δm = - 90 %	degradation of citric acid
	DTA : endothermic peak at 237°C		
300 - 560°C	TG : Δm =- 4,5 %		oxidation
	DTA : exothermic peak at 547°C		
	$(\Delta m)_{total}$ = 100 %	$(\Delta m)_{total}$ = 96 %	

Table II - Characteristics of the thermal degradation of citric acid

(Δm : weight loss)

Temperature	Air	Nitrogen	Comments
40 - 200°C	TG : Δm = - 41,5 %	TG : Δm = - 34 %	loss of H_2O
	DTA : endothermic peak at 150°C		
280 - 320°C	TG : Δm = - 21,5 %	TG : Δm = - 18 %	loss of functional group (- SO_3H)
	DTA : endothermic peak at 310°C		
500 - 600°C		TG : Δm = - 10 %	base polymer degradation
500 - 960°C	TG : Δm = - 34 %		
	DTA : exothermic "massif" due to oxidation		
	$(\Delta m)_{total}$ = 97 %	$(\Delta m)_{total}$ = 62 %	

Table III - Characteristics of thermal degradation of cationic IER

Temperature	Air	Nitrogen	Comments
40 - 200°C	TG : Δm = - 64 %	TG : Δm = - 56 %	loss of H_2O and - N $(CH_3)_3$
	DTA : endothermic peak at 155°C		
280 - 320°C	TG : Δm = - 15 %	TG : Δm = - 19,8 %	loss of functional group - N $(CH_3)_3$
	DTA : endothermic peak at 440°C		
500 - 600°C		TG : Δm = - 7,2 %	base polymer degradation
500 - 960°C	TG : Δm = - 19 %		
	DTA : exothermic "massif" due to oxidation		
	$(\Delta m)_{total}$ = 98 %	$(\Delta m)_{total}$ = 83 %	

Table IV - Characteristics of thermal degradation of anionic IER

(Δm : weight loss)

MELTING OF INCINERATOR ASHES USING A MICROWAVE FURNACE

Contractor:	CEA DCC/DPR/SCD
Contract No:	F12W CT91 0100
Duration of Contract:	July 1991 – June 1995
Period Covered:	January 1992 – December 1992
Project Leader:	J.J. Vincent

A. OBJECTIVES AND SCOPE

The purpose of this investigation is to design, build and test an inactive prototype microwave melting facility for incineration ashes, with a capacity not exceeding a few kilograms per hour.

The microwave melting technique will significantly reduce the ash disposal volume while ensuring chemical and mechanical stability comparable to that of the most favorable radioactive waste containment matrices. This technique is also particularly well suited for the treatment and conditioning of radioactive ashes, which are produced in relatively small quantities (about 10 m^3 per year) based on projections for the French MELOX mixed UO_2-PuO_2 oxide fuel fabrication plant.

B. WORK PROGRAMME

B.1 Bibliographic review.
Interrogation of data bases covering microwave melting (existing processes, operating conditions, dielectric properties of materials).

B.2 Laboratory study.
Specification and development of a glass composition for ash incorporation compatible with certain constraints:
- moderate melting temperature (1100°C),
- satisfactory microwave susceptibility,
- suitable glass leaching resistance.

B.3 Selection of a melting device.
- Generator power and frequency.
- Melter type: casting furnace or expendable crucible furnace.
- Energy transmission mode: single-mode or multimode.
- Crucible structure: cooled metal or refractory material.
- Glass casting mode: batch or continuous.
- Microwave cavity design.

B.4 Design and construction of the melting facility.

B.5 Testing and development.

B.6 Technical and economic assessment.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Task B1 (bibliographic review) was carried out during 1992. Existing processes were inventoried, and data on the dielectric properties of materials were compiled.

Task B2 (laboratory study) is nearing completion. The glass composition has been specified and tested, but leach tests have not been terminated.

Work is advancing on task B3 (selection of a melting device). The selected design calls for a cooled metal casting furnace heated by a single-mode generator operating at 915 MHz. Other devices continue to be investigated, however.

Work has been initiated on task B4 (design and construction of the melting facility) with SGN as the prime contractor.

Progress and Results

Task 1. Bibliographic Review

Existing Processes. Patent data bases and the IAEA data base were searched for the keyword *microwave*, yielding 80 references to publications and 60 references to patents. Most of the work in this area has been done by the Japanese (60–65%) and the Americans (25–30%). Only a few references to British and German work and none to French work were found.

Many of these documents concerned melting of dried radioactive sludge, generally low or medium-level waste. Patents covering ash melting processes have been filed by Kobel Co., New Japan Radio Co. Ltd. (NJR), and the JAERI. All these patents are for multimode (or highly degraded single-mode) systems in which microwaves are directed at right angles or obliquely to the material. These techniques have a number of drawbacks which we will attempt to avoid in designing a more advanced melter.

Dielectric Properties of Materials. A bibliographic search was conducted on dielectric relaxation mechanisms under the effects of a microwave field. The dielectric constants of glass component elements were compiled, revealing that no glass components are receptive to microwaves at room temperature, but that one of the principal components (aluminum oxide) is highly receptive at temperatures above 400°C. An additive capable of increasing the microwave susceptibility of the mixture is therefore required; magnetite (Fe_3O_4) was finally selected for its strong microwave absorption capacity at low temperatures.

Task 2. Laboratory Study

A glass composition was initially defined on the basis of process requirements: containment integrity (leaching resistance), low viscosity, and moderate melting temperature: the primary glass components are SiO_2, Al_2O_3, Na_2O and B_2O_3.

As this glass is not receptive to microwave heating, a suitable dielectric additive was required to ensure suitable low-temperature microwave susceptibility. Fe_3O_4 (magnetite) was finally selected for this purpose. An investigation of the effect of the magnetite concentration on the glass melting time (Figure 1) led us to adopt a concentration of 5 wt% in the final glass composition (Table I).

Task 3. Selection of a Melting Device

Single-mode operation was chosen to obtain a high specific power rating and ensure more uniform heating without the hot spots observed in multimode systems.

Microwaves directed parallel to the surface were adopted rather than perpendicular or oblique waves to increase the melting surface area and minimize hot spots.

Having selected these two techniques, we opted for a continuous casting melter using a cooled metal structure to limit corrosion. The facility will use a 25 kW 915 MHz generator to allow a throughput of several tens of kg/h.

A device similar to the one selected for this investigation has already been tested by the CEA at Cadarache: a cooled metal single-mode furnace rated at 6 kW and operating at 2450 MHz with a capacity of 2–3 kg/h (Figure 2). The tests confirmed the feasibility of the vitrification process, but several problems remain, notably occasional current overloads causing the generator circuit to trip, and excessive cooling rates resulting in poor glass homogeneity that is incompatible with radioactive containment requirements.

Task 4. Design and Construction of the Melting Facility

Work has begin to design and build a melter implementing the selected process, with SGN as the prime contractor. The facility is scheduled for completion in July 1993, and testing should begin before the end of the year.

Table I. Selected Glass Composition

SiO_2	37.0%
Al_2O_3	12.4%
Na_2O	16.6%
B_2O_3	15.2%
CaO	5.0%
Fe_3O_4	5.0%
CeO_2	2.9%
Fe_2O_3	0.3%
ZnO	1.9%
TiO_2	0.1%
MgO	1.4%
BaO	0.4%
Cl	1.3%
C	0.1%
S	0.4%

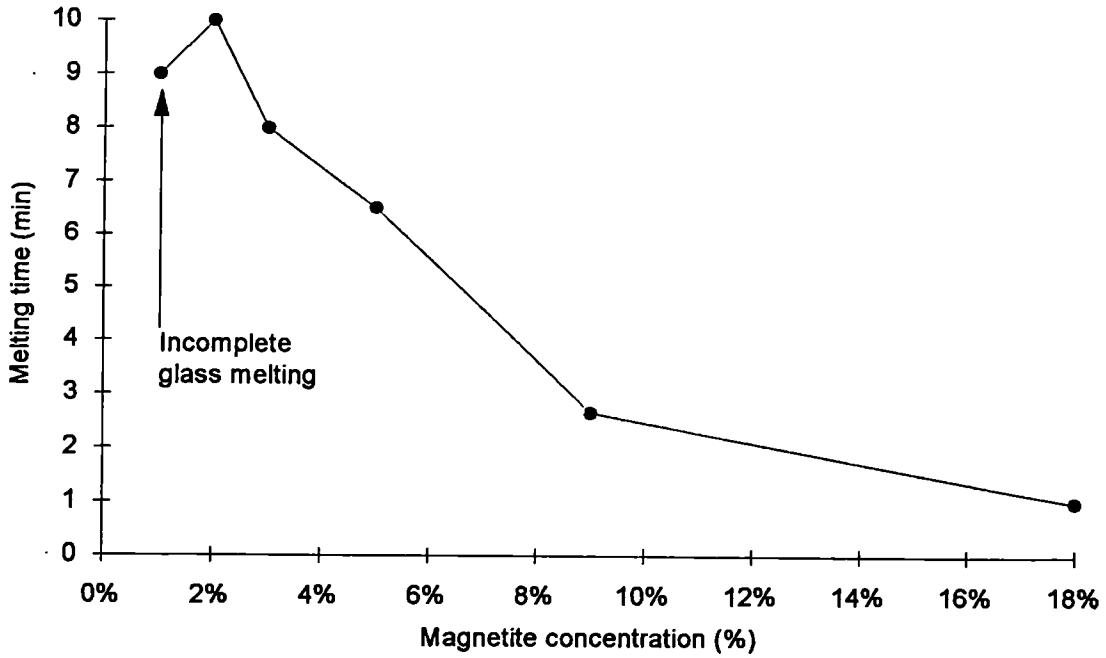
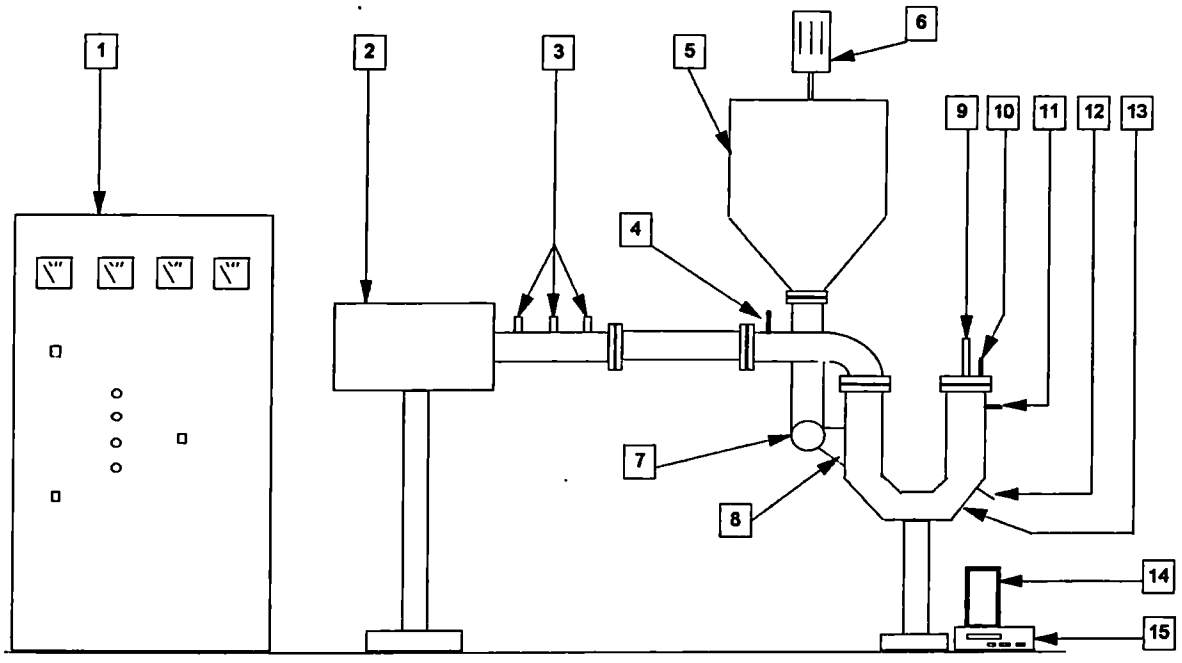


Figure 1. Melting Time versus Fe_3O_4 Content
Incident Power: 1 kW



1 - Generator
2 - Magnetron
3 - Piston attenuator
4 - Water outlet
5 - Feed hopper
6 - Blending motor
7 - Feed pipe
8 - Feed aperture
9 - Piston attenuator
10 - Gas outlet
11 - Water inlet
12 - Cooling air
13 - Casting nozzle
14 - Casting pot
15 - Balance

Figure 2. Melting Facility Schematic

PARLEMENT EUROPÉEN
BIBLIOTHÈQUE

Title:	Treatment of radioactive solvent waste by catalytic oxidation
Contractor:	ENEA
Contract N°:	FI2W-CT91-0108
Duration of contract:	from 1 October 1991 to 31 March 1994
Period covered:	January - December 1992
Project Leader:	Alfredo LUCE

A. OBJECTIVES AND SCOPE

As a result of past reprocessing campaigns performed in the EUREX pilot plant, about 26 m^3 of spent solvent were produced. Taking into account the difficulty to process this waste type (a mixture of tri-butyl-phosphate, tri-capryl-amine, kerosene and methyl-benzenes) according to existing technologies, this research activity aims at setting-up a suitable treatment process capable of reaching three major objectives:
1) reduction of the waste volume by a factor at least equal to 10;
2) oxidative destruction of the reduced volume waste;
3) compatibility of the processed waste with conventional immobilisation matrices like cement.
For the specific purpose, it is intended to investigate the potentialities of the combination of distillation with wet oxidation according to the management scheme reported in figure 1.
The research activity will comprise the implementation of the following items:
1) Laboratory scale distillation tests using genuine samples of EUREX spent solvent waste.
2) Wet oxidation experiments both on laboratory scale with genuine waste and on bench scale with simulated waste, using hydrogen peroxide in presence of a catalyst.
3) Cementation tests of the aqueous waste arising from the wet oxidation.
4) Preliminary design of a full scale treatment plant.

B. WORK PROGRAMME

The work programme includes the following tasks:
1. Conduction of laboratory scale distillation tests with genuine waste coming from the EUREX plant storage. Scope of the tests is the optimisation of the operating parameters in order to get a DF of the top fraction which satisfy incineration criteria in conventional plants.
2. Wet oxidation experiments
2.1. Laboratory-scale experiments. These experiments will be conducted using the bottom product generated during distillation tests of the genuine solvent waste.
2.2. Bench scale experiments. These experiments will involve processing of 3-5 litres batches of inactive simulated waste in order to quantify the scaling-up effect and to optimise the process parameters which enable a minimisation of the final aqueous waste volume.
3. Conduction of cementation tests using ordinary Portland cement (possibly with inorganic additives) on the inactive aqueous waste coming from the wet oxidation bench-scale experiments.
4. Preliminary design of a full scale treatment plant for processing the whole stock of the EUREX solvent waste, including the distillation section, the wet oxidation section and the interface with the cementation plant.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The first task of the programme (Distillation Tests) has been completed in line with the time schedule. We believe that the feasibility of the distillation as method to drastically reduce the volume of the waste has been demonstrated. More than 88% of the solvent waste can be distilled with a negligible rising of the activity, so that the top product of the distillation can be conventionally incinerated according with the environmental radioactivity receptivity.
The bottom residue needed for wet oxidation hot laboratory experiments has been produced but the tests haven't been started yet, due to internal problems of setting up the tests in safe conditions. However those problems have been overcome and the preparations for the tests have been completed.
A section of the cold technological hall of the EUREX plant has been modified for the cold bench scale wet oxidation experiments. The equipment needed has been supplied and the tests will start within January 1993.
The first approach to the problem of cementation of the residue has been done at the end of the year; an exhaustive campaign of tests will be started as soon as a sufficient amount of aqueous solution, coming from the bench scale tests, will be available.
Some more cold distillation tests are planned in 1993 in order to better define some design parameters concerning the Preliminary Design task.

Progress and results

1. Distillation Tests

The distillation tests has been carried out inside a laboratory fume hood. The equipment is completely borosilicate glass made, and consists of Reboiler, distillation column, phase separator and condenser. The distillation column is a packed type with Wilson helices packing. The main characteristics of the column are:

Internal diameter	25 mm
Packed height	300 mm
Wilson spiral diameter	3 mm

Estimated HETP = 30÷50 mm (height of packing equivalent to one theoretical plate).

Several hot tests have been conducted as described in the Progress Reports /1/ /2/, carried out utilising quantities of genuine waste ranging between 0.6 and 5 litres in batch steam distillation. Efforts have been made to maximise the decontamination factors and to minimise the operating time.
The described tests confirm the feasibility of the distillation process in order to obtain a substantial volume reduction of the waste before the chemical treatment.
Table I shows a resume of the main data concerning the distillation of about 5 litres of waste, DFs included.
If we report the above data in terms of the entire stock of Solvent Waste to be distilled we obtain the data of Table II, which shows the global ripartition of the activity between the streams. So the total residual activity in the distillate to be incinerated is:

$$\alpha+\beta = 2.21\ E+07\ Bq\ (\approx 0.6\ mCi)$$
$$\alpha = < 1.55\ E+04\ Bq\ (\approx 0.42\ \mu Ci)$$
$$\beta = < 7.52\ E+05\ Bq\ (\approx 0.02\ mCi)$$

(The γ activity released is of the same magnitude of the β one.)

In order to establish if this activity can be released to the environment the authorised discharge limits of the EUREX plant for the gaseous effluents has been examined (Table III). The achieved results show that the distillate can be conventionally incinerated, because all the residual activity can be completely released to the atmosphere without any filtration. The respect of the authorised discharge limits assures that the discharged activity is much below the limits of the local environmental receptivity.

The radionuclides limits for inhalation reported in the EEC directive have been also considered (EEC DIRECTIVE 3/9/1984, CE Official Gazette N° L265 5/10/1984).
After an estimation of the combustion gases coming from the combustion of the distillate the conclusion is that the radionuclides concentrations in the released gases are compatible with the established limits.

2. Wet Oxidation Experiments

2.1. Laboratory scale experiments

It has been decided to use the same installation used for the distillation tests with some modification, especially studied for the new safety requirements. So the reboiler will be used as reactor, while the packed column will be a high efficiency demister. This technical choice is being considered also for the future real plant, in order to obtain a very compact installation.
As described for the distillation the equipment is installed inside a laboratory fume hood; due to the safety consideration about explosion hazard, the reactor will be ventilated with N_2, in order to maintain the possible flammable gases always below the explosion limits.
Although some preliminary cold tests have been already done, full details about the setting up of the experiments, the safety consideration and the results of the tests will be given in the next semestrial report, when the complete outline will be probably available.

2.2. Bench scale experiments

Bench scale experiments with simulated waste have been prepared in order to quantify the scaling-up effect and to determine the process parameters which enable a minimisation of the final waste volume. Tests will involve processing of 3-5 litres batches of inactive simulated waste with about the same composition of the bottom product of the distillation, of course without contamination.
All the equipment has been installed inside a cold technological hall of the EUREX plant and consists of:
• Reactor borosilicate glass made, volume = 30 l., equipped with stirrer, heating, pH-meter, Temperature measurement, off-gas condenser, sampling.
• On-line monitoring of the off-gas flow-rate and composition, referring to main gaseous decomposition products (CO_2, CO, O_2).
• Other equipment: dosimetric pumps, instrumentation, data acquisition, etc.
Tests will be conducted within the first months of 1993, producing simulated aqueous waste to be used for the cementation tests.

List of publications

/1/ A.LUCE, F.TROIANI, Treatment of Radioactive Solvent Waste by Catalytic Oxidation, CEC Contract N° FI2W-CT91-0108, First Progress Report, April 1992.
/2/ A.LUCE, F.TROIANI, Treatment of Radioactive Solvent Waste by Catalytic Oxidation, CEC Contract N° FI2W-CT91-0108, Second Progress Report, October 1992.

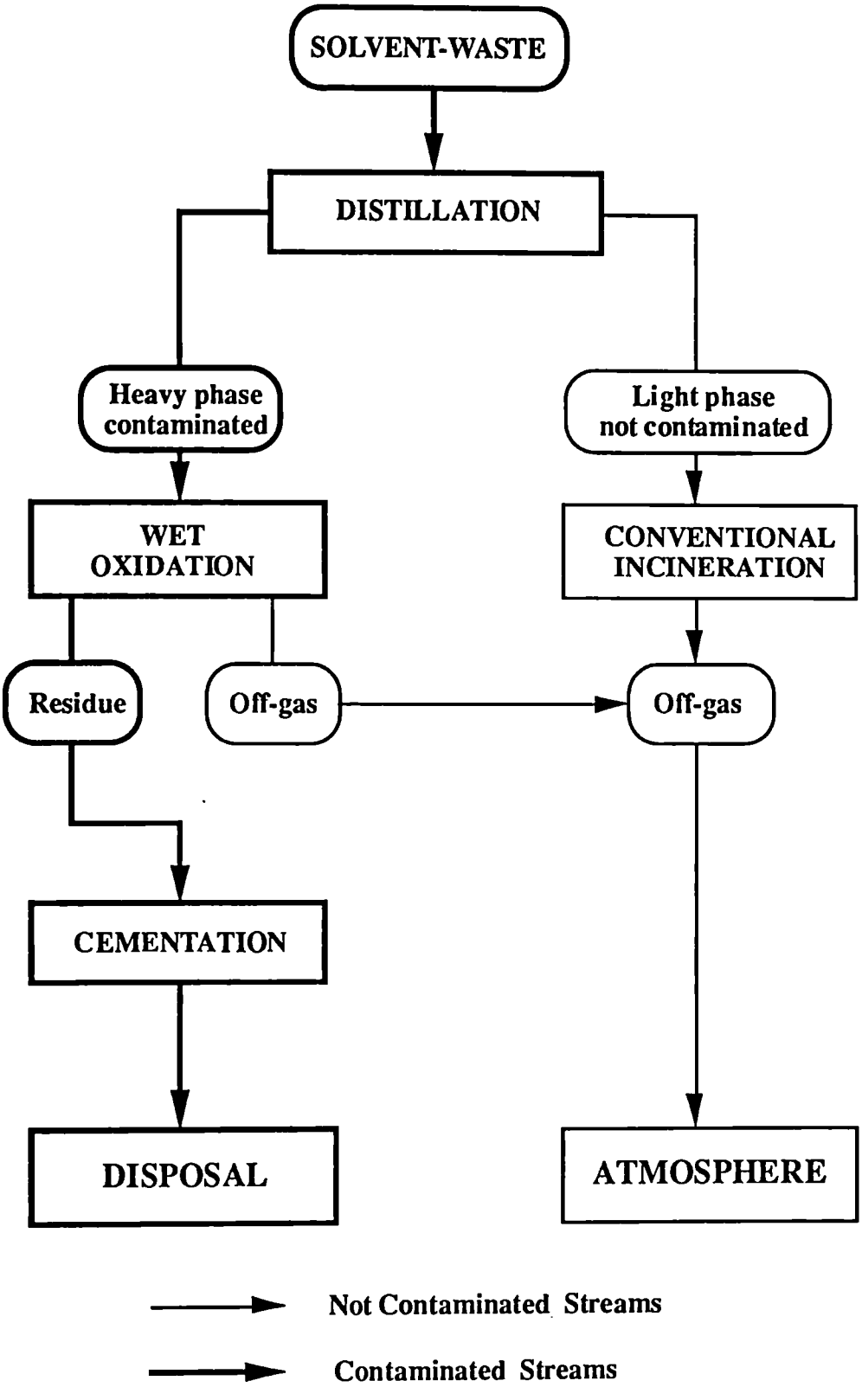


Figure 1 - Management Scheme for the EUREX Solvent-Waste

Table I - Resume of the Main Results

	α+β (Bq/l)	β (n.v.) (Bq/l)	α (Bq/l)	V (ml)	(%)
Solvent Waste	900000	176000	52500	4898	100
Distillate	1000	< 34	< 0.7	4333	88.5
Residue	7.96E+06	1.55E+06	4.65E+05	565	11.5
DFs	900	> 5000	> 50000		

n.v. = non volatile radionuclides

Table II - Ripartition of the Activity

	α+ β		β (n.v.)		α		Volume
	(Bq)	(Ci)	(Bq)	(Ci)	(Bq)	(Ci)	(l)
S.W.	2.25E+10	0.608	4.39E+09	0.119	1.31E+09	0.0355	25000
Distillate	2.21E+07	5.98E-04	7.52E+05	2,03E-05	1.55E+04	4.19E-07	22125
Residue	2.25E+10	0.608	4.39E+09	0.119	1.31E+09	0.0355	2875

Table III - Authorised Discharge Limits (ADL) for the EUREX Plant

Activity	ADL	Notes
Noble gases	≤ 2 E+04 Ci (1 year) ≤ 1 E+04 Ci (13 weeks) ≤ 2 E+03 Ci (24 hours)	
β-γ	≤ 3 mCi (1 year) ≤ 1.5 mCi (13 weeks) ≤ 0.3 mCi (24 hours)	In terms of equivalent ^{90}Sr, where: ^{137}Cs and ^{134}Cs = Activity/10 Other = Activity/100
α	≤ 0.5 mCi (1 year) ≤ 0.25 mCi (13 weeks) ≤ 0.05 mCi (24 hours)	

PRESS COMPACTION OF LWR HULLS

Contractor: KfK, Karlsruhe, Federal Republic of Germany
Contract No.: FI 2W - CT92 - 0118
Duration of contract: May 1992 - April 1994
Period covered: May 1992 - December 1992
Project leader: H. Frotscher

A. OBJECTIVES AND SCOPE

Within the framework of in-house R&D activities and under EC Research Contract FI 1W-0020-D, which expired in late 1989, the Karlsruhe Nuclear Research Center developed high-pressure compaction of hull and structural material wastes as an alternative conditioning technique.

In this phase of activities compaction tests with approx. 90 kg of radioactive hulls from the KKS dissolution campaign in WAK were to be carried out in Mol, but did not materialize for a number of technical and administrative reasons.

The current EC Contract, FI 2W-CT 92-0118 DOEO, and agreements signed between KfK and representatives of German electricity utilities have now made it possible to conduct these radioactive experiments at KfK-HVT/HZ with the WAK hulls so far kept in interim storage.

The German electricity utilities perceive an economic benefit in volume reduction and an advantage in repository safety arising from compacted hull waste, which must be accepted back in Germany under reprocessing contracts with foreign reprocessors. Within the framework of the contracts mentioned above, utilities also support planning for an industrial application of the technique as well as studies of the long-term behavior of the compacted product. The demonstration tests supply basic data for that planning and also furnish products to be used in studies of gas releases and leaching.

B. WORK PROGRAMME

1. PROVISION AND PROVING OF THE EXPERIMENTAL DEVICES
1.1 Manufacture of the hydraulik press
1.2 Licensing procedure for the compaction process in the hot cell
1.3 Provision of the digital signal processing
1.4 Manufacture of special hot cell plugs
1.5 Manufacture of the device for the coaxial double ring bending test
1.6 Manufacture of the device for the diametral compression test
1.7 Functional testing and optimization of the press and signal processing
1.8 Inactive operation of the experimental devices in mock up
1.9 Installation of the press in hot cell
1.10 Manufacture of the stainless steel cans.

2. EXPERIMENTAL PROGRAM
2.1 Transport of 18 hulls containers to the hot cells
2.2 Radiological characterization of hulls prior to the compacting
2.3 About 80 compactions of hulls in stainless steel cans at 275 MPa compression force
2.4 Mechanical and radiographical examinations of products
2.5 Dismantling and Disposal of the press
2.6 Disposal of excess hulls and products.

3. FINAL REPORT

LIST OF PUBLICATIONS

/1/ H. Frotscher, KfK,
Presentation of 3rd progress meeting of working group on task 2 on Oct. 21 to 23, 1992, at Lisbon (P).

C. Progress of Work

The main activities performed in the year under review comprised preparations for running the experiments. These were primarily procurement (press and digital measured data processing system) and design (ultimate load test systems and hot cell plugs) work for the test setup. In addition, the notification of change was drafted and filed in order to obtain the permit by the authorities to compact hulls in the hot cell.

LIST OF PUBLICATIONS

/1/ H. Frotscher, KfK,
Presentation of 3rd progress meeting of working group on task 2 on Oct. 21 to 23, 1992, at Lisbon (P).

Title	:	New macrocyclic extractants for radioactive waste treatment : Ionizable crown ethers and functionalized calixarenes
Contractors	:	CEA-Cadarache (F) - Universities of : Barcelona (E), Parma (I), Mainz (D), Belfast (IRE), Twente (NL) and Strasbourg (F)
Contract n°	:	FI2W-CT90-0062
Duration of contract	:	January 1991 - August 1995
Period covered	:	January 1992 - December 1992
Project leader	:	Coordinator : J.F. Dozol (CEA-Cadarache) (F) F. Lopez Calahorra (E) - A. Mc Kervey (IRE) - V. Boehmer (D) - R. Ungaro (I) - M.J. Schwing (F) - D. Reinhoudt (NL)

A. OBJECTIVES AND SCOPE

The main objective of this research project is to synthesise new macrocyclic compounds (ionizable crown ethers and functionalized calixarenes) capable of decontaminating a selection of real wastes (medium level reprocessing concentrate) to such an extent that these can subsequently comply with waste acceptance criteria for a near surface disposal site (waste de-categorisation). The selective cation removal concerns the following radionuclides : the actinides, the caesium and strontium. The second objective of the research is to develop a suitable separation technique enabling the use of low inventory of new macrocyclic compounds while showing potential for subsequent scaling up.
These new macrocyclic extractants have to demonstrate significantly higher decontamination and selectivity performances that those already recorded with more conventional ones (e.g. bidentate organophosphorous extractants, DC18C6 crown-ether...) for similar purposes.

This research activity will consist of the implementation of the following items :

- Identification of the liquid waste streams to be de-categorised as well as the target decontamination factors;

- Synthesis of "tailor-made" macrocyclic compounds capable of performing the desired waste decontamination;

- Setting-up of an experimental screening procedure for selecting the macrocyclic extractants deserving further development and testing;

- Determination of the extractive properties of a selection of new macrocyclic compounds (batch experiments);

- Development of suitable separation techniques;

- Implementation of continuous decontamination experiments with genuine waste;

- Appraisal of the results achieved and prospects for future developments and scaling-up.

Six European universities (Barcelona, Belfast, Mainz, Parma, Strasbourg and Twente) and one French nuclear research centre (Cadarache) are associated to perform the work programme described hereafter. The respective contribution of each participant is summarised in fig. 1. The whole research project is co-ordinated and supervised by the CEN-Cadarache.

B. WORK PROGRAMME

1- The EHIC Strasbourg tests all the macrocycles synthesized in the frame of the contract, after this screening (or simultaneously) the most promising products undergo extra tests in Cadarache.

1-1. Screening by extraction experiments of alkali, alkaline earth, lanthanides (and later thorium IV to simulate actinides IV) with the macrocycles.

1-2. Determination of the stability constants of the previuosly cited cations in methanol medium.

2- The laboratory of Cadarache tests after the screening carried out at Strasbourg the extractants prepared by the various universities involved in the project.

2-1. The conditions of utilisation of each extractant will be sought in order to use these compounds in liquid-liquid extraction (and in SLMs in particular).

2-2. Distribution coefficients are determined for several cations : ^{22}Na, ^{54}Mn, ^{60}Co, ^{85}Sr, ^{137}Cs, ^{152}Eu, ^{237}Np, ^{239}Pu, ^{241}Am.

2-3 Transport experiments are carried out for the macrocycles presenting high distribution coefficients.

2-4. The techniques rendering the use of these compounds possible are developed (supported liquid membranes, centrifuge extractors) and the most promising processes tested in hot cells.

3- The four universities (Belfast, Mainz, Parma, Twente) working on the synthesis and basic research of calixarenes devote their efforts to prepare selective extractants and work in close collaboration, but each of them works more specifically in the following areas :

3-1. Parma University synthesizes calixarene podands, calix crowns and calix spherands with acidic chains in order to remove caesium and strontium and functionalized calixarenes for the elimination of actinides.

3-2. Belfast University prepares new calixarenes with various functions (ester, ketone, amide...) and then switchable calixarenes.

3-3. Mainz University synthesizes tetraester derivatives of bridged calixarenes and also tetraamide derivatives and compounds with various functions on the "lower rim" of bridged calixarenes.

3-4. The University of Twente tests the potential of synthesized macrocycles for the separation/transport of cations via S.L.M. and if necessary modifies the structure of the macrocycles in order to improve the stability of the membrane and the transport of cations through this membrane.

4- The University of Barcelona synthesizes crown ethers with pendant ionizable groups such as phosphoric and sulfonic in order to allow for the removal of caesium and strontium from a highly acidic solution.

5- During the first two years, synthesis, basic studies, measurements of characteristics and of distribution coefficients of nuclides between organic and aqueous phases have been carried out.

6- Different kind of membranes will be built with macrocycles for the transport or the separation of cations.

6- The new process defined with functionalized calixarenes or ionizable crown ether will be compared with the process using CMPO and neutral crown ethers.

C. PROGRESS OF WORK AND OBTAINED RESULTS

1 - State of advancement

Since the beginning of the contract more than 40 macrocyles have been synthesized by the several Universities involved in the project and screened at the EHIC Strasbourg. About 20 were tested at Cadarache with nuclides in simulated liquid waste.

2 - Progress and results obtained in the various laboratories

2 - 1. European Higher Institute of Chemistry of Strasbourg

The research activity of the year 1992 can be divided in two periods : the first one as subcontractant of the University of Belfast and the second one, from september, as full contractant. About 40 new compounds have been screened toward alkali, alkaline-earth and lanthanide cations, mainly by cation picrate extraction experiments, from a neutral aqueous solution to dichloromethane, and by determination of the stability constants of the complexes in methanol.

Caesium removal. The best class of caesium over sodium selective compounds are the calix[6]hexaesters, from Belfast, and the calix-crowns, from Parma. Their excellent efficiencies are comparable and confirmed in the Cadarache conditions. The best three compounds so far are the *p*-dealkylated calix[6] hexabutylester, the 1,3 dipropoxy calix[4] arene-crown-6 and the *p*-dealkylated calix[6] hexaethylester. Their Cs^+/Na^+ selectivities, expressed by their disbribution coefficient ratios, range between 100 and 200. The calix[5] arene-crowns from Mainz are also Cs^+ selective but less than the latter because of a higher Na^+ extraction level. The pentaamides (6 compounds) and hexaamides (5 compounds) display only little selectivity for Cs^+ over Na+ whereas the tetraamides (10 compounds) are all selective for Na^+ and thus useless for caesium removal.

Strontium removal. The best candidate so far is the p-tbutyl calix[6] hexadiethylamide, from Belfast, with a Sr^{2+}/Na^+ of 14. This value is lower than the ones reported above for the Cs^+/Na^+ selectivity because of a higher degree of extraction of Na^+. In the same conditions the Sr^{2+}/Na^+ selectivity of DC18C6 is only 12.

Lanthanide complexation. The determination of the stability constants of Pr^{3+}, Eu^{3+} and Yb^{3+} complexes with 5 calixarenes carboxylic acids shows the formation of the fully deprotonated complex accompanied by protonated species. These calixarene-acids are lanthanide selective over sodium and strontium but their complexing ability is pH dependent and increases with decreasing acidity.

Miscellaneous. The capped calixarene amides, prepared jointly by Belfast and Mainz display no extraction nor complexation with alkali cations. The interpretation of the first tests on one ionizable crown-ether, the monosulfonated benzo18C6, from Barcelona, is presently in progress.

2 - 2. CEA Cadarache

The following macrocycles have been received and tested in Cadarache :

- Calixarenes from University of Belfast

Tetramer ester : 1
Tetramer amide : 1
Tetramer amide : 2
Pentamer amide : 2
Pentamer ester : 1
Hexamer ester : 3

- Calixarenes from University of Parma

Octamer ether : 1
Hexamer ether : 1
Tetramer hydroxamic acid : 1
Hexamer amide : 1
Tetramer amide : 1
Hexamer amide : 1
Tetramer amide : 1
Hexamer crowns : 2
Tetramer crown 6 : 4
Tetramer crown 7 : 1

- Ionizable crown ethers from Barcelona

Sulfonic crown 6 : 3
Sulfonic crown 7 : 2

Caesium removal

The measurements at Cadarache confirm those carried out at Strasbourg, the most efficient compounds for caesium removal are the calix[6]hexaesters from Belfast and the calixcrowns from Parma. Their selectivity for caesium towards sodium is higher than 10^4. Moreover these products are good carriers for caesium transfer through SLMs, they transport more than 80 % of caesium in less than 10 hours, although their concentration is only 10^{-2}M in the S.L.M.

Strontium removal

The best results for strontium removal are achieved with penta amide calix[5]arenes or hexaamide calix[6]arenes prepared at Belfast University, these products possess Sr distribution coefficients higher than those obtained with crown ether DC18C6.

Actinides removal

So far, no calixarene, contrarily to the CMPO, is able to extract all the valences of actinides. Calixcrowns and tetra amide calix[6]arenes, tetraester calix[4]arenes, although less effective than CMPO, allow to extract more than 90 % of plutonium. Tests carried with calixcrowns show that depending on the size of the crown, Plutonium or Neptunium can be transported quantitatively, but no transport of trivalent actinides occurs.

2 - 3. University of Belfast

The objectives of University of Belfast during 1992 were to synthesise a range of new chemically modified calix[4],[5] and [6]arenes with ligating functional groups on the lower rim with selectivity for caesium, strontium and lanthanide extraction. All new compounds have been submitted to EHIC Strasbourg for model extraction studies and stability constant measurements. Many of the compounds have also been supplied to CEA Cadarache.

The new compounds synthesised are :

1. Tetramer amides (10)
2. Pentamer amides (6)
3. Hexamer amides (5)
4. Bifunctional tetramer amides and esters prepared jointly with Mainz (7)
5. Tetramer thioamides (4)
6. Hexamer esters (3)
7. Tetramer acids (3)
8. Pentamer esters (2)

The principal conclusions of the Strasbourg measurements are for caesium removal : tetramer amides are not useful ; penta and hexaamides are slightly selective ; two of the hexaesters, the dealkylated ethyl ester and the dealkylated butyl ester, are highly selective for caesium over sodium showing the largest log Ke (Cs)/K_e (Na) values for all calixarene derivatives so far studied in the programme.

For strontium removal : the hexamer diethyl amide shows significant selectivity for strontium over sodium in extraction.

2 - 4. University of Mainz

In a joint effort with the group in Belfast (Pr Mc Kervey) several capped calix[4]arenes have been prepared by reaction of the 1,3-diacid chloride derived from t-butylcalix[4]arene and various diamines (including diaza crownethers). First complexation studies in Strasbourg revealed, however, no ionophoric properties, which are interesting for the target ions of this project.

Bifunctional tetraester and amide derivatives of t-butyl calix[4]-arenes (another joint topic with Belfast) have been mentioned there.

Four crownether derivatives of t-butyl calix[5]arene (1,3 calix[5]crown 5 to crown 7 and 1,2 calix[5] crown 6) have been synthesized for the first time. Two of them have been converted to the trimethylether in the cone-conformation, and one triester derivative was obtained. This further derivatization is complicated by conformational problems and/or by a strong complexation of alkali cations. The compounds studied so far in Strasbourg show appreciable Cs^+ over Na^+ selectivity, which however, has to be further improved.

The hexaethyl and methylester (as well as the hexaacid) of a new macrocycle consisting of three methylene linked biphenol units have been obtained by alkylation with ethylbromoacetate (one of the two possible stereo isomers) and by transesterification, respectively. Again Cs selectivity is found for the neutral ester ligands, while the ionizable ligands, like in the crown-ether series, still have to be studied (e.g. in membrane transport experiments).

2 - 5. University of Parma

The major attention in 1992 has been devoted to the removal of caesium cation by synthesizing various calixarene crown ethers. Both calix[4] and calix[6]arenes have been used as starting materials and the size of crown moiety has been varied in order to incorporate between five and seven oxygen atoms in the ring.

Calix[6]arene crown 5 and crown 6 derivatives have been synthesized and tested for their extraction properties.

The work on calix[4]arenes has been mainly focused on the synthesis of flexible or conformationally rigid crown ethers fixed in one of the possible conformations : cone, partial cone or 1,3 alternate. Following the preliminary extraction results, the synthesis of various calix[4] arene crown-6 derivatives fixed in the 1,3 alternate structure has been particularly investigated.

This structure, infact, reduces the sodium affinity of the ligands and, at the same time, increases the stability of the caesium complexes through the interaction of the cation with the polyether chain and the aromatic rings.

2 - 6. University of Twente

After the start of the participation in the project on September 1, 92 all the necessary equipment for the membrane transport experiments has been installed, and as long as no carriers are available for further testing, concentration has been focused on the synthesis of a bis (cyclohexyl) 18 crown 6 substituted with an NPOE functionality, to

make the molecule more lipophilic, as was agreed at the brainstorm meeting in Mainz (Sept. 92).

2 - 7. University of Barcelona

Complexation abilities of HSB18C6 were studied. The complexation abilities of HSB18C6 are not very different from the ones of its non ionizable relative 18C6. The sulphonic group attached to the aromatic ring of the crown ether seems not to produce an important effect on the complexation properties of the latter.

The extraction abilities of $(C_{17}\ CO)_2$ DB 18C6, $(C_{17}\ COH)_2$ DB 18C6 and $(C_{18})_2$ DB 18C6 have been studied (these compounds have been synthesized as precusors for new lipophilic and ionizable crown ethers). The low extraction abilities could be due to the high lipophilicity of those products.

Sulphonic acid derivatives, that are being synthesized at Barcelona, are expected to show higher extraction abilities.

pBenzo bis (ethylenoxy 16 crown 5), o benzo bis (ethylenoxy-16-crown 5), o benzo bis (ethylenoxy-19-crown 6) and its sulphonated derivatives have been synthesized, but the complexation measurements have not yet been carried out.

Title	Décontamination of Solid Alpha, Beta, Gamma Waste for De-Categorisation Purposes in Terms of Disposal Route
Contractor	Commissariat à l'Energie Atomique (CEA) - Centre d'Etudes Nucléaires de Fontenay-aux-Roses (CEN/FAR) - Département des Procédés de Retraitement (DPR)
Contract n°	FI2W/CT90/0070
Duration of contract	from April 1991 to March 1993
Period covered	January-December 1992
Project leader	J. Bourges

A. OBJECTIVES AND SCOPE

Nuclear activities in the radiochemistry building of Nuclear Research Center in Fontenay-aux-Roses, concern principally the study of fuel reprocessing and the production of transuranium isotopes. During these activities solid wastes are produced that are contaminated with α, ß, γ emitters for hot-cells studies and with α emitters only for glove-box experiments. In order to improve the management of these wastes, two facilities are engaged :

- ELISE, a group of glove-boxes for the treatment of α active solid wastes;
- PROLIXE, a hot-cell for the treatment of α, ß, γ active solid wastes.

In these facilities, leaching processes were developed in order to :

- decontaminate these wastes, especially in α emitters, to obtain a level of residual alpha contamination < 0.1 Ci/t of the conditioned wastes which will be suitable for surface site disposal;
- recover actinide elements and recycle redox agents.

The leaching process is based on the use of electrogenerated oxidizing agents (Ag(II)) in nitric acid or reducing agents (Cr(II), Ti(III), V(II) in sulphuric acid, which are particularly suitable to provoke the dissolution of plutonium dioxide.

B. WORK PROGRAMME

II. Laboratory scale studies

II.1. Oxidizing process : the following studies were scheduled : oxidizing dissolution of different compounds of plutonium such as fluoride, phosphate, carbide, nitride...; exhaustive alpha decontamination of zircaloy hulls of irradiated mixed oxide fuel by Ag(II) leaching method; electrochemical destruction of organic species.

II.2. Reducing process : characterization of redox couples, comparison of their performances and choice of reaction media will be realized.

II.3. Recycling of electrochemical mediators : the study of processes for recycling of silver will be performed.

III. Pilot scale experiments

III.1. Silver(II), leaching process : in PROLIXE and ELISE facilities, runs on about 20 kg of different kind (mineral, metallic, organic) of α, ß, γ wastes will be achieved. More than 1 500 kg of wastes will be treated in 2 years.

III.2. Recovery of actinides and redox mediators : the recovery of actinides will be systematically realized. The recycling of silver will be performed at pilot scale.

C. PROGRESS OF WORK AND OBTAINED RESULTS

The status of progress has not been forwarded to the Commission for 1993.

Title:	**Partition of Radioactive Wastes**
Contractor:	Kernforschungszentrum Karlsruhe (KfK)
Contract N°:	FI2W-CT90-0047
Duration of contract:	from 1st March, 1991, to 28th February, 1993
Period covered:	from 1st January, 1992, to 31st December, 1992
Project leader:	Z. Kolarik

A. *OBJECTIVES AND SCOPE*

- Separation of long-lived actinides and fission products would reduce the radiotoxicity of Purex process high-level wastes. This would lower the costs and risks of final waste disposal.
- The aim of the work is to obtain distribution data, which are applicable to the development of a solvent extraction process for the separation of plutonium, neptunium, americium, curium and technetium from the highly active Purex waste solution (HAW). The target decontamination factors are 50000 for Am and Cm, 1000 for Pu and 100 for Np.
- Application of solvent extraction for treatment of highly radioactive materials is well developed. Existing knowledge of the chemistry and engineering of the method can serve as a starting point for the project work.

B. *WORK PROGRAMME*

1. Compilation and assessment work, including the elaboration of a survey report and the formulation of conclusions for the start of the experimental work.
2. Measurement of distribution and kinetic data for the elements to be separated and for lanthanides, and the working out of a proposal of a flowsheet.

C. *PROGESS OF WORK AND OBTAINED RESULTS*

State of advancement

The experimental work was concentrated on
a) the separation of transplutonides(III) from lanthanides(III),
b) the possibility of reaching sufficiently high decontamination factors for actinides, and
c) the valency adjustment of neptunium.
The transplutonide/lanthanide separation was attempted by the extraction of solvated salts other than nitrates, using n-octyl(phenyl)-N,N-di-isobutylcarbamoylmethylphosphine oxide (OΦD(iB)CMPO) and tributyl phosphate (TBP) as solvating extractants. Am(III) and Eu(III) were used as representatives of the transplutonide and lanthanide groups respectively. An Am(III)/Eu(III) separation factor of 8 - 12 is reached in the extraction of thiocyanates solvated by OΦD(iB)CMPO. The separation efficiency is not improved by adding antagonists like trioctyl amine and 2-ethylhexanol or synergists like trioctylmethylammonium thiocyanate. The separation factor can be as high as 100, if di(2-ethylhexyl) dithiophosphates are extracted in the presence of TBP. The extraction in the presence of OΦD(iB)CMPO yields a separation factor as low as 2.0 to 2.5. Satisfactory decontamination factors can be reached in the repeated extraction of Am(III) and Np(VI) nitrates with OΦD(iB)CMPO and TBP respectively from simulated HAW. A less satisfactory decontamination factor is reached in the extraction of Pu(IV) nitrate with TBP. The oxidation of Np(V) to Np(VI) with nitrous acid in simulated HAW is completed within 2 - 5 min.

Progress and results

1. Extraction of transplutonide(III) and lanthanide(III) salts other than nitrates

We have previously shown /1/ that an Am(III)/Eu(III) separation factor of 8 - 12 is reached in the extraction of thiocyanates with OΦD(iB)CMPO. We tried to improve the separation efficiency by adding alkyl ammonium extractants to the system, namely trioctylammonium and trioctylmethylammonium thiocyanates (TOAT and TOMAT respectively). We measured the distribution ratios of trace Am(III) and Eu(III) as functions of the concentrations of TOAT (initially 0.002 - 0.02 M in the organic phase) or TOMAT (initially 0.0075 - 0.16 M in the organic phase), OΦD(iB)CMPO (initially 0.02 - 0.2 M in the organic phase), thiocyanate ions (initially 0.003 - 0.05 M in the aqueous phase), and HCl (initially 0.005 - 0.1 M in the aqueous phase). Lauronitrile (25 vol.%) modified dodecane was used as a diluent. TOAT causes a pronounced antagonistic effect, while a rather weak synergistic effect is observed in the presence of TOMAT. Unfortunately, neither TOAT nor TOMAT enhance the Am(III)/Eu(III) separation factor. Am(III) and Eu(III) form mixed OΦD(iB)CMPO-amine complexes, namely $[RH^+]_3[M(SCN)_6 \cdot nB^{3-}]$ with TOAT and $[R^+][M(SCN)_4 \cdot 3B^-]$ with TOMAT (RH^+ and R^+ are the trioctylammonium and trioctylmethylammonium cations respectively, B is a OΦD(iB)CMPO molecule, M is Am or Eu, and n is 2 or 3).

The Am(III)/Eu(III) separation factor is lowered to a value of 6 - 7, if the lauronitrile modifier (25 vol. %) is replaced by the originally suggested /2/ TBP modifier (33 vol.%). 2-Ethylhexanol (20 - 30 vol.%) lowers the Am(III)/Eu(III) separation factor to ~6. The alcohol suppresses the efficiency of the extraction with OΦD(iB)CMPO, and its addition could be needed if the separation of transplutonides(III) and lanthanides(III) desires a higher concentration of thiocyanate ions (~0.1 M).

A solution of di(2-ethylhexyl) dithiophosphoric acid (HDEHDTP) and TBP in dodecane has been reported to extract trace Am(III) selectively over Eu(III), indeed at initially 0.05 M Eu(III) in the aqueous phase /3/. We confirmed the necessity of the presence of the TBP synergist in the system, but we found out that the separation was only possible

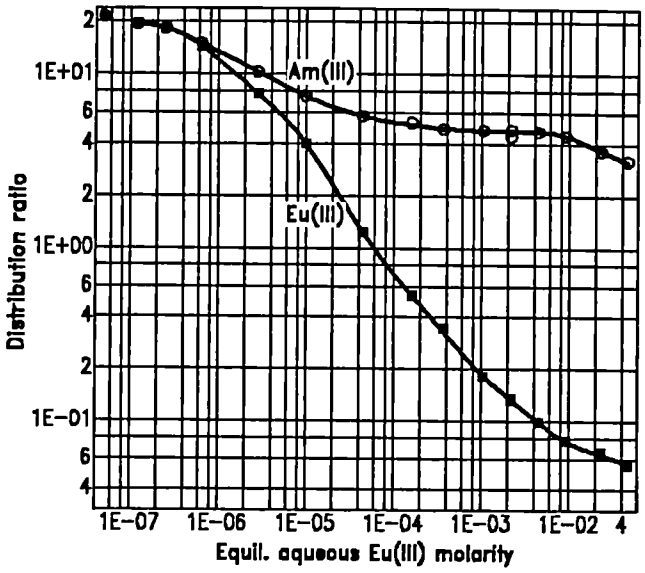


Figure 1. Am(III)/Eu(III) separation by the extraction of di(2-ethylhexyl) dithiophosphates in the presence of TBP: The effect of the Eu(III) concentration. Organic phase: 0.75 M di(2-ethylhexyl) dithiophosphoric acid + 0.25 M TBP in dodecane. Initial aqueous phase: 0.05 M HNO_3 + 1.0 M $NaNO_3$ + trace Am(III) + variable Eu(III). 22°C.

at macro concentrations of Eu(III). The distribution ratio of Eu(III) increases with decreasing Eu(III) concentration, and Am(III) is not separated from Eu(III) at trace concentrations of the metals (see Figure 1). The behaviour of Eu(III) can be explained by polymerization of a Eu(III)-HDEHDTP complex in the aqueous phase. Experiments with macro Am(III) amounts have not been possible in our laboratory and, thus, we have no information about the dependence of the distribution ratio of Am(III) on the Am(III) concentration. Nevertheless, the separation effect reported in /3/should be ascribed to different concentrations of Am(III) and Eu(III) in the system rather than to different stabilities of the extracted complexes of the metals.

OΦD(iB)CMPO enhances the extraction of Am(III) and Eu(III) by di(2-ethylhexyl) dithiophosphoric acid (Figure 2), causing a much stronger synergistic effect than TBP. Both elements are extracted at a rather high concentration of a mineral acid in the aqueous phase. The reverse effect, i.e. that of HDEHDTP on the extraction with OΦD(iB)CMPO is better visible in the presence of chloride ions than with nitrate ions present. The reason is that Am(III) and Eu(III) are strongly extractable by OΦD(iB)CMPO itself as solvated nitrates. The Am(III)/Eu(III) separation factor for trace metals in Figure 2 is unsatisfactory. It increases from 1.3 at 0.02 M OΦD(iB)CMPO to 2.14 at ≥0.16 M OΦD(iB)CMPO. Variations of the OΦD(iB)CMPO to HDEHDTP concentration ratio and of the Eu(III) concentration did not make it possible to achieve a separation factors of >3. Contrary to the system involving TBP, increase of the Eu(III) concentration suppresses the distribution ratio only as far as the loading of the solvent reduces concentrations of free OΦD(iB)CMPO and HDEHDTP.

2. Attainment of high decontamination factors

The attainment of high decontamination factors for actinides in repeated extraction may be impeded e.g. by adsorption on colloids or vessel surfaces or by the existence of minute fractions of actinides in stable inextractable forms. To check the role of such phenomena, we repeatedly contacted an actinide containing aqueous solution with equal

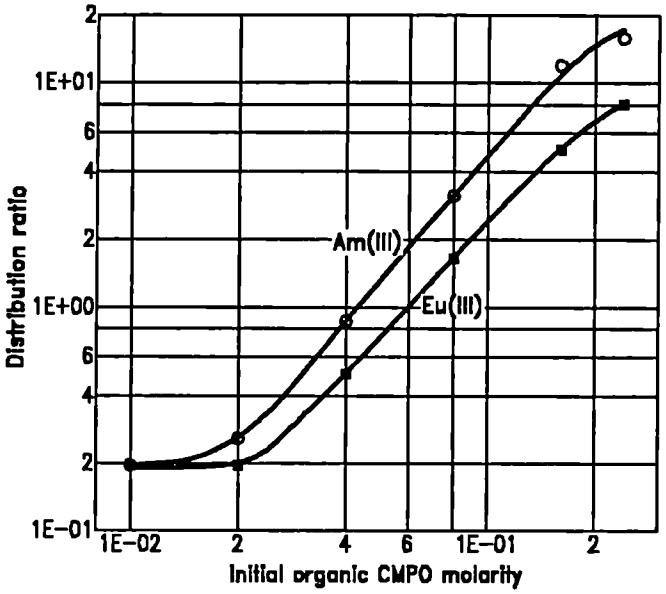


Figure 2. Am(III)/Eu(III) separation by the extraction of di(2-ethylhexyl) dithiophosphates in the presence of OΦD(iB)CMPO: The effect of the OΦD(iB)CMPO concentration. Organic phase: 0.10 M di(2-ethylhexyl) dithiophosphoric acid + 30 vol.% 2-ethylhexyl acetate modifier + variable OΦD(iB)CMPO. Initial aqueous phase: 0.5 M HCl + trace Am(III) and Eu(III). 22°C.

volume of a fresh organic phase. The number of contacts was 9 in each experiment. After each contact we measured the distribution ratio and the fraction of the actinide remaining in the feed. The repeated extraction of Am(III) from a simulated HAW solution with OΦD(iB)CMPO at a high HNO_3 concentration is shown in Figure 3 as an example. The attained decontamination factor is $\sim 2.5 \times 10^5$, i.e. higher than the target value 5×10^4. The Am(III) fraction left in the HAW solution did not decrease in the last three contactings, although the distribution ratio was ~5. The residual ^{241}Am radioactivity had most probably its origin in the usual contamination of the glove box. Very similar results were obtained in the extraction of Am(III) from the HAW simulate at 3 M HNO_3.

Neptunium was extracted from the HAW simulate with a 30 vol.% solution of TBP in dodecane. To oxidize Np(V) in the simulate to Np(VI), sodium nitrite was added to a concentration of 0.003 M before the first contacting. At initially 3.7 M HNO_3 in the simulate, the target decontamination factor 100 was reached after the 5th contacting and a value of ~5000 was attained after 9 contactings. The removal of Np from the HAW simulate was quite unsatisfactory at initially 6.3 M HNO_3. The distribution ratio of total Np was > 1 only in the first contacting. Then it decreased from the 2nd to 5th contacting, and in the 6th to 9th contacting it was as low as ~0.05 and corresponded to the distribution ratio of Np(V). ~15% Np remained in the HAW solution. Most probably nitrous acid decomposed at the high HNO_3 concentration to nitrogen oxides during the first and second contacts, and remaining Np(V) could not be oxidized in the following contacts.

Plutonium was also extracted with 30 vol.% TBP in dodecane. Its radioactivity in the extract was very low in the 5th to 9th contacting, and it could not be measured due to interferences by the radioactivity of ^{241}Am. The attained decontamination factor was lower than the target value 1000, namely 200 - 400 at two HNO_3 concentrations. The residual amount of Pu in the HAW simulate remained practically unchanged after the 7th to 9th contacts at 3.4 M HNO_3 and after the 5th to 9th contacts at 6.2 M HNO_3. In the latter case the distribution ratio of total Pu was in the 4th and 5th contacts markedly lower than

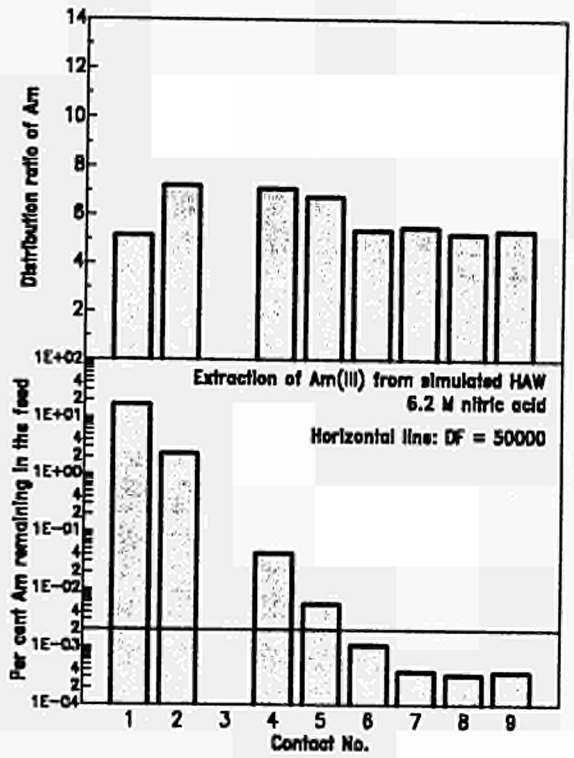


Figure 3. Removal of Am(III) from a HAW simulate in repeated extraction: The solvent was 0.2 M OΦD(iB)CMPO + 25 vol.% lauronitrile in dodecane, contact time was 2 min. Room temperature.

in the first three contacts. Thus, most probably a fraction of Pu existed in the simulate in a form inextractable with TBP. In our suggested flowsheet the residual Pu will be extracted by OΦD(iB)CMPO together with lanthanides and transplutonides, and will not escape into the alpha decontaminated waste solution.

3. Valency adjustment of neptunium(V)

The oxidation of weakly extractable Np(V) to well extractable Np(VI) by nitrous acid was further investigated. The aim was to reach a good extractability of total Np by 30 vol.% TBP in dodecane. The optimum nitrite concentration at 4 - 6 M HNO_3 is 0.001 to 0.005 M and a higher HNO_3 concentration within the above range supports the extraction of Np. In a simulated HAW solution the oxidation is completed in 2 - 5 min. Let us remember that an oxidation time of > 10 min is needed in pure HNO_3 solutions /1/.

3. References

/1/ COMMISSION OF THE EUROPEAN COMMUNITIES *Annual progress report 1991 on the community's research and development programme on radioactive waste management and storage, shared-cost action (1990-1994)*, EUR 14418 (1992), S. 165-9.

/2/ HORWITZ, E. P., KALINA, D. G., DIAMOND, H., VANDEGRIFT, G. F., and SCHULZ, W. W., *Solvent Extr. Ion Exch.* **3**, 75 (1985).

/3/ MUSIKAS, C., *Proc. Int. Symp. Actinide/Lanthanide Separations*, Honolulu, Hawai, USA, Dec. 16-22, 1984, p. 19.

Title :		**High level liquid waste partitioning by means of new completely incinerable extractants**
Contract n°		FI2W-CT91-0112
Contractors :	1/	**Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires de Fontenay-aux-Roses, Direction du Cycle du Combustible,**
	2/	**University of Reading, Department of Chemistry.**
Duration of contract :		**From October 1991 to September 1993**
Period covered :		**January 1992 to December 1992**
Project leaders :		**Charles MADIC** **CEA (coordinator)**
		Michael HUDSON **University of Reading**

A. OBJECTIVES AND SCOPE

High level waste partitioning constitutes one of the key step of any advanced management strategy for radioactive waste aiming at transmutation of long-lived radionuclides into short-lived ones.

The main objective of this research activity is the demonstration of the suitability of new types of diamides as well as triazine-based compounds for the removal of actinides from high level liquid waste and the subsequent purification of minor actinides from rare earths respectively.

This research activity is closely coordinated with that under study at the KfK-Karlsruhe on the same subject.

B. WORK PROGRAMME

This study will comprise the implementation of the following steps :

1. Synthesis of new organic extractants
    - 1.1. Synthesis of diamides
    - 1.2. Synthesis of triazine-based extractants
    - 1.3. Synthesis of alpha-hydroxo or 2-oxo carboxylic acids.
2. Extraction tests
3. Extractants stability
4. Partitioning flow-sheets
5. Counter-current experiments
6. Scaling-up of the preparation procedure for diamides/triazine-based extractants.
7. Solvent regeneration
8. Cooperation within the community.

C. PROGRESS OF WORK AND RESULTS

Advances

During the course of 1992, we have investigated a wide range of routes for the synthesis of diamides and alkyltriazines (TPTZ). Significant quantities of the diamides may be prepared by a modification of established reactions using malonyldichloride. A new route for the synthesis of alkylTPTZ compounds has been developed.

The extraction properties of diamide molecules have also been the subjects of numerous studies such as :

° suppression of third phase formation when extracting nitric acid or nitrate salts by diamides in solution in aliphatic diluents by the selection of proper alkyl groups of the diamide,

° study of the experimental conditions to achieve the Am(III)/Fe(III) separation by kinetic means,

° study of the actinide (III)/lanthanide (III) separation from aqueous thiocyanate/nitrate solutions using diamides extractants, alone or in synergistic combination with quaternary ammonium salts.

Progress and results

1.1. and 6 Synthesis of diamides extractants

The purity of the reagents which were being utilised in France was studied and it was established that the reagents were not pure as determined by mass spectrometry which is the principal method of analysis. In view of the fact that it is quite possible for minor component to play a significant role in the extraction of lanthanides and actinides, the nature of the minor components was investigated. It was established that the principal impurities were the hydrolysis products from the acid chloride. In addition, monoamides and another product, which probably comes from the secondary reaction between the acid chloride and the amine, were formed. Consequently, alternative methods which did not use the reactive malonyldichloride were initially investigated.

In view of the low reactivity and cost ot the malonyl diester, this was investigated as a suitable precursor for the diamides. The reaction of the diester of malonic acid and amines was investigated and found to give high yields for the reaction with ammonia. The reaction with amines, however, did not produce significant quantities of the diamides even when high pressures (10 bar) and temperatures (100°C) were used. Studies with the malonyl dichloride were then considered in great detail. It has been established that the principal cause of the formation of the impurities and the reported low yields (15 %) has been the lack of attention to the temperatures used for the initial reaction between the malonyl

dichloride and the amine itself. The malonyl dichloride is so reactive that it was considered that much lower temperatures than hitherto have been used should be investigated. Consequently, the temperature of mixing was reduced to -40°C and was not allowed to rise to more than -5°C during the addition of the amine. An additional stage of refluxing has also been incorporated. This modification has significantly increased yields and has allowed pure diamides to be prepared. A quantity (100 g 45 % yield) of the pure diamide ($Et_2NCOCH_2CONEt_2$) [1] has been prepared by this method.

In addition, the alkylation reaction to produce ($Et_2NCOCHRCONEt_2$) [2] has been investigated. The principal problem with previous studies has been that it has not been appreciated that the CH_2 protons are not strongly acidic is the case with the malonyldiamide. Consequently, a wide range of bases has been investigated for this reaction and it has been established that they have to be as strong as sodium ethoxide in order to extract one of the CH_2 protons. The conditions for the optimised reaction are that the diamide such as [1] needs to be refluxed with a sodium alkoxide prior to the addition of the alkyl bromide. Under these conditions, the yields of the compound [2] are high (ca.98 %). As required under the contract, a quantity (100 g) of the sample has been sent to Dr. Madic for studies at Fontenay-aux-Roses.

1.2. and 6 Synthesis of triazine derivatives

A wide range of methods of synthesis of the triazine (TPTZ) [3] and its alkylated derivatives (RTPTZ) [4] has been investigated. It has been established that the traditional methods of cyclisation of cyanopyridines using strong acids or bases which are successful for [3] do not work for [4] when the alkylated cyanopyridines are used. It has been clearly shown that one reason for the poor yields in the synthesis of [4] is that the intermediates formed are stable, which is not the case for [3]. Consequently, it has been necessary to investigate new methods for the synthesis of the alkylated TPTZ [4] derivatives. After many detailed studies, it has been established that novel conditions are required in order to convert the intermediates to [4]. The new high pressure route for the synthesis of the reagents gives the maximum yields (30 %) of the pure reagents such as trimethylTPTZ (MeTPTZ) [5]. This such an important advance in the synthesis of these compounds that the CEA will shortly consider patenting this method of preparation. Consideration will also be given to patenting compounds such as [5] because these could have significant advantages over the traditional TPTZ derivatives with respect to the hydrophobicity of the extractants. Currently, there are attempts to improve the yields of this process. It is possible that an additional advantage may be gained using a catalyst such as a lanthanide. It has also been suggested that iron(III) may also be used. A small quantity (2 g), of [5] has been sent for studies at Fontenay. Further quantities will be sent in the near future.

2. *Extraction tests*

Optimisation of the structure of the diamide to avoid third phase formation.

When developing liquid-liquid extraction processes, it is very important to select extracting molecules, or solvent mixtures, thus avoiding the formation of third phase i.e. splitting the organic phase into two parts when extracting solutes. For example, for the well known TRUEX process, based on the use of the carbamoylmethylphosphine oxide (CMPO) extracting agent, it was necessary to use a modifier, such as the tributylphosphate (TBP) in order to suppress third phase formation occurring during the extraction of nitric acid or metallic nitrates by CMPO solutions in aliphatic hydrocarbon diluents which are the preferred diluents for industrial applications. Another possibility is to suppress third phase formation by the CMPO extractant is to use lauronitrile as a diluent, as demonstrated by Z.KOLARIK at KfK (Germany). Third phase formation during the extraction of nitric acid or metallic nitrates by diamides is also observed. In order to suppress that problem and to be able to use an aliphatic hydrocarbon diluent, we decided to optimize the structure of the diamide extractant.

Third phase formation during the extraction of nitric acid at room temperature by various diamides (malonamides), of general formula (RR'NC(O))2CHR", were studied. It was clearly shown that an increase in the length of the alkyl groups R, R' or R" increases the solubility of the nitric acid-diamide solvates in the aliphatic diluent used, named TPH. For example with R=CH_3, R'= n.C_4H_9 , an increase in the length of radical R" induces a great effect on the minimun of the concentration of the aqueous nitric acid necessary for diamide third phase formation during nitric acid extraction. For example,these nitric acid concentrations were : 3.5 ; 4.7 and 9.6 M for, malonamides with, respectively R" = $C_{12}H_{25}$, $C_{14}H_{29}$ and $C_{18}H_{37}$. Moreover it was shown that increasing the degree of branching of the R" group does not have any effect on the third phase phenomenon. However, introducing one or two ether functions into the R" radical decreases the nitric acid concentration required for the appearance of the third phase.

Third phase formation is also observed when extracting metallic nitrates by diamides solutions in TPH. This phenomenon was studied in the case of the extraction of Nd(III) and U(VI) nitrates. Good results were obtained, especially for the two malonamides : ($CH_3C_4H_9NC(O))_2CHR"$, with R" = $C_{14}H_{29}$ and $C_{18}H_{37}$. For example, 0.041 and 0.15 M Nd(III)-loaded organic solutions can be obtained by extraction from 4 M aqueous nitric acid solutions with respectively these two diamides (0.65 M) diluted with TPH. The loading capacity was lower in the case of the extraction of U(VI) nitrate. It appears that, up to now, the diamide dimethyldibutyltetradecylmalonamide, DMDBTDMA, seems to be a good compromise for the development of a HLLW partitioning process. We named this process by the acronym DIAMEX, for DIAMide EXtraction.

Influence of various chemical features on the Am(III)/Fe(III) separation

Fe(III) is always present in liquid wastes. Its presence is due to the corrosion of the equipment by aqueous acidic solutions, mainly nitric and its separation from the minor actinides, especially Am(III), must be studied for the design of a minor actinide HLLW partitioning process. This problem is acute for the diamide extractants which possess a rather good affinity for Fe(III) nitrate, in particular high aqueous nitrate ion concentrations.

Kinetic or thermodynamic factors were considered for this Am(III)/Fe(III) separation.

For diamides with alkyl R" groups, it was shown that the rate of Am (III) nitrate extraction is rapid in comparison with that of Fe(III), and consequently their mutual separation via kinetic means could be considered, for example with the use of fast centrifugal contactors. With R" an ethoxy radical, no such difference is observed in the kinetics of the extraction of Am(III) and Fe(III) but at equilibrium Am(III) is extracted more than Fe(III) : a moderated separation factor close to 7 or 8 is obtained. Other parameters influencing the Am(III)/Fe(III) separation were studied, and the results are summarised below :

° parameters with a positive effect on the separation factor :

1/ increase of the diamide concentration,

2/ increase of the Fe(III) concentration ;

3/ use of continuous phase emulsion mode,

4/ increase of the aqueous nitric acid concentration : an optimum is obtained for the range 4 to 5 M.

° parameters with a negative effect on the separation:

1/ use of a benzenic diluent instead of the TPH,

2/ the presence of large concentrations of nitrate salts in the effluent.

The results seem to be sufficient for the design of a flow-sheet for Am(III)/Fe(III) separation using the difference in the kinetics of extraction with diamides extractants. Nevetheless, it will be necessary to try to improve such a separation by the use of selective Fe(III) complexing agent.

Actinide (III)/ lanthanide (III) group separation by diamide extraction from thiocyanate-nitrate media.

Following a first extraction cycle using diamide, a general minor actinide partitioning process must include the subsequent Ac(III)/Ln(III) group separation.

To achieve this goal, the possibility to use a diamide extractant was considered, alone or in synergistic combination with quaternary ammonium salts. The principle of the separation consists in the extraction of thiocyanate complexes of trivalent ions. It is well known that polarisible ligands such as SCN^- ions, possess a greater affinity for trivalent actinides than for trivalent lanthanides.

With the diamide extractant dimethyldibutylpentadecylmalonamide (DMDBPDMA) diluted in TPH extraction of Am(III) and its separation from Ce(III)

and Eu(III), which were used as representatives of light and medium lanthanides, was observed in moderate concentrations of thiocyanate ions in aqueous solutions. Separation factors (S.F) close to 6 were observed. With the addition of quaternary ammonium salts such as trilaurylmethylammonium or trioctylmethylammonium to the diamide organic phase, synergistic phenomena are observed with a greater increase of the affinity of the solvent for Am(III) leading to a substantial increase in the separation factors between Am(III) and the lanthanides. For example, excellent S.F(Am/Eu) equal to 20 has been observed. Such an increase in the separation between Am(III) and Ln(III) may be due to the fact that the extracted complexes contain four thiocyanate ions in the case of the synergistic mixtures, instead of three for the extraction of metallic salts wih diamide alone.

If encouraging results concerning the Ac(III)/Ln(III) group separation have been obtained using such a system, it must be mentioned that it does not fulfil the requirements for the design of a good process. This difficulty lies essentially in the non incinerability of the thiocyanate ion. Other work using alkyl TPTZ derivatives will be done in this field next year.

8. *Cooperation within the community*

Upon the request of M. Lucien CECILLE, Charles MADIC attended a meeting in Brussels on September 9th, 1992, in order to discuss with Z. KOLARIK, L. CECILLE and J. RIESGO VILLANUEVA, the new orientations of the research work to be realized by Z. KOLARIK, at KfK (Germany), on the design of HLLW minor actinide partitioning TRUEX type process.

Part A3

Task 3

"Characterisation and Qualification of Waste Forms, Packages and their Environment"

Topic 1	Waste form characterisation and performance
Topic 2	Containment and barrier properties of the near-field (including modelling)
Topic 3	Radionuclide assay : development of standard methods and equipment for specific applications
Topic 4	Quality control of waste conditioning

Task 3

Topic 1 Waste form characterisation and performance

FI2W/0012 The behaviour of Pu, Am, Np and Tc during the corrosion of the Cogema glass R7T7 in salt solutions.

FI2W/0020 Consequences associated with gas production in geological repositories (PEGASE).

FI2W/0025 Characteristics of bitumenized radioactive waste.

FI2W/0026 Natural analogues of bitumen matrices in a deep repository.

FI2W/0027 Aqueous corrosion of nuclear glasses: influence of disposal conditions.

FI2W/0028 Effect of insoluble active dissolution fines on fission product glasses.

FI2W/0031 The corrosion of nuclear waste glasses in a clay environment: mechanisms and modelling.

FI2W/0032 Basic leaching for pure Beta long-lived emitters in radioactive wastes.

FI2W/0055 Chemistry of the reaction of as-fabricated and high burnup spent UO_2 fuel with saline brines.

FI2W/0077 Container properties ensuring safety: gas emission, biodegradation, corrosion.

FI2W/0094 Gas generation in supercompacted waste products.

FI2W/0099 Impact of additives and waste streams constituents on the immobilisation potential of cementitious materials.

Task 3

Topic 2 Containment and barrier properties of the near-field (including modelling).

FI2W/0022 The effect of microbial activity on the near and far fields of a deep repository.

FI2W/0030 Corrosion of selected packaging materials for disposal of heat-generating radioactive wastes.

FI2W/0035 Theoretical and experimental study of degradation mechanisms of cement in the repository environment.

FI2W/0040 The performance of cementitious barriers in repositories waste in practice.

FI2W/0096 Completion of the corrosion programme in Boom clay (in situ experiments).

Task 3

Topic 3 **Radionuclide assay : development of standard methods and equipment for specific applications.**

FI2W/0010 Determination of fissile material in waste package by neutron transport interrogation.

FI2W/0034 0109 Inventory and characterisation of important radionuclides for safety and storage-correlation to key nuclides easy to measure in waste types.

Topic 4 **Quality control of waste conditioning.**

FI2W/0009 Construction and testing of a computer tomography assembly for routine operation.

FI2W/0014 Behaviour of low-level radioactive waste under fire accident conditions.

FI2W/0018 Non-nuclear non-destruction testing methods to determine free water, gas pressure and matrix level in waste drums.

FI2W/0019 Test for process control during treatment of low and medium radioactive waste in practice.

FI2W/0021 Establishment of non-destructive or partially destructive test procedures for determining the characteristics of waste containers.

FI2W/0023 Non-destructive characterization of radioactive waste packages by advanced radiometric methods.

FI2W/0107 High Energy Accelerator Tomography

Task 3 - Characterisation and qualification of waste forms, packages and their environment

A. Objectives

- Determination of the relevant properties and performances of waste forms and their environment (Characterisation)
- Development and validation of models and data bases describing the long-term evolution of disposed waste (Modelling)
- Improvement of the control of radioactivity in the waste and the quality of waste products/packages.

B. Research topics dealt with under the 1985-1989 Programme

In the previous programme, the following main research actions were pursued :

- Characterisation of low and medium level wastes :

  Eleven waste forms were selected for joint investigation and specified as reference formulations for conditioned LLW and MLW. Many of the characteristics of these waste forms relevant to the long-term safety in different disposal environments were determined with simulates and, as far as available, with real waste specimen.

- Testing and evaluation of high active and special alpha-bearing waste forms :

  During the period 1985-1989 the development of new candidate waste forms for the High Level Liquid Waste Stream was reduced in favour of extended testing and evaluation of the industrial reference borosilicate formulations. Corrosion, nuclide leaching, radiation damage and thermal stability were investigated in laboratory test series with inactive and spiked simulates.

- Study of container and buffer/backfill materials :

  The coordinated action on container corrosion launched in the second programme was concluded : corrosion rates and mechanisms of carbon steel, Ti-Pd and Hastelloy were determined under representative conditions.
  A variety of argillaceous and cement-based buffer materials were tested to determine suitable formulations for the various repository options.

- Development of a standard waste hostrock interaction test :

  The Repository Systems Simulation Test which permits the testing of HLW glass formulations in conditions representative of geological disposal was developed and validated in a Round-Robin campaign by 14 laboratories.

- Development of methods for the Quality Assurance of Waste Packages :

  Non-destructive test methods such as computer tomography and active neutron interrogation techniques for assaying alpha emitters as well as techniques and procedures for sampling solidified waste were the most important items of a wide range of R&D projects.

C. Present programme (1990-1994)

1. Waste form characterisation and performance

- Characterization of heterogeneous waste forms
- Effects of radiation, corrosion, biodegradation, etc. on waste form stability
- Gas generation by corrosion, radiolysis and biodegradation
- Effect of inclusions on waste form crystallisation and stability
- Chemistry of reaction of spent fuel with saline brines
- Mechanisms of nuclide release under repository conditions

2. Containment and barrier properties of the near-field

- Effect of microbial activity on the near-field
- Theoretical and experimental study of degradation mechanisms of cement in the repository environment
- Modelling and testing of the hydration of backfill and sealing materials
- Corrosion of selected packaging materials for disposal of heat generating radioactive waste

3. Radionuclide Assay : development of standard methods and equipment for specific application

- Establishment of a European basis for the determination of relevant nuclide concentrations in industrial LLW and MLW : Study of existing methods and compilation of data bases, evaluation of currently used scaling factors and correlation.
- Development of equipment and methods for the assaying of LLW and MLW including the validation of scaling correlations for relevant emitters.
- Development of methods for measuring (checking) the nuclide inventory of conditioned TRU-wastes

4. Quality control of waste conditioning

Research actions to develop methods permitting the measurement and certification of compliance with quality requirements/criteria. Subjects being addressed include :

- Establishment of sampling procedures and techniques
- Verification of chemical composition
- Detection of unwanted or undeclared substances
- Detection/measurement of waste/matrix interaction, gas generation and release, container corrosion and swelling
- Measurement of physical properties of waste products and packaging
- Homogeneity, thermal stability, etc.

D. Programme implementation

The above topics and areas of research are being tackled under 28 contracts, the majority of which are multi partner and trans-european. Further details are provided in the summary reports listed hereafter.

Retention of Pu, Am, Np and Tc in the Corrosion of COGEMA* Glass R7T7 in Salt Solutions.

Contractor:	Kernforschungszentrum Karlsruhe
Contract:	F12W0012
Duration of contract:	Januar 1991 - December 1994
Period covered:	February 1992 - December 1992
Project Leader:	Dr. Werner Lutze, Institut für Nukleare Entsorgungstechnik

-- *We were advised by CEA Marcoule to use a different designation for the glass. The glass investigated here was fabricated by CEA Marcoule closely simulating the chemical composition of the glass produced by COGEMA at La Hague in their vitrification plants. The glass from Marcoule is designated CEA R7T7 in the text. --

A. Objectives and Scope

High-level radioactive waste from the reprocessing of German spent fuel is vitrified at La Hague. Glass blocks will be returned to Germany and must be disposed in the deep underground eventually. The repository is under construction and will be located in the Gorleben salt dome. The repository constitutes a system of technical and natural barriers (multibarrier system) against the release of radionuclides. The glass is one of the technical barriers. A detailed understanding of the glass performance must be obtained for all conceivable accidental conditions including contact with water. The respective results shall be used to describe source terms in the framework of safety analyses.
The subject of this investigation is to study the chemical durability of the highly radioactive French borosilicate glass R7T7 in one of the three German "standard" salt solutions as a funtion of time and temperature. This work complements previous investigations on the durability of a very similar but non-radioactive CEA glass by measuring the release behaviour of Pu, Am, Np and Tc.

B. Work programme

1. Installation of the hot cells: One hot cell has to be equipped with crushing, milling and sieving devices to prepare glass powder. The other cell has to be equipped with three ovens, devices to handle autoclaves, a balance, a pH-Meter and sampling and filtering devices.

2. Modification of analytical techniques: Tc, Pu, Am and Np have to be separated from concentrated salt solutions for activity measurements (α,β,γ spectrometry).

3. Equipment for corrosion tests: Tests sall be performed in autoclaves. Previously used Teflon liners for inactive glass

have to be replaced by tantalum to resist both radiation and chemical corrosion.
4. Corrosion test conditions: Powdered CEA R7T7 (4.5 g, average grain size 86 µm) shall be corroded in 25 mL (S/V = 10,000 m^{-1}) of salt solution at 110, 150 and 190°C for 45, 90, 180, 360, 720 and about 1000 days (individual experiments in duplicate for each time and temperature).

5. Solution analyses: Samples shall be taken after completion of each experiment. The leachates shall be filtered to separate colloids. Concentrations of B, Si (glass formers) and of Tc, Pu, Am and Np shall be determined. pH shall be measured in the unfiltered leachate.

6. Analysis of corrosion layers: Sample surfaces will be observed under the light microscope and in the SEM. Host phases for actinoids and Tc will be searched and analysed, if possible.

C. Progress of work and obtained results

State of advancement

The report covers the period from February to December 1992. Work performed under this contract includes the following:

1. Reinforcement of the shielding of the experimental cell for the glass corrosion experiments.

2. Equipment of the hot cell
The cell was equipped with ovens, autoclaves, argon hood and purge system, a balance, a pH meter and specially manufactured tools to handle the autoclave. Cold tests were performed with the equipment.

3. Preparation of the CEA R7T7 powder and the leachant for the corrosion tests.
The previously prepared CEA R7T7 powder was sieved to obtain the desired size fraction (86 µm average grain size). The powder was then transferred to the hot cell in which the corrosion experiments are performeded.
The concentrated magnesium rich salt solution was prepared and the stock transferred into the cell.

4. Experiments were performed with the newly designed autoclaves (tantalum liner and gaskets) to guarantee tightness.

5. Several 45 day corrosion experiments were performed with inactive R7T7 glass to compare corrosion data with previous obtained results

6. The analytical procedures for the quantitative detection of Tc, Np, Pu and Am and some other radionuclides were tested by

The salt solutions were prepared by dissolving analytical grade chemicals at 80°C in deionized water. The composition (in g/L) is: 4.13 NaCl, 1.42 KCl, 438.90 $MgCl_2$, 29.90 $CaCl_2$, 0.07 $CaSO_4$. The solution is stable and clear at room temperature.

The autoclaves were modified to withstand the γ-irradiation. The Teflon liner was replaced by a tantalum liner. This required extensive testing of the performance of gasket materials to guarantee long-term tightness of the autoclaves. Gold, graphite and elastomere gaskets were tested and graphite was selected.for the corrosion experiments with the radioactive CEA R7T7. Gold is also suitable but is too expensive. Tightness was tested in a series of 45 day experiments at 190°C with only salt solution in the autoclave. In case of gold and graphite gaskets, losses of water were less than 10^{-2} % of the liquid.

In order to test the analytical procedure for non-radioactive elements, four 45 day corrosion experiments were performed with simulated CEA R7T7 glass. After completion of the tests, the leachates were analyzed for eight glass constituents by ICP-AES. Table 1 contains the results.

	Li ppm	Sr ppm	B ppm	Mn ppm	Zn ppm	La ppm	Pr ppm	Nd ppm
HMI(*)	742	138	1843	231	982	195	58	175
KfK	551	128	1886	194	847	876	49	175
KfK	558	126	1858	192	853	177	54	175
KfK	534	130	1878	194	897	179	50	179
KfK	590	129	1872	199	875	178	50	180
average KfK	563	128	1872	195	868	177	51	177

Table 1: Comparison of concentrations of glass constituents in leachates from this study and from previous corrosion experiments (44 day and 45 day experiments, 190°C, S/V = 9,050 m^{-1}, Mg salt solution).
(*) results from previous experiments by W. Lutze an R. Müller, Hahn-Meitner-Institut Berlin.

These results are compared with those previously found with the Teflon lined autoclaves. The results show that no significant difference between the two types of experiments can be detected. The maximum deviation of 30% in the case of lithium appears to be high, but, as shown in our annual report for 1992, the interpretation of the corrosion process is not affected. The concentration of boron in solution is a measure of the advancement of the corrosion process. This value is in excellent agreement with previous results.

The surface of the corroded glass was examined (Fig.2) by SEM-EDX. The typical alteration phases (powellite-type, cerianite-type and Mg,Al,Si-compounds were found in agreement with what was found in previously experiments.

dissolving some of the CEA R7T7 and comparing the results with those given by CEA Marcoule.
7. A short term corrosion (45 days) experiment was performed at 190°C with the radioactive CEA R7T7 to test and assure the safe functioning of all remotely handled operations before, during and after the experiment. This included sampling and analyses of the solution, filtering procedures and the recovery of the glass powder and sample preparation for SEM-EDX surface analyses.

8. The corrosion experiments with the longest test duration, 360, 720 and 800 days, were started for all temperatures, 110°, 150° and 190°C.

Progress and results

CEA R7T7 powder with a grain size fraction of 72 µm to 100 µm, average grain size 86 µm, was prepared from the as delivered cylindrical glass block (8.6 cm diameter, 11.5 cm length). The block was crushed in a 100 kN hydraulic press. The fractured material was further treated in a jaw breaker and the resulting pieces of glass were milled in a centrifugal mill until small enough particles were obtained to provide optimum yield of the desired size fraction. Figure 1 shows the mashines used for the powder production in the background and the glass, after passing through the jaw breaker, in the foreground.

Figure 1: Jaw breaker (left), centrifugal mill (middle) and sieving mashine (right). Powdered CEA R7T7 in the foreground.

Powdered radioactive CEA R7T7 was dissolved in 1 N HNO3 and radiochemical analyses were performed. Table 2 contains the results. The data are compared with those provided by CEA Marcoule. As seen, the agreement between the measurement of the two laboraties is good.

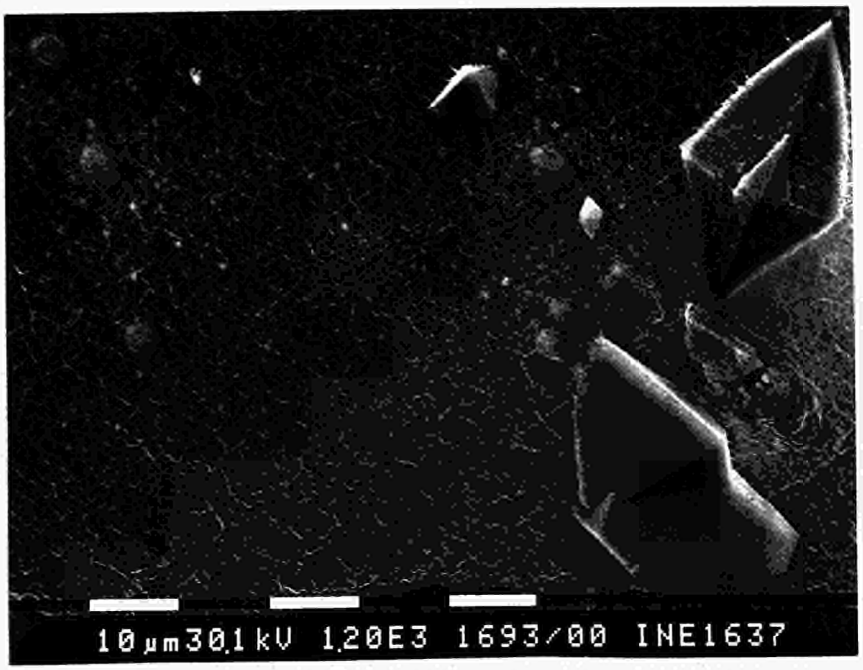


Figure 2: SEM micrograph of inactive glass corroded in soln. 2 for 45 days at 190°C. Pyramids: powellite-type phase, spherical particles: cerianite-type phase, background: Mg,Al,Si-compounds.

	KfK	CEA Marc.		KfK	CEA Marc.
nuclide	Bq/mg	Bq/mg	nuclide	Bq/mg	Bq/mg
Pu-238	2.4 E5	2.4 E6	Tc-99	2.0 E1	no value
Pu-239/40	4.4 E3	2.7 E3	Cs-134	2.2 E3	2.2 E3
Np-237	7.4 E0	no value	Cs-137	4.7 E5	4.7E5
Np-239	2.7 E1	no value	Eu-154	4.1 E3	no value
Am-243	2.7 E1	no value	Eu-155	1.0 E4	no value
Cm-244	7.0 E2	5.2 E2	Sb-125	1.5 E3	1.9 E3
			Am-241	2.1 E4	2.1 E4
			Co-60	1.5 E2	1.2 E2

Table 2: Specific activity of various radionuclides in CEA R7T7 glass .(Column 2: determined by α spectrometry; column 5: determined by γ spectrometry.

In September 1992 all long-term corrosion experiments (360, 720 and 800 days) were started at 110, 150 and 190°C in the hot cell.

In order to test all manipulations necessary to successfully complete corrosion experiments in the future, a 45 day experiment with radioactive glass has been carried out. At the end of the experiment the following procedure was executed: Opening of the autoclave after cooling; immediate measurement of pH (result: pH = 3.55), see figure 3, filtration of the leachate through a 0.45 µm filter; fitration of the filtrate through a $0,18x10^{-2}$ µm filter; measurement of radioactivity for various radionuclides in the two filtrates. The results of the activity measurements are listed in table 3. The values for Tc and Np are still missing.

Figure 3: Measurement of pH in the radioactive leachate in the hot cell.

	filtered 0.45 µm		filtered 1.8xE-3 µm	
radionuclide	Bq/ml	norm. mass loss [g/m^2]	Bq/ml	norm. mass loss [g/m^2]
Co-60	3.0 E3	2.3	2.8 E3	2.1
Cs-134	2.7 E4	1.4	1.3 E4	0.66
Cs-137	7.3 E6	1.8	3.2 E6	0.78
Pu-238	3.4 E4	0.016	1.3 E4	0.006
Pu-239/240	3.8 E2	0.0097	3.3 E2	0.008
Am-241	3.0 E4	0.16	9.3 E3	0.05
element (*)	ppm		ppm	
B	1872	4.7	-	-

Table 3: Specific activities and normalized mass losses of radionuclides measured in the leachate of the 45 day corrosion experiment at 190°C before and after microfiltration.
(*) from Table 1

The comparison of the normalized mass losses (NL) of the radionuclides with that of boron (table 3) shows that only fractions of the activities are found in solution, e.g. 40% for Co and 15% for Cs (last column). The low NL values for actinoids indicate that these elements form insoluble secondary phases. Comparison of the third and the last column in table 3 shows that fracions of the radioactivity in the leachate can be filtered. The nature of radionuclide containing phases is not yet known. Further measurements (activities on the filters and on the container walls) and SEM/EDX analyses of the particulates are necessary before the results can be discussed in detail.

Title : **Consequences of gas production in geological repositories (PEGASE)**
Contractors : ANDRA, ENRESA, GRS
Contract No: FI2W/0020
Duration of contract : 1 August 1991 to 31 July 1994
Period covered : 1 January 1992 to 31 December 1992
Project leader : S. Voinis (ANDRA Coordinator), M.A. Cunado (ENRESA), W. Müller (GRS)

A. OBJECTIVES AND SCOPE

This project intends to model the overall impact of gas production in the nearfield and in particular on the groundwater flow, the durability of engineered barriers and on the radionuclide migration. The wastes forms will include spent fuel, vitrified wastes, medium level waste. The different rock formations envisaged are granite rock and salt. This project is divided in four stages :

1. Description of processes
2. Analyse of gas transport mechanisms
3. Modelling of the system
4. Calculations in specific disposal conditions

B. WORK PROGRAMME

B.1. Description of processes

This step will consist in identifying the mechanisms for gas formation in the different waste repositories considered in the project scenarios from bibliographic or experimental studies and to establish the common data for the development of the models and for calculations. Analytical laws will be defined through this study to be integrated in the future modelling.

B.2. Analyse of gas transport mechanisms

The transport concerns the near-field and the host-rock. A listing of the main phenomena will be identified and studied.

B.3. Modelling of the system

The modelling will be based on specific developments or on already existing models for the different repository conditions considered by each participant.

B.4. Calculations

The calculations will be performed for the repository conditions defined by the participants. The aim of these calculations is to verify that engineered barriers and waste matrix are still playing their safety role in the presence of gas. The other aim is to discuss the results and their consequences on the future research.

C. PROGRESS OF WORK AND OBTAINED RESULTS

C.1. Task 1

C.1.1. Data reference and bibliographic synthesis

On the basis of an exchange of information; working group 1 (ANDRA/ENRESA/GRS) created for Task 1 has finished two reports :

- Data reference : the characteristics of wastes, concepts are described in this chapter.
- Bibliographic synthesis : a compilation of the description concerning the potential gas formation mechanisms is finished.

This synthesis has been used for the establishment of the gas formation codes.

C.1.2. Gas formation codes

Two codes have been developed. The name of the first one is GASFORM which has been developed by ENRESA/INITEC. It evaluates the consequences associated with the production of gas in underground storage facilities for radioactive waste. The model is intended to include spent fuel; glasses, and intermediate level wastes.

The model calculates the gas generation due to the following mechanisms : canister corrosion, cladding corrosion, microbial degradation, external radiolysis, internal radiolysis, radioactive decay and water vaporization. The scheme in annex 1 shows the structure of GASFORM code.

A first application with this code has been made for the ENRESA concepts. Preliminary calculations have shown that the generated gas from canister corrosion is one order of magnitude greater than that produced by cladding corrosion, two orders greater than microbial degradation and three orders greater than radiolysis and radioactive decay. The water vaporization is insignificant. This code will be coupled with the transport model that will be developed by ANDRA/BERTIN.

Another code has been developed by GRS. Its name is GABI. GABI's code is charged to calculate the gas formation due to the corrosion canister and internal radiolysis. Concerning the corrosion, two anaerobic metal corrosion reactions can be selected for inner and outer container corrosion.

In fact, a preliminary evaluation has been made to determine the most important phenomena to model. This GABI code will be coupled to the diphase code TOUGH2 or PHOENICS. The scheme in annex 2 presents the results obtained with the GABI's code for the GRS concept.

- A first evaluation has been made by ANDRA for the external radiolysis and corrosion canister mechanisms. The calculation has been made with analytic laws (hand calculations).

In this next year, a benchmark will be intended to compare essentially the GABI and GASFORM codes. Same scenarios and data must be defined. Results will be obtained in the middle of 1993.

C.2. Gas transport

C.2.1. Transport in salt

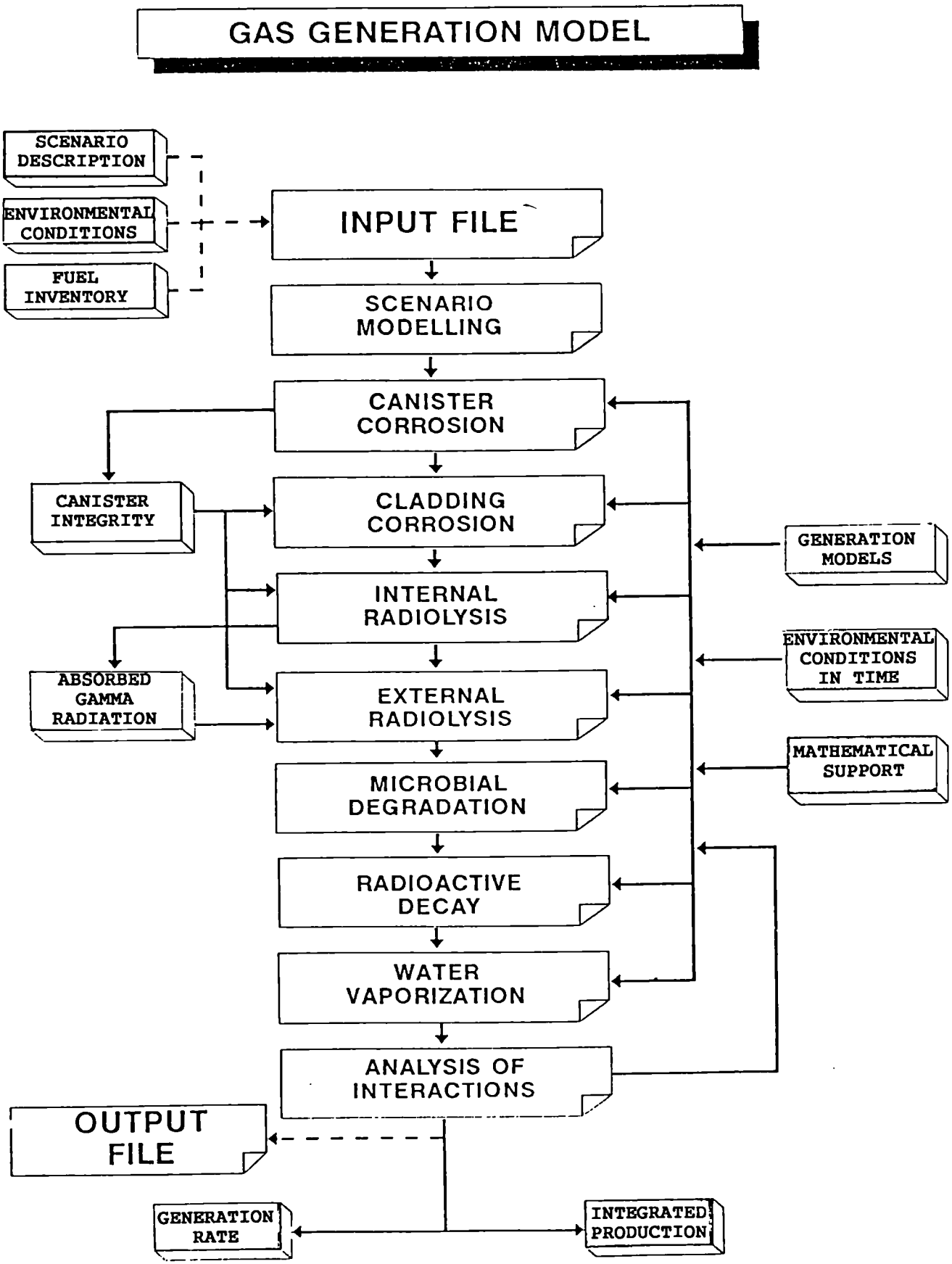
GRS is studying the coupling between PHOENICS or TOUGH2 to GABI. Some tests are necessary to understand well these two transport codes and some adaptations are necessary for the GRS concept and scenarios applications. In fact, the gas formation in the near-field is not independent of the gas transport. The coupling is very important. The limits conditions will be well identified.

C.2.2. Transport in granit

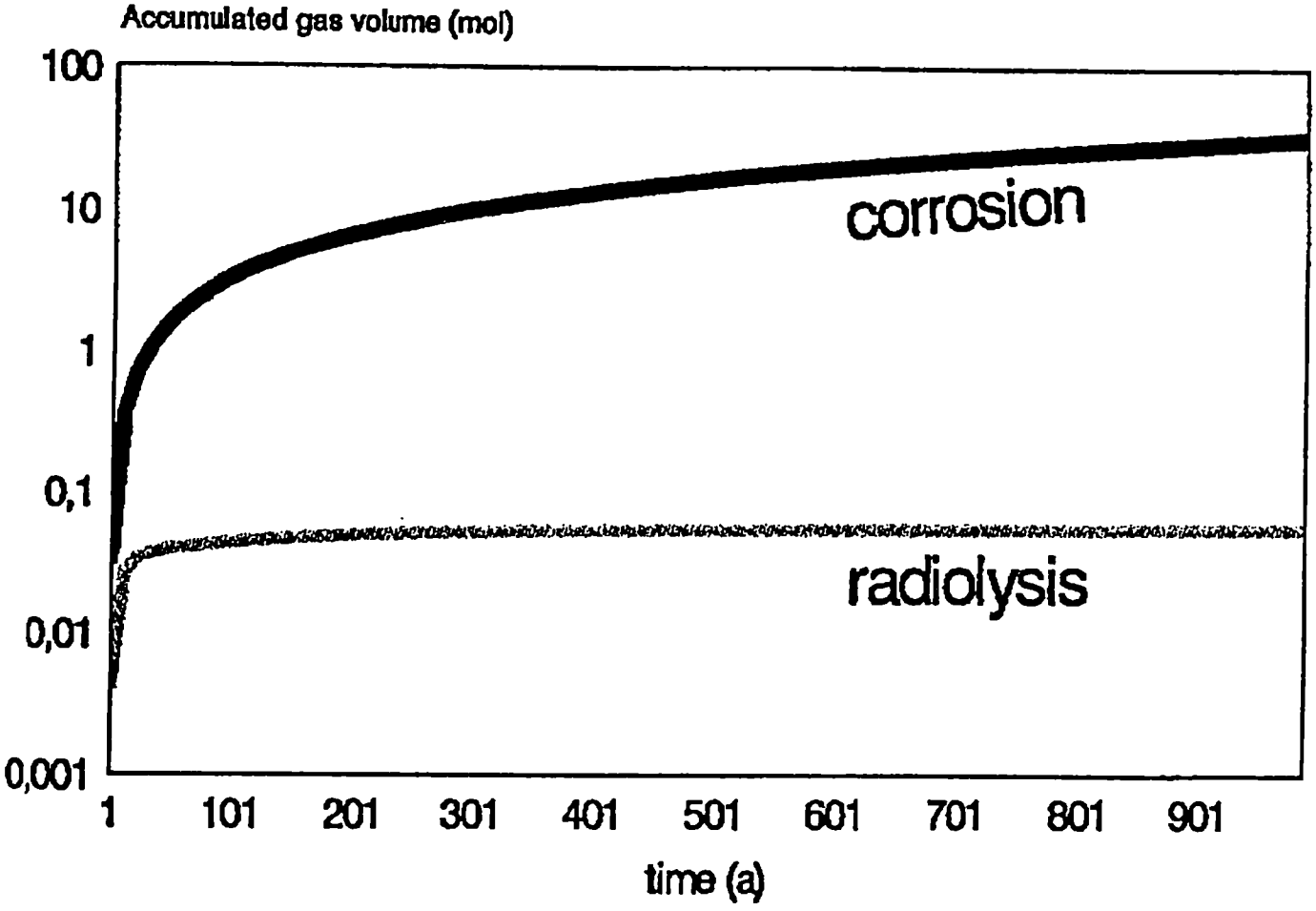
A physical analysis has been made to determine the predominant phenomena and parameters to be integrated in the global codes. One aspect of the work after will be to couple GASFORM to this. The scheme in annex 3 shows the different phenomena taken into account in the model.

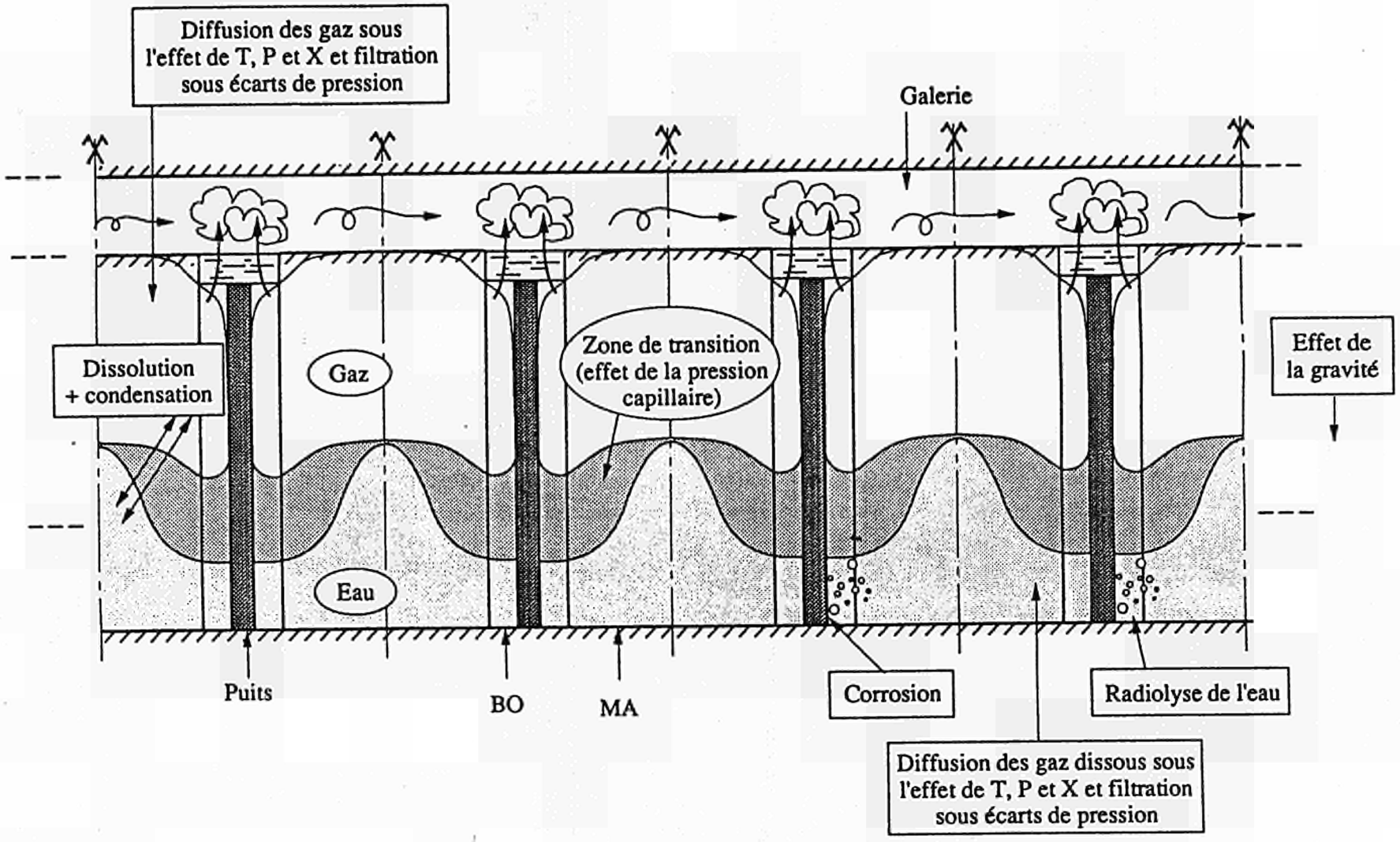
Specifications of this code is still to be discussed before doing the informatic development. The organisation of the code will be presented in the PEGASUS meeting.

ANNEX 1


GAS GENERATION MODEL
SCENARIO DESCRIPTION
ENVIRONMENTAL CONDITIONS
FUEL INVENTORY
INPUT FILE
SCENARIO MODELLING
CANISTER CORROSION
CANISTER INTEGRITY
CLADDING CORROSION
INTERNAL RADIOLYSIS
ABSORBED GAMMA RADIATION
EXTERNAL RADIOLYSIS
MICROBIAL DEGRADATION
RADIOACTIVE DECAY
WATER VAPORIZATION
ANALYSIS OF INTERACTIONS
OUTPUT FILE
GENERATION RATE
INTEGRATED PRODUCTION
GENERATION MODELS
ENVIRONMENTAL CONDITIONS IN TIME
MATHEMATICAL SUPPORT

ANNEX 2


Accumulated gas volume (mol)
100
10
1
0,1
0,01
0,001
corrosion
radiolysis
1
101
201
301
401
501
601
701
801
901
time (a)


Diffusion des gaz sous l'effet de T, P et X et filtration sous écarts de pression
Galerie
Dissolution + condensation
Gaz
Zone de transition (effet de la pression capillaire)
Effet de la gravité
Eau
Puits
BO
MA
Corrosion
Radiolyse de l'eau
Diffusion des gaz dissous sous l'effet de T, P et X et filtration sous écarts de pression

Title : **CHARACTERISTICS OF BITUMINIZED RADIOACTIVE WASTES**
Contractants : CEA/DCC (Cadarache et Saclay), SCK/MOL, NIRAS-ONDRAF, RISO NATIONAL LABORATORY
Contract n ° : FI2W-CT90- 0025
Period covered :01-03-92 to 31-12-92
Project leader : M.BRUNEL, Task leaders : MM.VAN ISEGHEM, DE GOEYSE, NOMINE, BRODERSEN

A.OBJECTIVES AND SCOPE

The objective of this study is to investigate the leaching behaviour of the bitumen encapsulation of representative and homogeneous reprocessing sludges or concentrates wastes under geological disposal conditions.

The influence of the bitumen matrix and the type of waste treated will be closely examinated.

The present study will include realistic disposal scenarios and comparaison of Eurobitum and M80/100,M40/50 and MR90/40 will be possible in regards to efficiency confinement of radioactivity.

The tests that should enable us to evaluate encapsulation stability are steady leaching tests in different media conditions constitued by water (CEA CADARACHE and SACLAY), by a cement/clay mixture and clay/clay water mixture(SCK MOL and CEA SACLAY) with different size samples from a few cm3 to the full size bitumen block.

Understanding of water uptake in and release of dissolved materials when bituminized materials are disposed of under saturated as well as unsaturated conditions and quantification of swelling, swelling pressure and leaching phenomena are improved by RISØ NATIONAL LABORATORY.

The small size samples of bituminized coprecipitation sludges will be prepared by CEA CADARACHE.

B. WORK PROGRAMME

B.1. Sampling

Samples are taken from an inactive and an active drum or are fabricated in suitably equipped shielded cell. The size of the samples is between 20 cm3 and 200 l.

B.2. Inactive leaching tests

Tests are carried out by SCK Mol Laboratory in a cement/clay mixture and a clay/clay water mixture, at 23°C and 40°C, for duration until 480 days. Emphasis will be on leaching kinetics of inactive waste constituents.

B.3. Active leaching tests

Tests are carried out in similar conditions as B.2 (media, temperature, duration) by SCK MOL for the small saples (20cm3) and by CEA SACLAY for 200 l, 20 l,2 l and 0.2 l samples. Leaching tests in water will be performed on 0.4 l samples in

static and uncontinuous conditions by CEA CADARACHE and on 200 1,20 1,2 1 and 0.2 1 for CEA SACLAY. Emphasis will be on leaching processes and kinetics of the active waste constituents.

B4. Migration of water and ions through membranes of bituminized products.

Uptake of water into bitumenized waste is important for the understanding of the long-term behaviour of the material.
Diffusion of tritiated water and ^{134}Cs ions is studied using membranes made from pure bitumen, bitumen mixed with crystals of soluble salts such as $NaNO_3$ or with insoluble sludge particles, for example $BaSO_4$. The measurements of the amounts of diffused materials are supplemented by measurement of the electrical conductivity over the membrane. This gives additional information about the migration mechanisms and the quality of the membranes.

B5. Swelling and swelling pressure.

Unrestricted swelling, water uptake and Na-leaching from samples of bitumenized materials containing soluble salts are followed using a weighing technique and chemical analyses of the leachants. The materials are simplified versions of typical waste products. This makes it possible to investigate the influence of single parameters such as bitumen type, salt content, crystal size, presence of sludge particles, etc.
Pressure development due to water uptake in confined samples of similar materials is also investigated using a technique where swelling caused by water penetrating through a cement mortar barrier results in replacement of mercury from a bottom reservoir up in a long capillary tube.

B6. Model describing water uptake and leaching.

A research model describing the water uptake in bituminized materials containing soluble salt has been developed. The dynamics of the swelling and the generation of an internal solution-filled pore structure are modelled on the micro scale. Some simplifying assumptions about geometry of the system, etc. are made. The water is supposed to be transported as vapour through the bitumen films surrounding the crystals. Diffusivities for tritiated water obtained in the above-mentioned membrane experiments are utilized.

C. PROGRESS OF WORK AND OBTAINED RESULTS

C.1. CEA CADARACHE

A shielded cell has been prepared for the fabrication of small size active samples.

This cell is a 30 m3 parallelepiped with a tight 8 m3 tank. It is equipped with four remote manipulators and two rectangular observation parts, fitting for cendrillon type flasks (liquids) and Padirac RD15 type flasks (solids).

1992 was devoted to the internal equipment of the cell. The interior equipment which will enable us to carry out the coating are:

- for the synthesis and spiking of the waste:

The requisite equipment for this operation is a decanting mixer that will allow us to fabricate the sludges required for encapsulation using real or spiked effluents; means for measuring the chemical oxygen potential, the pH and the dry extract are provided.

- for coprecipitation sludges encapsulation:

The cell is equipped with a one liter stainless steel mixer with heated double casing; it also has a condenser for distillate hold-up during encapsulation and a sludge flow valve. All these equipments can be remote operated and both the driving and monitoring operations are outside the cell.

All these equipment are now tested and are ready to work. The fabrication of inactive samples will be possible during march 1993 and the fabrication of active samples after the inactive fabrication.

C.2. NIRAS-ONDRAF

During the first semester of 1992, the full size drums of inactive Eurobitum were selected for taking inactive samples. A prototype tube for sampling was developed, designed,constructed and tested at SCK/CEN. Tests of sampling on inactive Eurobitum waste simulates confirmed that cylindrical Eurobitum samples can be taken from drums by core-cutting and by pressing the sampling tube into Eurobitum product.

During the secondsemester of 1992,a sampling tube for sampling inactive Eurobitum samples for leaching tests was costructed. We are considering to patent this tube in 1993.

For the sampling in an active Eurobitum drum, the work began by the selection of the drum to be sampled; the concept and the procedure for sampling in regards of contraints which not allowed the transfer of this drum in SCK/CEN to be sampled. In this new context, the active drum will be sampled at the Eurobitum plant: the sampling procedure is now written and the construction of the equipment for sampling the active drum at a distance of 4 meters will be elaborated. It will be tested on an inactive drum.

C.3. SCK MOL

The concept of leaching tests to investigate the behaviour of bituminized reprocessing coprecipitation sludges under geological disposal conditions was elaborated during the first semester of 1992 and the experimental set up of the leach tests is designed.

The radionuclides which can be used as tracers and with which the active bitumen samples will be doped were selected following several criteria which are:

- the inventory of the radionuclides in the active waste form,
- the precision and the accuracy with which the concentration of these radionuclides can be measured in the leachant,

- the importance of the radionuclides in terms of their mobility in the Boom clay layer (data from performance assessment studies for the Boom Clay Formation under the Mol site),
- radiation protection regulations and safety limitations during the leaching tests.

Leach tests on inactive and active CEA bitumen will start at SCK/CEN as soon the bitumen samples are available.

C.4. CEA SACLAY

During 1992,leaching tests on several species of bituminized waste form have been undertaken in the leaching facility of CEA in SACLAY.

In one way, the preparation of different samples which size are respectively 0.2, 2, 20, and 200 liters have been fabricated to start a leaching scale effect study.

In another hand, M80/100 bitumen samples have been prepared.

The first three months results for scale effect are available : for the 137 Cs, it has been seen that there is probably not a scale effect when changing the size sample; the preliminary conclusion will be probably not the same for the 60Co. but, tests are continuing to confirm these conclusions.

C.5. RISO NATIONAL LABORATORY

- Eight membrane experiments have been made, but so far results are only available for the first four. Three types of French bitumens (Mexphalt 40/50, 80/100 and R90/40) were employed. The diffusivities for water were found to agree with previous measurements. There was not much difference between the three types of bitumen, nor were there any large effects of the presence of soluble salt crystals.

- Eight samples made from the same three bitumens mixed with 20 or 10 weight% $NaNO_3$ crystals (and 30 % $BaSO_4$ in the last four) were studied using the unrestricted swelling technique. The swelling rates were low as found previously for similar materials. An interpretation model for the results have been made. An example of the output is shown in Fig. 1 illustrating the swelling and water penetration. The pore structure developing below the surface is divided into two layers, an upper one with open water-filled pores from which the $NaNO_3$ is leached, and a lower one where water is present in droplets of saturated sodium nitrate solution. The modest rate of swelling is partly compensated by a simultaneous contraction which probably is caused by out-diffusion of air trapped during casting of the sample. If the contraction had not occured the swelling would have followed the upper curve marked sw.

- Six samples of similar materials are studied using the confined sample technique. All had developed a certain pressure, up to 1.9 bar for the highest one. The systems are somewhat difficult to set up, but otherwise the principle is well suited for the purpose. It should be stressed that the pressure is not hydrostatic but an internal osmotic pressure due to the fact that the water uptake is faster than the leaching of ions from the samples.

- The dynamic model of water uptake in a row of uniformly sized $NaNO_3$ crystals functions quite well. It is being extented to account for leaching also. Test runs so far seem to be in fair agreement with the experimental results obtained with free-swelling samples.

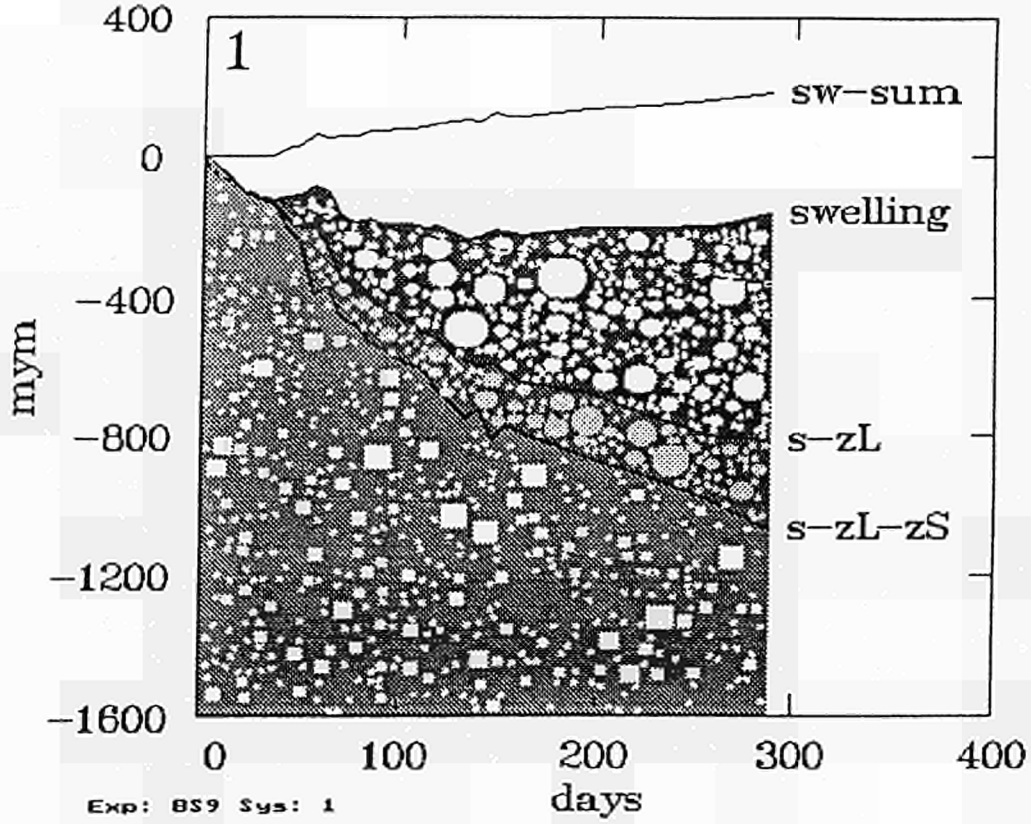


Fig.1. Swelling and water uptake in a sample of Mexphalte R90/40 containing 20 weight% $NaNO_3$ crystals.

Title: Organic matter and uraninite from the Oklo natural fission reactors - Natural analogous of radioactive waste- containing bitumen and UO_2 irradiated fuel.

Contractors: CEA/DSD Cadarache, CREGU/CNRS Nancy
Contract No: FI 2W - CT90 - 0026
Duration of contract: June 1991 - December 1995
Period covered: January 1992 - December 1992
Project leader: P. Holliger, DSD/SCS Cadarache, France

A. OBJECTIVES AND SCOPE

Bitumens are used for the solidification of low-activity alpha containing wastes and their long-term behaviour in a geological deep repository remains questionable. It is thus proposed in this work to gain understanding on this issue by studying analogues of technological bitumens which have been poorly investigated, from this viewpoint, until now. The two billion years old fission reactors discovered in the Oklo uranium ore (Gabon) and embedded in clays, uraninite, Organic Matter (OM) and sandstones, provide opportunity to examine the state of preservation of radionuclides-containing matrices. They are a priori favourable, as natural analogous, because of the long time scale involved and the presence of stable daughters of fission products and transuranium elements generated by the fission process which induced radiation effects.

This programme is specially aimed at investigating the relationship between radiation effects, due to various particles emitted by alpha decay of uranium and during fission reactions, and changes in the structure of the organic matter. In the Oklo s.l. U-ore, we intend to characterize the different types of (U + OM) phases, ranging from "invisible" U-rich OM to millimetric uraninites inclusions within the OM, in order to estimate the specific consequences of radiation damages.

The original experimental procedure relies on the characterization of radiation-induced structural and chemical modifications with a variety of physico-chemical techniques. On powdered samples, we first analyse the Total Organic Carbon (TOC); ^{13}C NMR and infrared spectroscopies will provide interesting results which allowed the different types of bitumens and kerogens to be discriminated. Infrared Spectroscopy and Raman microanalyses appear to be appropriate techniques for the in-situ characterization of the OM during the radiolytic alteration process. These analyses, coupled with $^{13}C/^{12}C$ isotope data and ion images (in-situ microscale cartography) obtained by SIMS (the ion microprobe), would allow us to discriminate more accurately the different OM samples selected for this study.

Another aspect of this programme is to calibrate the radiation effect induced by increasing doses of well-defined particles (mass, energy) in order to help interpret the direct characterization of samples naturally irradiated during the functioning of reactors. For comparison with Oklo, OM from the Lodève U-ore may constitute an other good analogous; indeed, the U-rich mineralization is younger (jurassic age) and, as at Oklo, was controlled by migrated OM.

B. WORK PROGRAMME

Task 1: Geochemical characterization of the Oklo organic matter.
B.1.1 Sampling and Global geochemistry (CEA, CREGU)
B.1.2 In-situ characterization of the Organic Matter, by coupling Infrared and Raman spectroscopies (CREGU) and electron and ion microprobes techniques (CEA).
Task 2: Experimental study of the mobility of uranium and fission products.
B.2.1 Characterization of the OM from the nuclear reactor zones before leaching experiments : U - Fission products in-situ analyses by using the ion microprobe (CEA).
B.2.2 Leaching experiments (CREGU) and new characterization.
Task 3: Experimental study of radiation effects
B.3.1 Irradiations and calibration experiments (CEA)
B.3.2 Modifications of the structure and chemical composition of the OM by radiation effects: characterization by spectroscopy and microprobe techniques (CREGU, CEA).

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

During this first stage of the contract we started to apply the original methodology in order to test its applicability and to identify possible experimental problems which may have arisen. We studied some samples collected from both inside reaction zone 9 and from outside (reference). The sampling of this material is not an easy task at Oklo because the organic matter cannot always be easily distinguished in situ from other faciès (e.g. uraninite-rich ones). Only subsequent petrographical observations and chemical analyses, when back to the laboratory, can confirm the appropriateness of the collected samples to this investigation. The OM samples, from various petrographic areas outside the U-ore, in the U-ore and in the reactor zones, have been carefully selected. Polished sections and powders have been made and a complete sampling is now achieved.

PROGRESS AND RESULTS

B.1.1 Sampling and Global geochemistry

Sampling at Oklo (CEA)

Organic material is almost ubiquitous in the environment of the Oklo deposit. The ampelites of the Francevillian formations contain up to 8% of total organic carbon (TOC) while the FA sandstones content averages 1%, but locally, in the South of Oklo, reaches a tens of pourcent. Reactors 7-9 are extremely rich in organic matter (U/C up to 50% in weight); a part of uranium fissioned and remained there in the form of UO_2 inclusions within OM. In these zones, OM acted as a moderator in the same way as water; ion microprobe analyses show that most of fission products were retained in ^{235}U-depleted uraninite grains. Four samples of the reactor cores 8-9, with $^{235}U/^{238}U$ ratios ranging from 0.578% to 0.680%, have been selected. Zone 10, larger than the reactor zones 7-9, contains organic matter but with heterogeneous distribution. Mixed U + C mineral phases, within reactor core at the bottom of zone 10, have

been sampled in March 1992 (gallery D.81N). At the total, eleven samples from zone 10 have been prepared for this study. The two reactor zone areas 7-9 and 10 are petrographically different and it would be useful to compare the characteristics of OM each other. Reactor 13 shows a unique configuration with a massive uraninite reactor core, compacted a long time after the reactions occured. This zone is located only about ten meters near to a magmatic intrusion which cuts cross the Oklo U-ore, in the E-W direction, and was dated 750 Ma. This event played a prominent role by remobilizing - recrystallizing large amounts of uranium and organic matter in the South part of the Oklo U-ore. Two samples of OM from zone 13 have been collected; one, in a fracture within fine sandstone just below the "faciès-pile" and the other, at the contact with the dolerite intrusion. Besides, twelve samples from outside Oklo reactor zones, and in Okelobondo area have been prepared. Al these samples are now being studied by using the different analytical techniques which have been proposed in this programme.

In order to classify the Oklo OM samples relative to the radiation dose which was absorbed, some theoretical calculations have been done. The radiations are mainly of two types: - one corresponds to the decay of ^{238}U in equilibrium with its daughters. For a sample where U content is 10%, uranium has thus deposited a dose of $5x10^{12}$ rads, for two billion years. The other is related to the fission process (10^4 shorter than the age of the U-ore) and the radiation dose is 10 greater than the first one, in a sample with a ^{235}U depleted value of 0.6%. On account of the high values of the radiation dose, these effects may have induced important changes in the structure of the OM by bond-breaking, ionization, formation of ^{13}C-depleted volatile products, ...

Characterization of the Organic Matter (CREGU)

Organic matter from the Oklo deposit is highly aromatic. Atomic H/C ratios remain below 0.4 and aromaticity factors generally exceed 75%. This high structural organization is mainly induced by the combined effects of radiolysis and thermal alteration. Both kerogens (dispersed sedimentary organic matter) and bitumens (residues of migrated oil) display high molecular orientation and various oxidation levels. However, organic material spatially associated with the nuclear reactors, generally displays an apparent lower maturity than that of the mineralized or unmineralized organic material sampled outside the reactor rones. Pyrolysis-gas chromatography, ^{13}C nuclear magnetic resonance (^{13}C NMR) as well as elemental analysis studies, have confirmed this statement. Such chemical composition could be attributed either to the presence of late bitumens (migrated after the nuclear reactions occured) or to the combined effects of temperature, pressure and radiolysis in hydrous conditions.

The structure of the Oklo organic material does not favour the utilization of conventional organic geochemistry techniques. As far as extractable compounds yields remain below 1%, analytical tools such as gas chromatography or mass spectrometry are not efficient. Solid-state techniques including C-H-O-N-S analyses, ^{13}C NMR and infrared (IR) spectroscopies could provide interesting results. Methyl/methylene ratio, degree of substitution of aromatic rings as well as aromaticity factors (see figure 1) were determined by ^{13}C NMR. They revealed that bitumens from the reaction zones display very contrasted characteristics, which are not typical of highly radiolized organic material.

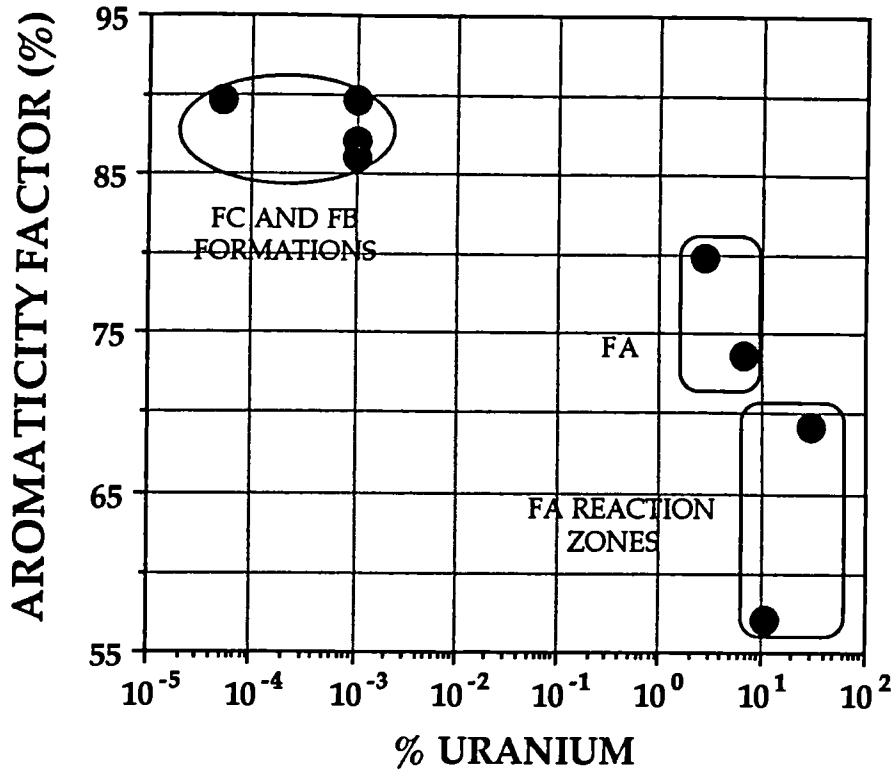


Figure 1 : Aromaticity factor and U content relationship on different bitumens, sampled outside and in reactor zone 9

However, it has also been shown that different generations and different types of structures of OM can coexist in the same sample. Then, bulk sample techniques are no more efficient and only give an averaged image of the chemical composition of the OM.This is why we developed a methodology which is mainly based on the use of in-situ investigation techniques.

B.1.2 In-situ characterisation of the OM (CEA, CREGU)

The ion microprobe technique (or SIMS)

Because of the little quantity required for an analysis free of pollution, the Secondary ion mass spectrometry (SIMS) appears to be an appropriate technique for an isotope investigation on microminerals. This technique in situ has already been successfully used in the Oklo research programme (*Radwast Programme, Task 4: "Oklo-Natural analogous"*) for isotopic micro-distribution maps and to determine the individual isotopic distribution of the elements (U and fission products). The methodology for U-Pb dating on small-sized uranium oxide and galena samples has been also developed and allowed to propose a geochronological sequence of the main geological events at Oklo (see Figure 2).

In addition, the SIMS technique allows to measure precise $^{235}U/^{238}U$ ratios on U-oxides microphases in a short time (1 hour, with an accuracy of 0.3% at 2σ). In situ controls of ^{235}U isotope abundance in uranium oxides have

thus permitted the identification of four new reaction zones where ^{235}U has been measured depleted down to 0.4% (normal value 0.725%) in zone 13.

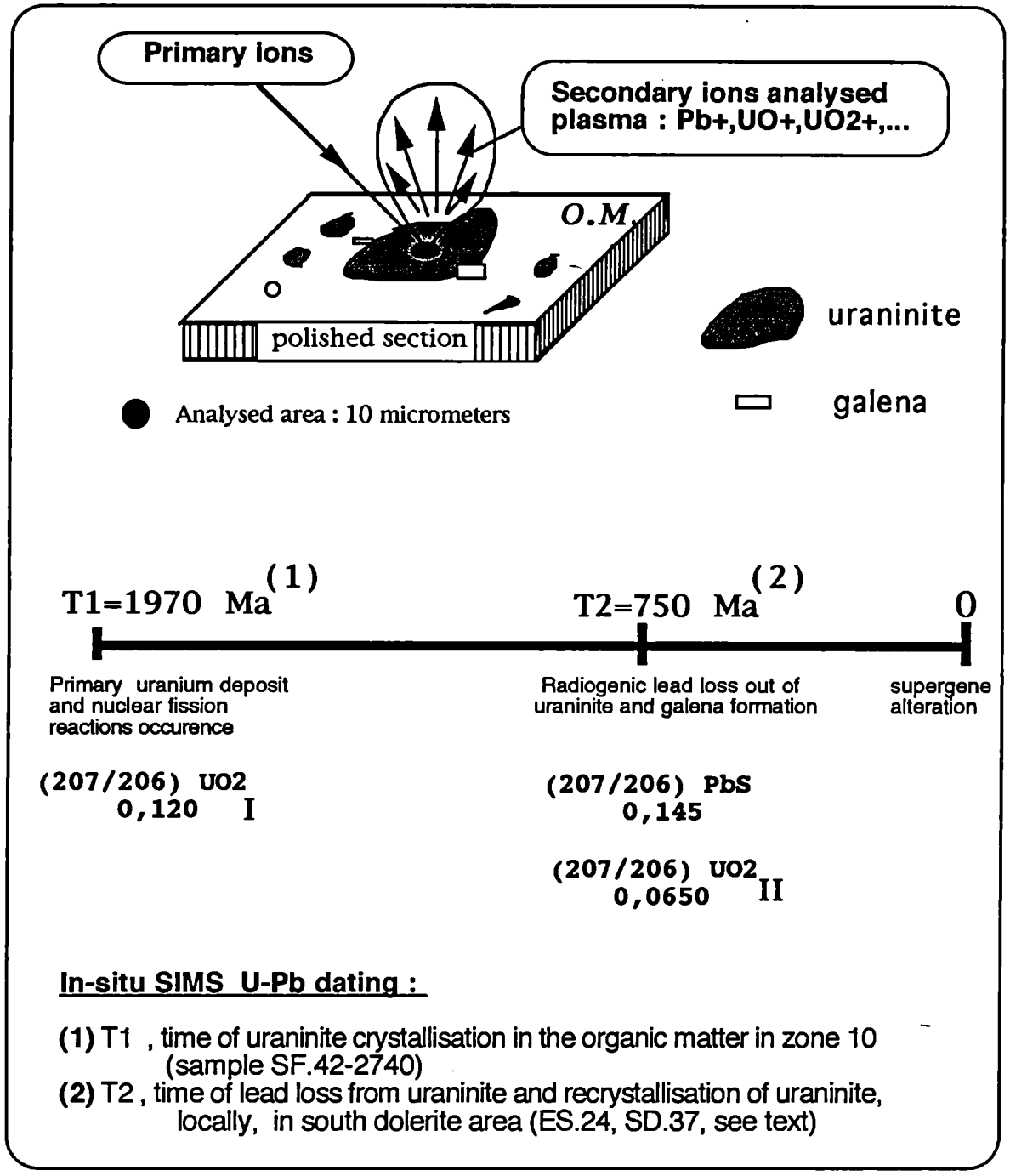


Figure 2 : The ion microprobe technique and its use for U-Pb datings of the different paragenesis of OM on Oklo samples.

The microspectroscopy techniques (CREGU)

Besides transmission electron microscopy and SIMS provide evidences for the occurrence of various types of OM, Raman and Infrared microspectroscopies are also able to provide reliable information and to characterize either different types of OM or alteration processes. Raman spectra have already provided sufficient information to infer the degree of

organization of these highly aromatic structures Preliminary investigations in transmission micro-infrared spectroscopy allowed the radiolytic effects around uraninite grains to be circumvented (aliphatic and aromatic CH removal, relative concentration of C=C bonds).These analyses obtained by spectroscopies techniques, coupled with $^{13}C/^{12}C$ isotope data and ion images (in-situ microscale cartography) obtained by SIMS (the ion microprobe), would allow us to discriminate more accurately the different OM samples selected for this study.

B.3.1 Calibration experiments for the study of radiation effects

Another aspect of this part of our programme is to calibrate the radiation effect induced by increasing doses of well-defined particles (mass, energy) in order to help interpret the direct characterization of samples naturally irradiated during the functioning of reactors. The original experimental procedure relies on:

- ion bombardment with varied ions of appropriate mass and energy in order to simulate alpha particles, alpha recoils and fission fragments. At this stage, we used either ion implanters for low energy heavy ions or accelerators for high energy ions.
- surface analysis with Rutherford Backscattering Spectrometry (RBS), intended to detect stoichiometry changes, particularly after leaching. In addition, this technique provides near-surface elemental depth profiles, which potentially help decipher the leaching mechanism.

During this first stage, we started to apply this methodology in order to test its applicability and to identify possible experimental problems which may have arisen. We studied some samples collected from both inside reaction zone 9 and from outside (reference). Some difficulties occurred because the bitumens of Oklo revealed to be quite fragile in the high vacuum conditions necessary for ion bombardment and analysis and to ion beam effects. In addition, as the release of light volatile organic components was susceptible to contaminate the sample chamber, it was necessary to develop an experimental procedure minimizing these effects by coating both sides of samples with a thin coating of aluminium (30 nm). Another difficulty stems from the relative brittleness of these bitumens which tend to break into small pieces during the leaching experiments, notably when performed at high temperatures (> 100°C). The samples were thus embedded in an epoxy resin and subsequently polished with ethylene-glycol as a polishing solvent in order to avoid artefacts (hydration and leaching).

The only ion bombardment runs so far performed involved low energy (1 keV/amu) lead ions which have been shown in previous studies dedicated to nuclear glasses and ceramics to conveniently simulate alpha recoils. These studies demonstrated that such particles are responsible for atomic displacements and structural modifications in inorganic ionic or covalent compounds which explain most of the property changes linked to alpha decay. In contrast, we do not expect such particles to be the most damaging ones for bitumens because ionization effects are likely dominant in organic matter. However, it was quite convenient to start the present study with low-energy heavy-ions bombardment because the associated radiation effects are already quite well calibrated. During these preliminary implantations no macroscopic degradation of the organic material has been observed at least up to doses of lead ions as high as 10^{14} ions/cm^2 which corresponds to about $2x10^{19}$ alpha disintegrations per g.

Up to now, the expected effect of irradiation on the leaching behaviour could not be evidenced. We thus intend in the near future to apply a technique which allows the detection of subtle effects. In this approach, the sample is covered with an electron microscope grid acting a partial mask during irradiation which delineates a regular succession of irradiated and unirradiated zones. Any difference between these two types of zones in terms of contrast or level would be easily detectable even by means of Nomarski interferential optical microscopy and could be further investigated with infra-red microscopy. In addition, whenever the leaching of such material surface induces step heights between the two types of zones (reflecting the effect of radiation damage on aqueous corrosion), measurement of the differential leach rate could be performed with a profilometer.

RBS characterization of samples

Our main observations are the following:

- the shape of the RBS spectra on unleached samples is characteristic of a highly heterogeneous uranium distribution. In effect, these spectra cannot be conveniently fitted by a simulation with the computer code RUMP, developed at Cornell University, USA, assuming a homogeneous distribution. The best fit corresponds to a mean carbon/uranium ratio of 200. Moreover, the slope of the experimental spectrum (towards lower energies), as compared to the theoretical one, is an indication of some "rugosity" within the matrix which is best interpreted by the existence of dispersed U-rich grains.

-Complementary observations of the samples with an optical microscope and with a scanning electron microscope do indeed confirm the presence of numerous uraninite grains (UO_2) distributed throughout the material. Although this fact could be anticipated because it has been already described at Oklo and also reported for U-ore deposits of the same type, we expected to find zones of sufficient size (compared to the RBS beam spot of the order of 1 mm) where uranium would have been homogeneously distributed in the bitumen as organo-metallic complexes. Unfortunately, it does not seem to be the case.

- the shape of the RBS spectra on leached samples clearly demonstrates a modification in the uranium concentration. Indeed, one does not observe neither a surface accumulation or a marked depletion but, instead, a general impoverishment of the bitumen reflected by a steady lowering of the experimental spectra which systematically lies below the theoretical ones. Due to the heterogeneous distribution of uranium such a feature is quite difficult to interpret with certainty. Two possibilities may be suggested:

- true uranium leaching over a significant thickness of the sample (probably > 1 micrometer). This would involve the fraction of uranium atomically complexed with the organic matrix.

- release of UO_2 grains by mechanical breakdown of the matrix in which they are imbedded. Indeed, such a behaviour could be anticipated as the immediate surrounding of such grains is known to be highly damaged by natural alpha decay.

The discrimination between these two hypotheses is hard although the observed trend of general uranium decrease pleads for a significant loss of uraninite grains. Moreover, we do not know yet the fraction of uranium in the form of uraninite grains and of organometallic complexes so that quantative assessment of RBS spectra is not possible.

AQUEOUS CORROSION OF NUCLEAR GLASSES: INFLUENCE OF DISPOSAL CONDITIONS

Contractor:	CEA - CEN Valrhô, DPR/SCD
Contract No:	FI 2W 0027
Duration of Contract:	April 1991 - April 1995
Period Covered:	January 1992 - December 1992
Project Leader:	N. Jacquet-Francillon

A. OBJECTIVES AND SCOPE

Geological disposal of vitrified high-level waste packages will expose the containment glass to multiple complex chemical reactions (involving the host rock, the engineered barrier materials and the nuclear glass) due to the presence of the water vector in the repository environment. The presence of environmental or local site materials affects (increases or decreases) the glass matrix corrosion rates and the degree of radionuclide containment. It is therefore essential to characterize and quantify the potential reaction mechanisms in a geological disposal complex. The investigation begins at laboratory scale; the experimental approach also allows the development of a nuclear glass dissolution model applicable to actual repository conditions.

Three major avenues of research will be investigated in a programme combining an experimental approach and modeling of relational processes: < basic research on aqueous corrosion of nuclear glass; > the effect of the host rock on R7T7 glass alteration; and fi the development of models describing glass behavior in repository conditions.

B. WORK PROGRAMME

B.1 Basic research on aqueous corrosion of nuclear glass

1. The effect of glass composition on the initial dissolution rate, the solubility limit and equilibrium pH, and the role of new phases on glass dissolution kinetics will be investigated by varying the concentrations of the following components: MgO, SiO_2, Al_2O_3, B_2O_3 and fission product oxides.
2. Role of exterior ions: metallic cations (Al, Fe, Zn, Pb and Mg) and canister corrosion products; effect of the ionic strength.
3. Investigation of the interface gel layer: physical and chemical properties, thermodynamic properties and stability.

B.2 Influence of the disposal site

1. Equilibrium limits with various host materials: granite, clay (ref 448 and 802), schist and salt.
2. Parameter experiments at 90°C in the presence of schist (different types and grain sizes), clay, granite or salt (clear halite and cloudy halite).
3. Integral experiments with granite, clay and schist.

B.3 Development of a glass behavior model

1. Mechanistic model
2. Geochemical model (thermodynamics and kinetics of R7T7 glass dissolution, interactions between R7T7 glass and corrosion products, interactions between R7T7 glass and host materials: granite, clay or schist).

C. PROGRESS OF WORK AND OBTAINED RESULTS

Part I: Basic Research on Aqueous Corrosion of Nuclear Glass

Effect of Glass Composition

When MgO is added even in small amounts (2% and 5%) to the standard R7T7 glass composition, the "final" dissolution rate under near-saturation conditions (simulated by high SA/V ratios) increases substantially. The DISSOL geochemical code was used to calculate solution saturation with respect to various magnesian minerals. Most of the magnesium silicates tested are supersaturated in solution, and thus liable to precipitate. X-ray emission chemical microanalysis and electron microdiffraction confirmed that the glass alteration products included magnesian smectites and micas. It is therefore highly probable that the sharp increase in the "final" dissolution rates observed after adding MgO is related to precipitation of magnesium silicates. However, we were unable to reproduce the experimentally observed corrosion kinetics using a rate law based exclusively on the H_4SiO_4 activity in solution.

R7T7 glass samples were prepared by varying the SiO_2 content from –10% to +15% with respect to the standard composition. Increasing the SiO_2 content by 15% resulted in a four-fold drop in the initial dissolution rate, and a 13-fold drop in the long-term rate under near-saturation conditions. Conversely, lowering the SiO_2 content by 10% caused the initial and long-term corrosion rates to increase by less than a factor of 2.

Role of Metal Canister Corrosion Products

The R7T7 glass corrosion rate increased substantially in the presence of metallic corrosion products. It should be noted, however, that the corrosion products used in these experiments were obtained by acid dissolution and soda precipitation of NS 24 alloy scraps (i.e. the canister material). The high specific area of these specimens is certainly not representative of slow canister degradation in a geological repository, and constitutes an extreme limit.

Glass alteration and the time during which the corrosion rates remained high were proportional to the amount of corrosion products in the environment. With 0.5 g of canister corrosion products, the rate remained constant at an average of 0.12 $g \cdot m^{-2} d^{-1}$ throughout the longest test period (from 7 to 364 days). The rate diminished after 84 days with 0.05 g of corrosion products, and after only 28 days with 0.005 g of corrosion products. By comparison, the R7T7 glass corrosion rate from 7 to 364 days in pure water at the same SA/V ratio is 0.01 $g \cdot m^{-2} d^{-1}$.

The corrosion products result in a slightly acid pH (4.5–5.5 at 90°C) for as long as they are present in large quantities. The pH becomes basic as the corrosion rates diminish.

Increased R7T7 glass corrosion in the presence of canister corrosion products is attributable to the persistence of low H_4SiO_4 activity in solution. The duration of the low activity is directly related to the quantity of corrosion products involved.

Effect of the Interface Gel

The diffusion barrier properties of the interface gel were investigated by flowing experiments at 90°C. The best fit between experimental and calculated results was obtained with an apparent silicon diffusion coefficient in the gel of between 5×10^{-14} and 1×10^{-13} $m^2 \cdot s^{-1}$ (Figure 1).

Part II : Influence of the Disposal Site

Equilibrium Limits with Various Host Materials

Static leaching experiments at 90°C with a high SA/V ratio (5800 m^{-1}) were conducted for periods of over one year with R7T7 glass powder samples and pulverized environmental materials (granite, clay, salt and schist) to determine whether new glass-water-host rock equilibria allow the system to reach the very low corrosion rates observed when the medium is "saturated" with respect to the glass. In all four media, the glass dissolution rate dropped by over two orders of magnitude from the initial rate, indicating that near-saturation conditions were reached, even in the presence of crushed environmental materials. However, the "residual" corrosion rate observed in clay (approx. 6×10^{-3} $g.m^{-2}d^{-1}$) was higher than in granite or schist (approx. 1×10^{-3} $g.m^{-2}d^{-1}$), although this difference cannot be attributed to lower H_4SiO_4 activity at equilibrium in clay.

Static Leaching Experiments at 90°C with an SA/V Ratio of 50 m^{-1} in the presence of Various Materials

Considerable glass alteration was observed in natural moist clay (i.e. without prior conditioning by soluble silica). The alteration was much lower in the presence of crushed granite or schist, although greater than in double-distilled water; the finer the material grain size, the greater the long-term glass alteration. R7T7 glass showed only slight alteration in French halite, whether pure or containing fluid inclusions.

Integral Experiments Simulating Granite, Clay and Schist Media

The "TAV 6" experiment simulating a granite repository environment has been in progress for over 9 years. Glass alteration remains very slight, and is controlled by the pseudo-flow due to the solution sampling procedure. Four integral clay tests were initiated in 1992 : two of them will be terminated after 6 months and the others after 2 years. Two integral schist tests were also initiated in 1992 for periods of 6 months and 2 years.

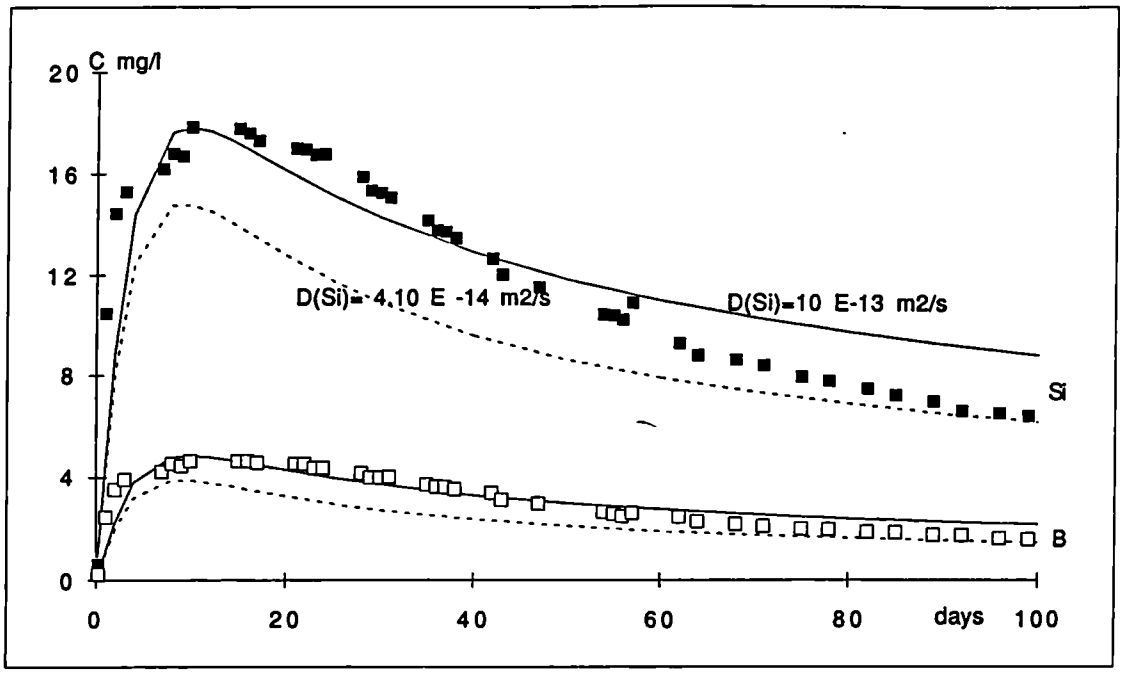
Part III : Development of a glass behaviour model

LIXIVER Code

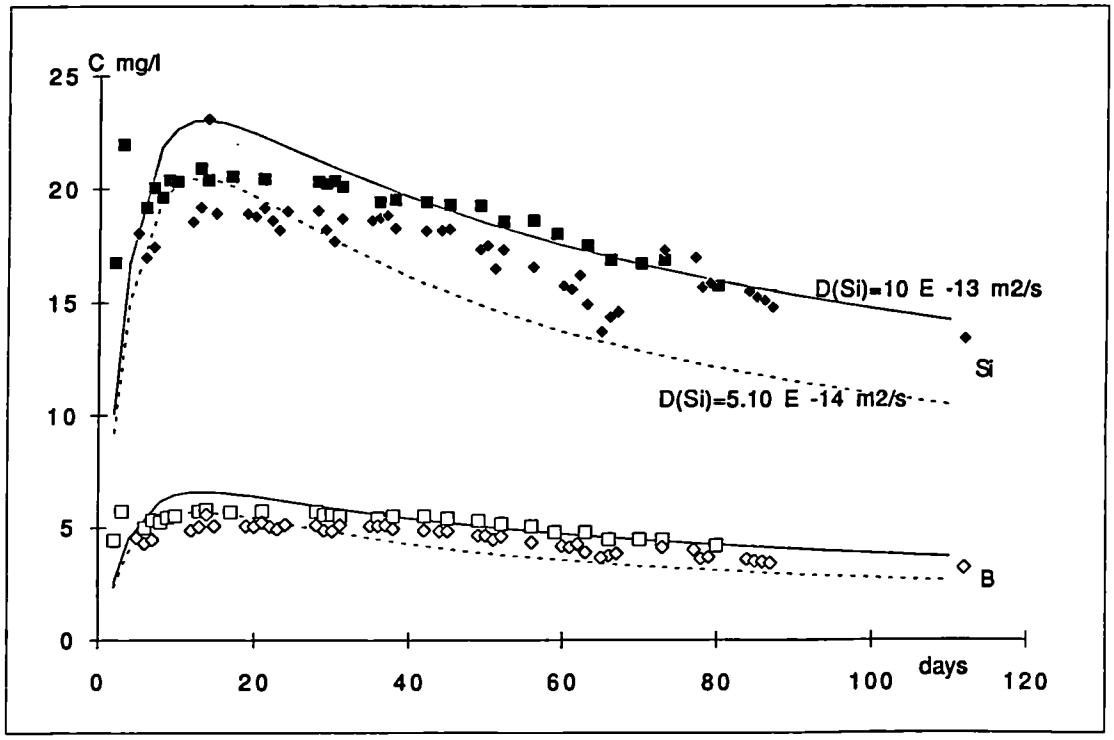
Development of work on the LIXIVER code, which takes account of the surface reaction (first-order law), diffusion in the gel layer, silicon consumption and pH calculations, was completed in 1992. Figure 1 is an example of the correlation between model predictions and experimental data. The fit is less accurate for static experiments, and a thorough analysis has been undertaken to identify the weak points in this type of modelling, base exclusively on the H_4SiO_4 activity at the reaction surface.

KINDIS Code

The KINDIS code, coupling a first-order kinetic law with the DISSOL geochemical code, continued throughout 1992, with allowance for flowing conditions and possible supersaturation with respect to the mineral phases. This work will be discussed in detail in 1993.



FLOW RATE : 122 ml/d



FLOW RATE : 60 ml/d

Figure 1. R7T7 glass leaching at 90°C with two different flow rates:
Boron and silicon concentrations predicted by the LIXIVER code (curves) and measured experimentally (points).

EFFECT OF INSOLUBLE ACTIVE DISSOLUTION FINES ON FISSION PRODUCT GLASSES

Contractor:	CEA - CEN Valrhô, SCD
Contract No:	FI 2W - 0028
Duration of Contract:	March 1991 to February 1995
Period Covered:	January 1992 to December 1992
Project Leader:	N. Jacquet-Francillon

A. OBJECTIVES AND SCOPE

Insoluble particles, known as fines, present in fission product solutions consist of cladding fragments or undissolved fission products, notably platinoids. At La Hague, these fines are vitrified with the fission product solution in the T7 facility. Platinoids are found in soluble or insoluble form with other particles. Regardless of their initial state, the platinoid elements ruthenium, rhodium and palladium are insoluble in the glass.

As a result, the amorphous glass mass contains heterogeneous inclusions comprising notably highly radioactive Ru and Rh, with substantial thermal power. It is therefore necessary to ascertain whether the SON 68 18 17 L1C2A2Z1 reference glass composition is a suitable containment matrix for these active insoluble dissolution fines. The experimental programme will include the fabrication and characterization of glass rods containing actual active fines.

B. WORK PROGRAMME

B.1 Development of an analysis method for glass containing dissolution fines.

B.2 Development of a nondestructive gamma-scanning method to measure the radionuclide distribution and the true activity.

B.3 Fabrication of glass rods containing actual active fines; quantification of the fines, and notably the platinoids, in the glass.

B.4 Preparation of test specimens after gamma scanning.

B.5 Measurement of glass containment properties at room temperature and at 90°C; determination of glass alterability at 90°C.

B.6 Leaching of test specimens at 100°C in Soxhlet devices.

B.7 Characterization of glass microhomogeneity.

B.8 Repeat steps B.4 through B.7 on glass samples submitted to a heat treatment cycle.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Progress and Results

A glass composition designated A130, containing actual fines from dissolution of fuel irradiated in the Advanced Prototype Boiler (CAP) at Cadarache, was produced in the *Vulcain* cell. The principal characterization tests specified in the contract have been completed on this sample.

- Procedures for dissolution by alkaline melting and analysis of the major glass components have been qualified; however, platinoid analysis in the fines and in the glass remains a difficult problem.
- Gamma scanning showed uniform radionuclide distribution in the glass, although a slight excess of ruthenium was observed at the end of the casting phase. Specific activity measurements by gamma scanning have been qualified to determine the quantity of radionuclides in the glass and to allow comparison with glass radiochemical analysis results.
- Leach testing at 90°C showed satisfactory aqueous corrosion resistance. The normalized mass losses after 21 days were the same for both the as-cast and heat-treated glass specimens, and were comparable to the results obtained for inactive R7T7 glass.

A second glass composition designated A131, containing fines from reprocessing fuel from the *Phénix* fast breeder reactor at Marcoule, was also produced in the *Vulcain* cell. When cast, the melt was initially fluid and flowed smoothly, but its viscosity increased, resulting in intermittent flow. Two rods, weighing 422 g and 190 g, were obtained.

The platinoid content of this glass, determined after an initial analysis of the fines suspension, was 0.44%. This figure will require confirmation by additional analysis of the solution and of the glass.

The radiochemical balance at various points in the vitrification facility showed little radionuclide volatilization: virtually all the initial activity was found in the glass.

The fines dissolution and analysis procedures have not been finalized. Acid and alkaline dissolution methods provide diverging results, notably with regard to the platinoid content. Additional tests are now in progress.

THE CORROSION OF NUCLEAR WASTE GLASSES IN A CLAY ENVIRONMENT : MECHANISMS AND MODELLING

Contractor :	NIRAS/ONDRAF Brussels
Contract N° :	FI2W0031
Duration of contract :	March 1991 - February 1995
Period covered :	January 1992 - December 92
Project leader :	R. Gens (NIRAS/ONDRAF, coordinator)
Project leader SCK :	P. Van Iseghem

A. OBJECTIVES AND SCOPE

The present project is the third part of a programme which started in 1981. This programme studies the performance of various simulated HLW-glasses in one of the reference repository environments, the Boom clay, with the aim to elucidate corrosion mechanisms in clay media and to propose a source term for the radionuclide release into the nearfield. The objective of the present project is to enlarge the already existing database by the use of corrosion accelerating conditions (accelerated tests) and more complex media (integrated tests) and to model the long term interaction between glass and clay environment, which is the final goal of the project. In the accelerated tests, SA/V (glass surface area to solution volume) and temperature are used as the corrosion accelerating parameters. To obtain a high SA/V the glass is powdered. In the integrated tests glass corrosion is studied in the presence of canister/overpack corrosion products and backfill.

The S.C.K./C.E.N (Mol, Belgium) was appointed for the practical execution of the programme.

B. WORK PROGRAMME

B.1. Accelerated tests, inactive: powdered samples of glasses SON68 and SM539 are exposed to distilled water (DW), synthetic interstitial claywater (SIC) and a mixture of 500 g Boom clay and 25 g Fe_2O_3 per liter synthetic interstitial claywater (called "CCSICM + CP"). The SA/V values are 500, 2500 and 10000 m^{-1}, the experimental temperatures are 40, 90 and 150°C. The maximum test duration is 720 days.

B.2. Accelerated tests, active: grains of glasses SON68 and SM539 are exposed to the same media as sub (B.1.). The glasses are doped with either Pu/^{134}Cs/^{90}Sr or ^{237}Np/^{99}Tc/^{55}Fe/^{241}Am. The SA/V value is approximately 400 m^{-1}. The experimental temperature is 90°C. The maximum test duration is 360 days.

B.3. Integrated tests, inactive: a first series of powdered samples of glasses SON68 and SM539 is exposed to a mixture of 250 g Ca-bentonite, 250 g Boom clay and 25 g Fe_2O_3 per liter synthetic interstitial claywater. A second series of powdered glasses is exposed to a mixture of 475 g Boom clay, 25 g Cibelcor P40 cement and 25 g Fe_2O_3 per liter synthetic interstitial claywater. The SA/V values are 500 and 2500 m^{-1}. The experimental temperatures are 40, 90 and 150°C. The maximum test duration is 720 days.

B.4. Integrated tests, active: grains of glasses SON68 and SM539 are exposed to a mixture of 250 g Ca-bentonite, 250 g Boom clay and 25 g Fe_2O_3 per liter synthetic interstitial claywater. The glasses are doped with the same radionuclides as for the active accelerated tests. SA/V, temperature and test durations are also the same as sub (B.2.).

B.5. Modelling of the dissolution behaviour of the glass matrices in the studied clay disposal surroundings.

Table I shows a overview of the 1991 - 1995 test programme.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

By the end of 1992, the inactive accelerated tests, more than half of the inactive integrated tests and all active tests with Pu/^{134}Cs/^{90}Sr doped glasses had been started. Many of these tests are already finished. The tests with ^{237}Np/^{99}Tc/^{55}Fe/^{241}Am doped glasses are in preparation. Orientating discussions have taken place to assess the need for an adaptation of the GLASSOL kinetical model.

Progress and results

B.1. Inactive accelerated tests

The inactive tests at 40, 90 and 150°C have all been started. The following tests were finished: 90 and 360 days at 40°C; 28, 90, 180 and 360 days at 90°C; 20 and 90 days at 150°C.

The acceleration of the glass corrosion is expressed in an increase of the boron concentration in the leachate and a decrease of the normalized boron losses and glass mass losses with increasing SA/V. In general the corrosion rate is higher for SM539 than for SON68 and increases in the order SIC < DW < CCSICM+CP. At higher SA/V the difference between the B concentrations in CCSICM+CP and the other media becomes smaller. This suggests that the corrosion enhancing effect of Boom clay decreases with increasing SA/V, and thus possibly also with time. Plots of the solution B concentrations at 90°C as a function of SA/V.time or SA/V.time$^{0.5}$ generate single curves, suggesting diffusion controlled corrosion in DW (SON68 and SM539) and SIC (SM539). The B plots for CCSICM+CP did not yield single curves at 90°C, but the corrosion of SM539 appeared to be proportional with time in this medium at 150°C. In general, the data obtained with glass coupons do not fit well with the data obtained with glass powders. One of the causes of this misfit may be a bad estimate of the actual SA/V ratios, especially in the tests with glass powders.

B.2. Active accelerated tests

The tests with the Pu/^{134}Cs/^{90}Sr doped glasses have been started. The tests lasting for 90 and 180 days are finished. The results of the radiochemical analyses are not yet available.

B.3. Inactive integrated tests

The tests at 40, 90 and 150°C with Ca-bentonite as backfill material have been started, as well as the tests at 40°C with cement as backfill material. For the bentonite series, the following tests were finished within 1992 : 90 days at 40°C; 28 and 90 days at 90°C; 20 days at 150°C.

At this stage of the programme, no conclusions can be drawn about the effect of the bentonite on glass corrosion.

B.4. Active integrated tests

The tests with the Pu/^{134}Cs/^{90}Sr doped glasses have been started. The 90 days tests are finished. The results of the radiochemical analyses are not yet available.

B.5. Modelling

Originally it was planned to use the geochemical PHREEQE code, coupled with the kinetical GLASSOL code. In the course of 1992 it became clear that the GLASSOL code needs some improvements to meet the needs, imposed by the test programme. In this respect, a basis for collaboration with experts, not directly involved in the programme, is being discussed.

Table I : Overview of the corrosion tests of the 1991-1995 programme

Test Conditions	Accelerated tests		Integrated tests	
	Inactive	Active	Inactive	Active
Temp (°C)	40 90 150	90	40 90 150	90
Media	DW SIC CCSICM+CP	SIC CCSICM+CP	BC+SIC+CP+BF1 BC+SIC+CP+BF2	BC+SIC+CP+BF1
SA/V (m^{-1})	500 2500 10000	400	500 2500	400
Duration (days)	20(1,2) 28(1,3) 90 180(1) 360 720(3)	90 180 360	20(1,2) 28(1,3) 90 180(1) 360 720(3)	90 180 360

DW : distilled water
SIC : synthetic interstitial claywater
CCSICM: concentrated clay - synthetic interstitial claywater mixture
BC : Boom clay
CP : corrosion product (Fe_2O_3)
BF1 : backfill bentonite
BF2 : backfill cement
(1) : not at 40°C
(2) : not at 90°C
(3) : not at 150°C

Title : **Basic Leaching Tests for Pure β Long-lived Emitters in Radioactive Wastes**

Contractor	:	CEA Cadarache
Contract No	:	F12W/CT-90/0032
Duration of contract	:	01.05.1991 to 30.04.1994
Period covered	:	01/01/1992 to 31/12/92
Project leader	:	C.Riglet (CEA Cadarache)

A. OBJECTIVES AND SCOPE

The technical solution under study to store long-lived radioactive wastes consists in :
- embedding them in suitable confining matrixes (glass, cement, bitumen);
- and burying the coats in stable geological sites where the radioactivity will decrease naturally.

The valuation of the confining capability of the matrixes used - determined by implementing leaching tests - enables us to assess the reliability of the process. Safety studies indicate that the long-term risk mainly stems from long-lived radionuclides.

In this context, the research contract is related to a basic leaching study of pure β and α long-lived emitters in real and simulated wastes, in order to collect basic results about these radionuclides which are critical for the safety analysis of disposal storage and for which no reliable data are available at present.

B. WORK PROGRAMME

B.1. (CEA - CIEMAT)
- Working organisation
- Setting-up of a working programme
- Harmonization of the leaching procedures

B.2. (CEA)
- Definition and manufacturing of the samples
- Implementation of the leaching experiments
- Collection of the data and interpretation

B.3. (CIEMAT)

- Selection of the types of wastes, the cement formulae and of the elements to be taken into account
- Implementation of the leaching experiments with simulated wastes
- Optimisation of the analytical procedures
- Collection of the data and interpretation

B.4. (CIEMAT)

- Implementation of the leaching experiments with actual resins
- Collection of the data and interpretation

B.5. (CEA - CIEMAT)

- Interpretation of the data
- Comparative study of the various experiments
- Final evaluation

C. PROGRESS OF WORK AND RESULTS OBTAINED

STATE OF ADVANCEMENT

B1 : This task have been completed.

B2 : CEA programme

During the period under review, all the bituminous and thermo-setting resin coats (containing "STE3 LH" sludges or - sodium borate - evaporator concentrates) were manufactured. The scheduled leaching tests for the samples in demineralized and Evian waters, in leachants at a pH of 6 and 8, and in leachants containing EDTA, were carried out. Leaching results corresponding to the first renewal sequences were obtained. Six evaporator concentrate/cement coats have yet to be manufactured. As a result of some technical difficulties relating to the availability of the irradiator at Cadarache, the leaching tests under irradiation were cancelled. The collection of the data as well as the interpretation of the results are in progress.

B3 and B4 : CIEMAT programme

The experimental work is also proceeding favourably. The reference leaching tests in demineralized water at different temperatures (25, 40 and 50°C) and the tests performed in "El Cabril" underground water and in leachants containing complexing agents are progressing. Nevertheless, the leaching procedure finally adopted will require a greater experimental duration than initially estimated.

The necessary analytical procedures have been optimized. As far as the leaching tests with actual resins are concerned, samples of ion-exchange resins from two Spanish nuclear power plants have been collected and analysed for the further implementation of the experiments.

PROGRESS AND RESULTS

B.2.1. Manufacturing of the samples :

Bituminous coats : The synthetic "STE3 LH" sludges were manufactured according to the same process as that used at La Hague, with a pilot STE3 machine (scale 1/50). The doping elements UO_2, ThO_2, $NaTcO_4$, AgI, $CsNO_3$ were added to the sludges after the primary and secondary decantations and the system was then well mixed. The simulated evaporator concentrate wastes were prepared following a procedure that consisted in preparing a highly concentrated (160 $g.l^{-1}$) sodium tetraborate solution to which the various doping elements were added. The resulting suspension was stirred for homogeneisation. The bituminization of these wastes (wastes : 50% - bitumen : 50%) was carried out with a mixing-machine of GUEDU type at 130°C.

Thermo-setting resin coats : For these types of coats, the wastes must be dehydrated and turned into powder. After decantation and removal of the liquid phase therefore, the "STE3 LH" sludges were centrifuged and dried into a drying-oven at 65°C. The dry matter was finely ground. The doping elements were added to the powder and the system was shaken for homogeneisation. As regards the evaporator concentrates, the initial sodium tetraborate powder was doped with the selected elements and the system was well shaken for homogeneisation. The embedding of these wastes into thermo-setting resins (wastes :50% - RTD : 50% of which resin LX195D07T : 36% and hardener D6M5 : 14%) was performed using a mixing-machine of GUEDU type.

B.2.2. Implementation of the leaching tests :

Preliminary experiments were carried out before implementating the leaching tests at a fixed pH (pH of 6 and 8) : In order to buffer the leachants without introducing complexing agents unlikely to be found in natural conditions, a ($CO_2/HCO_3^-/CO_3^{2-}$) buffer was experimented. The aimed pH value was obtained by bubbling a CO_2/N_2 gaz mixture (10% CO_2 - 90% N_2) into a closed vessel containing demineralized water, to which a known concentration of sodium bicarbonate was added. The initial concentration of HCO_3^- in the leachant was calculated by using the equilibrium constant of the (CO_2/HCO_3^-) system and the final pH objective. We thus verified that the pH could be stabilized at a fixed value over a large period of time using this technique. After these satisfactory first results, the leaching experiments with the actual coats were carried out and the stability of the measured pH during the first sequences of the tests confirmed the validity of the methodology.

B.2.3. Collection of the data and interpretation :

The conditioning of - sodium borate - evaporator concentrates into bitumen is proving to be inadequate due to fast degradation of the top surface of the samples in contact with the leachant, whatever its nature (demineralized or Evian water, leachants at a pH of 6 and 8). This evolution is interpreted as being due to sodium tetraborate dihydrate - stable at the bituminization temperature - changing into sodium tetraborate decahydrate, stable at room temperature. This results in swelling and cracking of the coats and consequently in an acceleration of the leaching rates of the embedded wastes.

"STE3 LH" sludge / bitumen coats (figures 1a,1b,1c) : The releases of U and Tc do not significantly vary as a function of the composition of the leachant. The leaching velocities are about 3.10^{-7} cm/day for U and 4.10^{-6} cm/day for Tc. Cs and Th are hardly detectable in any type of leachants, which reveals an infinitely small leaching velocity for these elements. As for I, the leached fractions, which are quite moderate in demineralized and Evian water (leaching velocity about 10^{-5} cm/day) increase drastically in the leachants in a bicarbonate medium at a pH of 6 or 8. The difference of behavior of I is connected to the chemistry of this element in carbonate medium.

Evaporator concentrate / bitumen coats (figures 1a, 1b, 1c) : The leached fractions of U are quite similar in demineralized water, Evian water and in leachants at a pH of 6 (leaching velocity about 10^{-5} cm/day) whereas much higher releases in leachants at a pH of 8 were observed; This significant difference is connected to the increase of UO_2 solubility in a carbonate medium due to the formation of a $UO_2(CO_3)_3^{4-}$ complex. As regards Tc, the leached fractions in demineralized or Evian water are similar but exceed those obtained in leachants at a pH of 6 and 8 by a factor of 4. The presence of bicarbonate in the leachant seems to partially prevent the release of Tc. Significant quantities of Cs were detected in demineralized and Evian waters (leaching velocity about 10^{-6} cm/day) but no release of Cs in leachants at a pH of 6 and 8 was detected. As regards I, the results evince a great influence of the carbonate medium (leachant at a pH of 8) in comparison with demineralized and Evian waters or leachants at a pH of 6 (in which the leaching velocities are about 10^{-5} cm/day).

Although the initial quantity of Th added to the samples was quite high (5g of ThO_2 per sample), this element was not detected in any of the leaching tests implemented at present, which reveals a much lower solubility of ThO_2 in aqueous media in comparison with UO_2, the same amount of which was initially added to the specimens.

B.3.1. Selection of wastes and cement formulae :

Taking into account the results of the reference leaching tests, formula 2 was modified by changing sulphate resistant cement into BFS for the specimens earmarked for the leaching tests with complexing agents. The initial compositions of the specimens, used for both the reference leaching tests and the tests where complexing agents are present in the leachants, are shown in table 1.

B.3.2. Reference leaching tests :

A cumulative leaching period of 420 days has been already completed and most of the analytical results are now available. The leaching rates for formula 1 constituents are collected in table 2. A relationship between the leaching rates of the elements and the radius of the solvated ions in aqueous media (published in the litterature) can be deduced from the available results : the greater the radius of the solvated ion, the lower the leaching rate.

B.3.3. Leaching tests with complexing agents :

A cumulative leaching period of 110 days has been completed but only a few analytical results are available at present. Those leaching tests are performed at 40°C using either the "El Cabril" underground water or solutions of EDTA (2,5 mM/l) or solutions of trimethylamine (6 mM/l) as leachants. A sufficient quantity of "El Cabril" water has been collected for these experiments and a chemical analysis of the water has been carried out.

B.3.4. Analytical procedures :

One sample of DUOLITE and two samples of EPIFLOC 21 H resins from two nuclear plants have been collected and analysed. The results, in Bq/g of sample, are summarized in the following table :

	DUOLITE Sample	EPIFLOC Sample	
^{90}Sr	9.15E+3	4.9 E+1	(sample 1)
		1.03E+4	(sample 2)
^{63}Ni	4.69E+5	3.45E+3	(sample 1)
		5.70E+3	(sample 2)

As the ^{63}Ni radioactivity of the Epifloc samples is not high enough for detectable quantities of this isotope to be obtained in the leachants during the tests, additional ^{63}Ni will be introduced into the specimens at the manucfacturing stage.

B.3.5. Leaching tests with actual resins :

These experiments should start in March 1993.

Table 1
Initial compositions of the ion-exchange resin/cement specimens

CONSTITUENT	FORMULA 1	FORMULA 2	MODF. FORM 2
Resin	10.25 % EPIFLOC	9 % DUOLITE	9 % DUOLITE
Cement	50.00 % BFS	56.00 % Sulph Rest	56.00 % BFS
Water	38.45 %	31.00 %	31.00 %
Lime	1.30 %	4.00 %	4.00 %
Ni-63	700.5 μCi *	307.7 μCi	680.7 μCi
Sr-90	79.6 μCi **	15.6 μCi	39.1 μCi
Al	2.8 g	2.0 g	3.3 g
Fe	1.2 g	3.0 g	1.4 g
Ca	24.4 g	38.3 g	30.8 g
Mg	1.4 g	0.4 g	1.7 g
Na	0.7 g	2.3 g	0.8 g
K	0.5 g	0.6 g	0.6 g
SiO_2	17.7 g	17.5 g	21.1g

* 760.6 μCi in the specimens used for leaching tests with complexing agents
** 43.7 μCi in the specimens used for leaching tests with complexing agents

Table 2

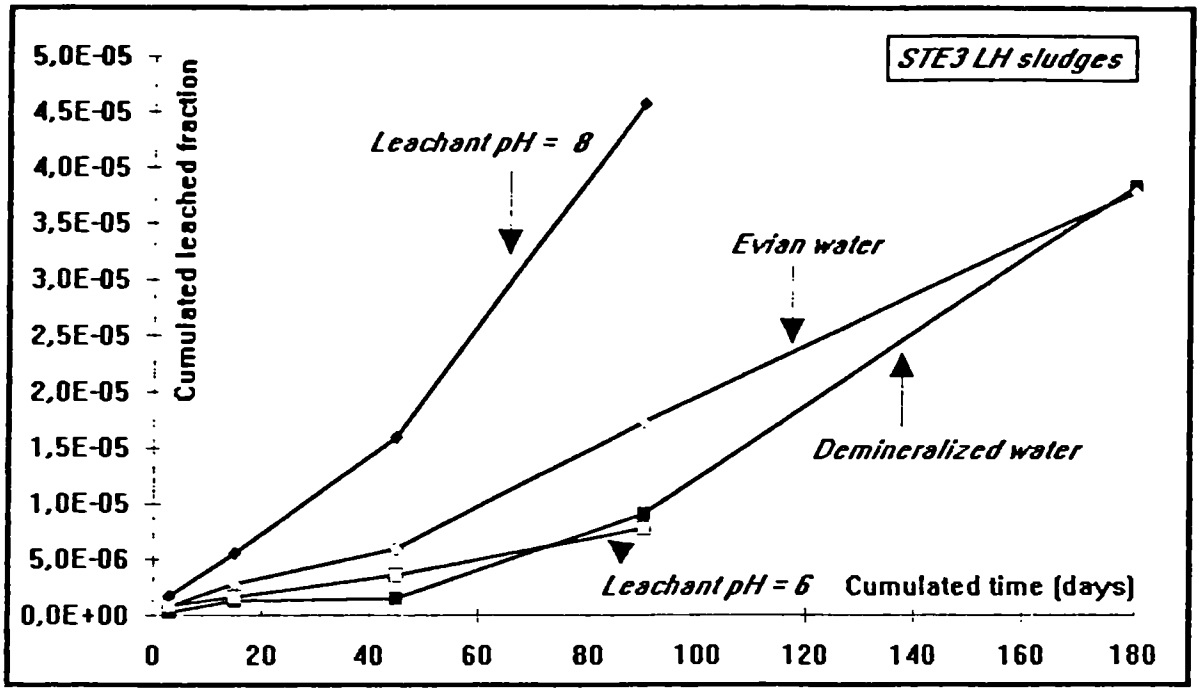
Results of the leaching tests for the immobilized ion-exchange resins

- Reference leaching tests at 25, 40 and 50°C
- Formula 1
- Leaching rate in cm/day

ELEMT	°C	DAYS							
		3	15	45	91	182	270	365	455
K	25	3.6E-2	7.6E-3	1.5E-3	6.5E-4	4.8E-4	3.9E-4		
	40	4.9E-2	9.0E-3	1.8E-3	8.2E-4	4.8E-4	3.4E-4		
	50	5.9E-2	9.8E-3	2.4E-3	1.0E-3	5.2E-4	3.7E-4		
Na	25	2.8E-2	4.4E-3	8.0E-4	3.4E-4	2.3E-4	1.9E-4		
	40	3.3E-2	4.8E-3	8.7E-4	3.9E-4	2.3E-4	1.5E-4		
	50	3.7E-2	5.0E-3	1.0E-3	5.1E-4	2.5E-4	1.7E-4		
Sr 90	25	8.7E-3	2.4E-4	9.8E-5	4.5E-5	3.6E-5	2.3E-5	2.0E-5	
	40	1.5E-2	6.2E-4	1.4E-4	9.8E-5	2.6E-5	2.5E-5	1.7E-5	
	50	1.7E-2	9.3E-4	1.7E-4	1.3E-4	1.6E-5	1.2E-5	1.5E-5	
Ca	25	3.1E-4	5.5E-6	7.7E-6	3.0E-6	2.5E-6	5.8E-6		
	40	1.9E-4	1.8E-5	1.8E-5	2.0E-6	1.2E-6	4.6E-6		
	50	3.9E-4	1.2E-5	1.5E-5	1.1E-6	1.1E-6	7.7E-6		
Mg	25	2.2E-4	-	-	1.5E-6	1.1E-6	8.3E-7		
	40	1.4E-4	-	-	2.2E-6	1.0E-6	4.9E-6		
	50	1.3E-4	-	-	2.8E-6	1.3E-6	1.0E-6		
Al	25	1.7E-4	8.4E-5	5.8E-6	7.9E-7	1.9E-7	2.6E-7		
	40	2.6E-4	6.9E-5	8.1E-6	1.9E-6	8.6E-7	5.4E-7		
	50	4.0E-4	6.6E-5	9.1E-6	1.9E-6	5.5E-7	5.4E-7		
Fe	25	6.4E-6	4.2E-6	9.1E-7	4.8E-7	1.7E-7	1.1E-6		
	40	7.8E-6	4.6E-6	9.1E-7	4.5E-7	1.8E-7	4.4E-7		
	50	1.2E-5	3.2E-6	1.4E-6	3.0E-7	1.2E-7	3.9E-7		
Ni 63	25	4.2E-7	1.7E-7	1.6E-7	2.4E-7	8.9E-8	2.6E-7	7.9E-8	
	40	1.3E-6	4.0E-7	2.2E-7	3.5E-7	4.8E-8	2.6E-7	4.6E-8	
	50	1.4E-6	8.5E-7	1.8E-7	6.7E-7	4.0E-8	1.0E-6	3.3E-8	

Figure 1
Comparison of the leaching behavior of the "STE3 LH" sludge and the - sodium borate - evaporator concentrate / bitumen coats in various leaching conditions

Figure 1a : Uranium



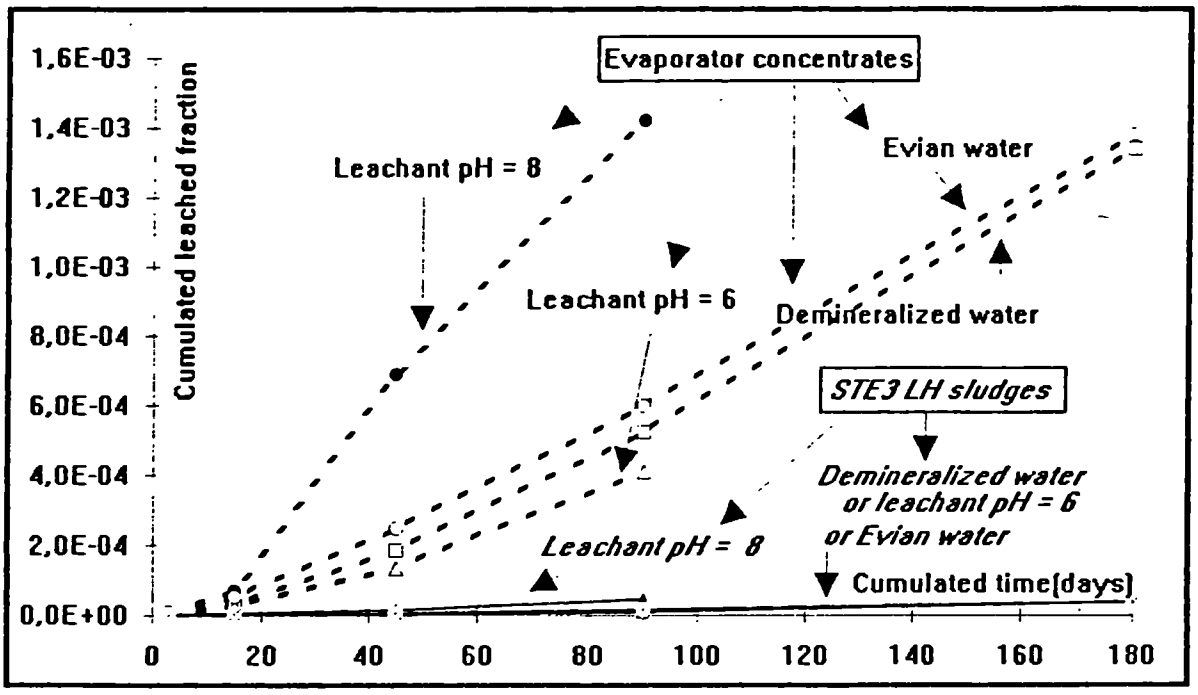
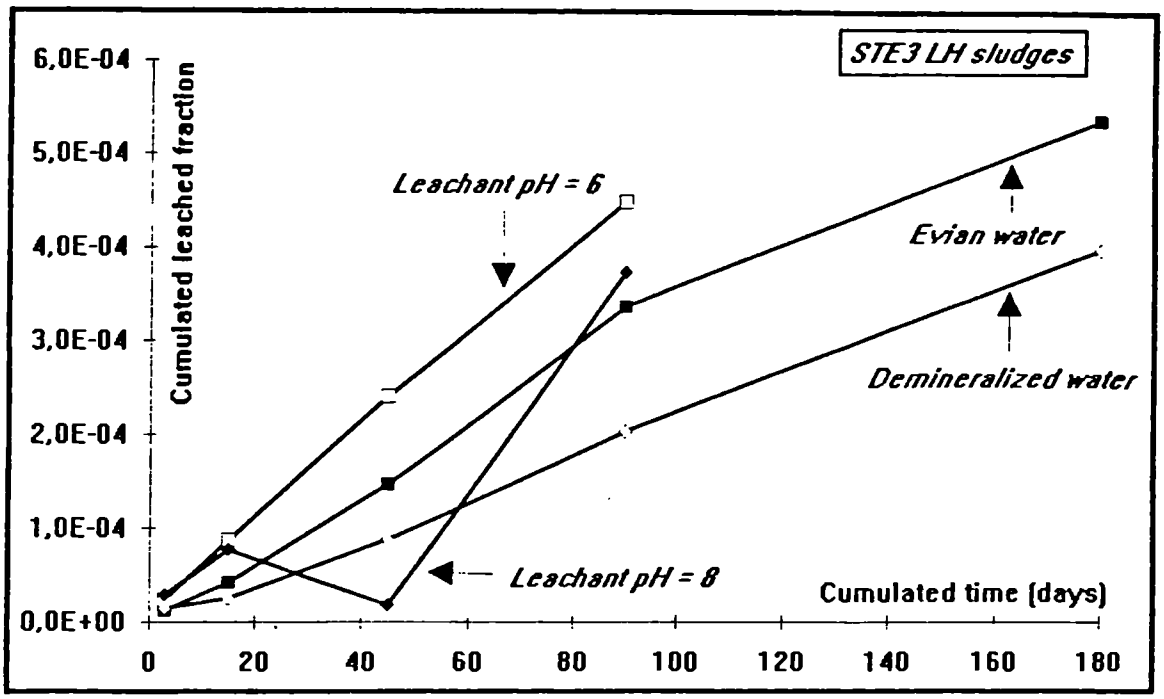


Figure 1b : Technetium



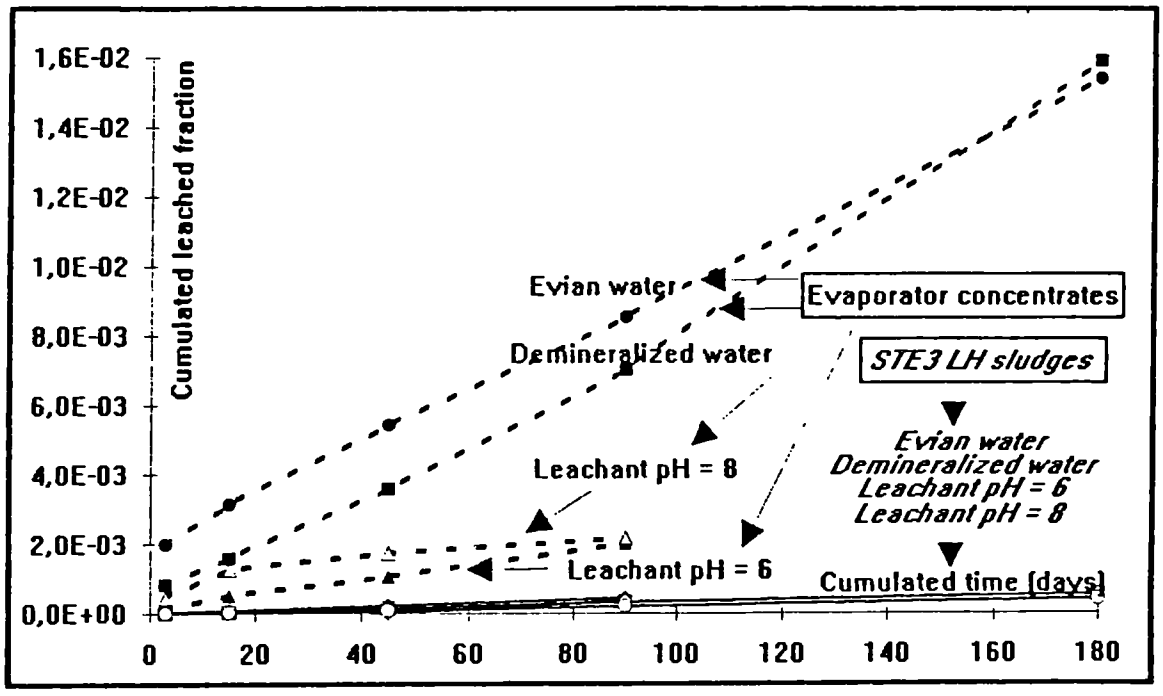
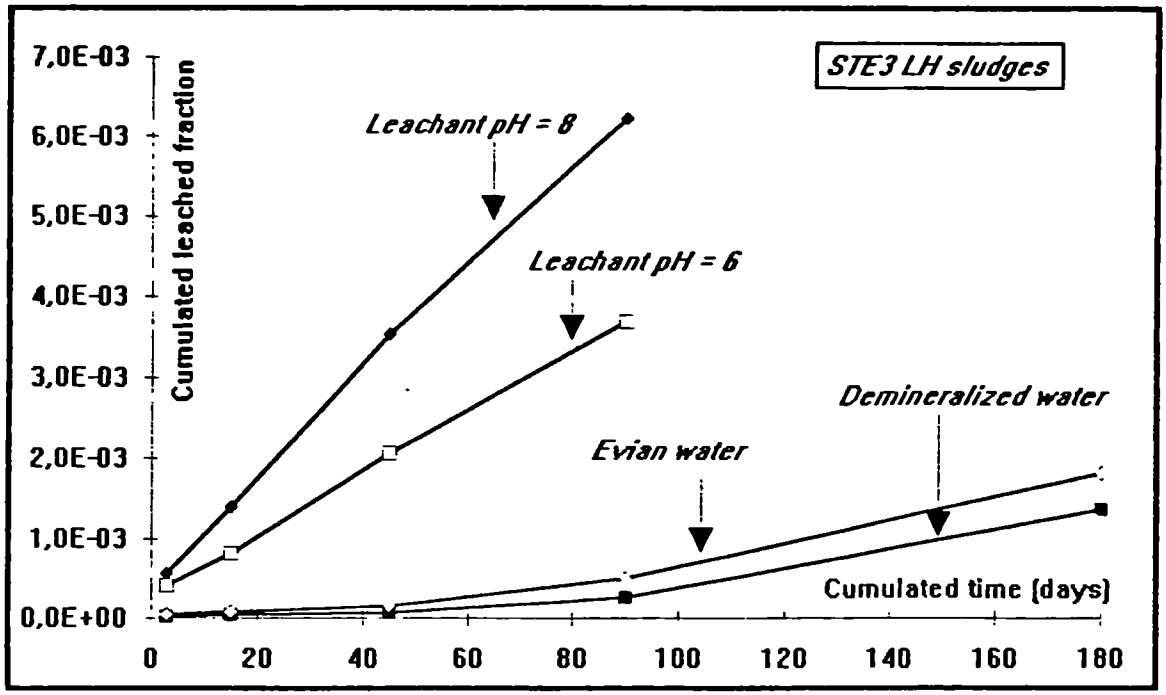
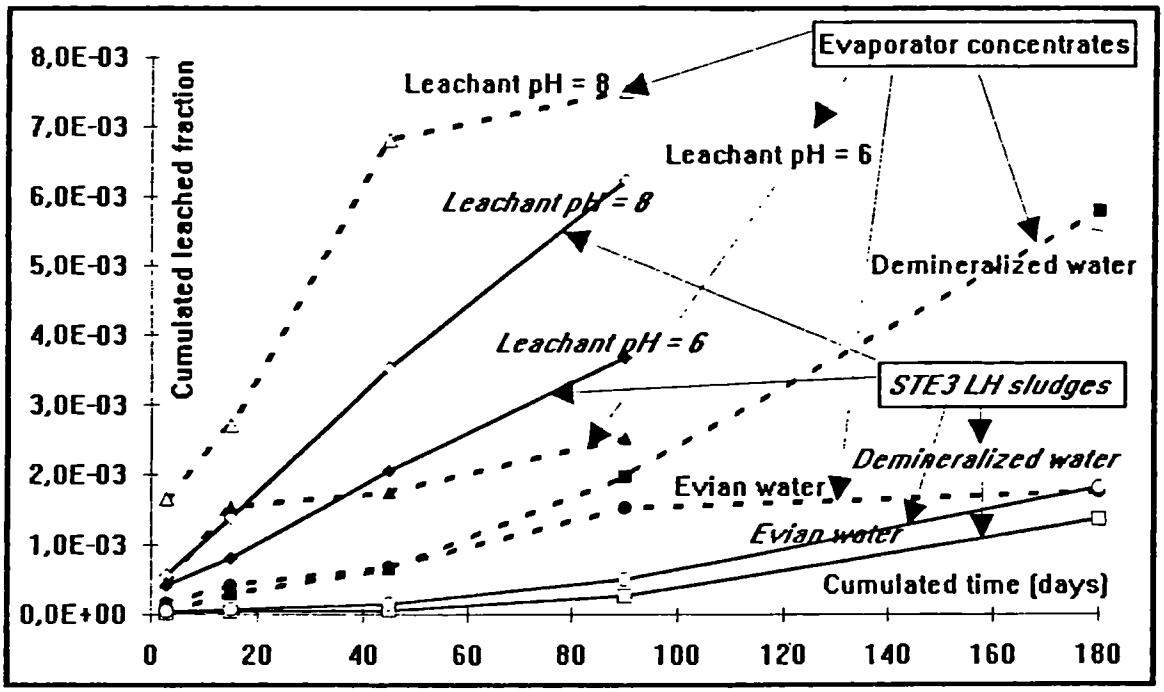


Figure 1c : Iodide





Title: **Chemistry of the Reaction of Fabricated and High Burnup Spent UO_2 Fuel with Saline Brines**

Coordinator: Kernforschungszentrum Karlsruhe GmbH, Institut für Nukleare Entsorgungstechnik, B. Grambow, A. Loida, K. Müller

Participant: Empresa Nacional de Residuos Radiactivos S.A., Departamento de Ingenieria (ENRESA), J. Gago

Subcontractor: Universidad Politecnica de Cataluña (UPC), I. Casas, J. de Pablo, J. Giménez, M.E. Torrero

Contract No. **F12W/0055**

Duration of contract: from 1.3.1991 to 28.2.1995

Period covered: 1.1.1992 - 31.12.1992

Project Leader: B.Grambow

A. Objectives and Scope

The research program aims at characterization and qualification of the chemical durability of unprocessed high burnup UO_2 fuel as a barrier against radionuclide release for disposal sites in salt formations. The reaction behavior of the fuel with saline brines is going to be studied as a function of time, temperature, redox potential, and surface area in order to give insight into the corrosion mechanisms and sources of radionuclide release. Additionally, the solubility of unirradiated UO_2 in salt brines is studied for comparison with the reaction behavior of the irradiated material in order to identify radiolysis and burnup effects and in particular to identify and quantify solubility effects in the degradation of the fuel matrix. Eventually, the ongoing work will provide a basis for modeling, bridging over the gap between experimental results and performance assessment for long-term storage of the fuel in a repository in salt formations in case of brine intrusion.

B. Work Program

I. General preparations, analytical techniques, and sample preparations

II. Characterization of the durability of spent UO_2-fuel in saturated NaCl brines

III. Solubility tests with unirradiated UO_2

IV. Modeling of the reaction behavior of spent fuel with salt brines

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

During the reference year high burnup spent fuel samples were prepared under Ar-atmosphere, hot cell equipment was improved and spent fuel corrosion experiments were started. The accumulated corrosion time is about 100 days. Radiochemical separation techniques were employed and leach solutions were analyzed.
Dissolution tests with unirradiated UO_2 in salt brines have been performed to study the effect of oxygen partial pressure on reaction rates and solution concentrations of Uranium. A preliminary model has been presented describing the effect of particle size on UO_2 dissolution rates.

Progress and results

I. General preparations, analytical techniques, and sample preparations

Samples (cm sized segments, mm sized fragments and μm sized powders) were prepared from a high burnup (50 MWd/kg U) UO_2-fuel rod of the PWR-Reactor Gösgen, and were transferred under N_2 atmosphere to the reaction vessels. Hot cell equipment was improved, in particular an apparatus was designed and constructed, allowing remote automatic solution sampling with a syringe. A centrifuge was put in place for ultrafiltration of solution samples. Radiochemical analyses and separation techniques were employed allowing analyses of the nuclides Pu238, Pu239/240, Pu241, Am241, Am243, Cm244, Cm242, Np237, Np239, Tc99, Cs 134, Cs137, Ru106, Ag110m, Eu154, Eu155, Ce144, Sr90, Sb125 and Uranium.

II. Characterization of the durability of spent UO_2-fuel in saturated NaCl brines

Corrosion tests were started except for tests at 150°C. The tests comprise "washing" steps, where the Cs gap inventory should be removed by exposing the fuel to the leachant (95% saturated NaCl or deionized water) under Ar atmosphere for two periods of one month and afterwards replacing the total solution volume by fresh leachant. Subsequently static corrosion of the fuel samples is initiated. Aliquots of the solution are sampled periodically under Ar atmosphere and the time dependence of the spent fuel dissolution behavior is deduced exclusively from analyses of filtered and ultrafiltered solution samples. At test termination the final solution volume will have been reduced to about half of its initial value, solid samples will be analyzed for surface alteration effects and in particular for identification of solid reaction products.

The washing steps were completed and resulting leach solutions were analyzed. As expected, the solutions are characterized by high Cs contents. About 2% of the Cs inventory of the fuel was washed out. Other nuclides analyzed were Pu238, Pu239/240, Pu241, Am241, Am243, Cm244, Cm242, Np237, Np239, Tc99, Ru106, Ag110m, Eu154, Eu155, Ce144, Sr90, Sb125 and Uranium. Fractional release was in the order of 10^{-3} to 10^{-5} with values in the high range for Sr90, Ag110m, Tc99 and low values for the actinides and rare earth elements. Typical results for the two washing steps are shown in Figure 1 for NaCl solutions. Roughly 50 days after begin of the static tests, first solution samples were taken but were not yet analyzed.

III. Solubility tests with unirradiated UO_2

Samples of unirradiated UO_2 were exposed to either NaCl rich or $MgCl_2$ rich brines under CO_2 free gases with oxygen partial pressures of 0.05, 0.21 and 1 atm. A comparison of data for NaCl and $MgCl_2$ rich solutions are shown in Figure 2. Rates and solution concentrations increased with increasing oxygen partial pressure and logarithm of the initial dissolution rates were found to be correlated by a slope of 0.7 with the logarithm of the partial pressure of oxygen. In air saturated solutions rates in $MgCl_2$ rich brines were about twice as high as the rates in NaCl dominated brines.
The effect of particle size on the dissolution rate was studied in $NaClO_4$ solutions. The results show a fast initial dissolution rate during the first 15 days and subsequently the rates decreased significantly. This behavior was rationalized and modelled by initial dissolution of an oxidized UO_2 surface film and the decrease in the rate was explained by the kinetics of oxidation of unoxidized UO_2 .

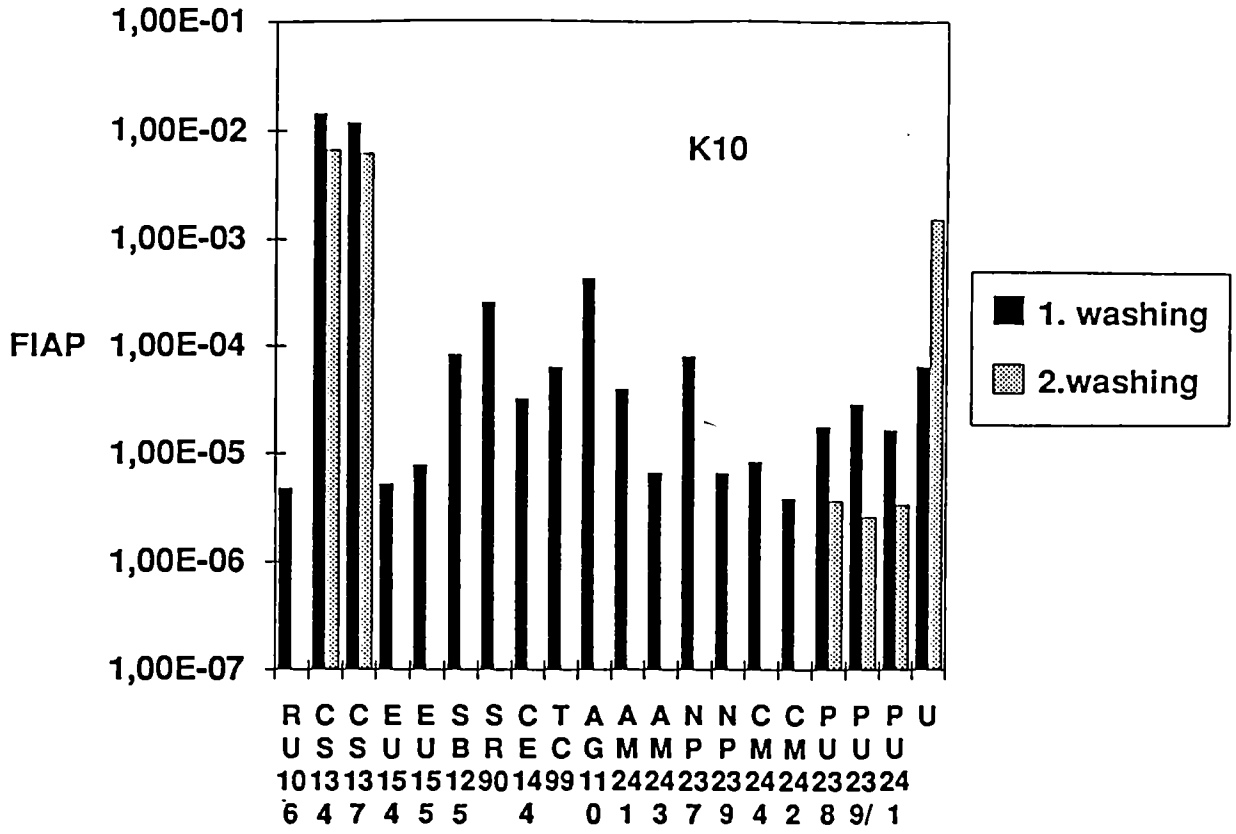


Figure 1: Fractions of spent fuel inventories in the aqueous phase (FIAP) after 1. washing (30 or 31 days) and 2. washing (42 days) of the sample K10 in NaCl solution (95% saturated) at room temperature

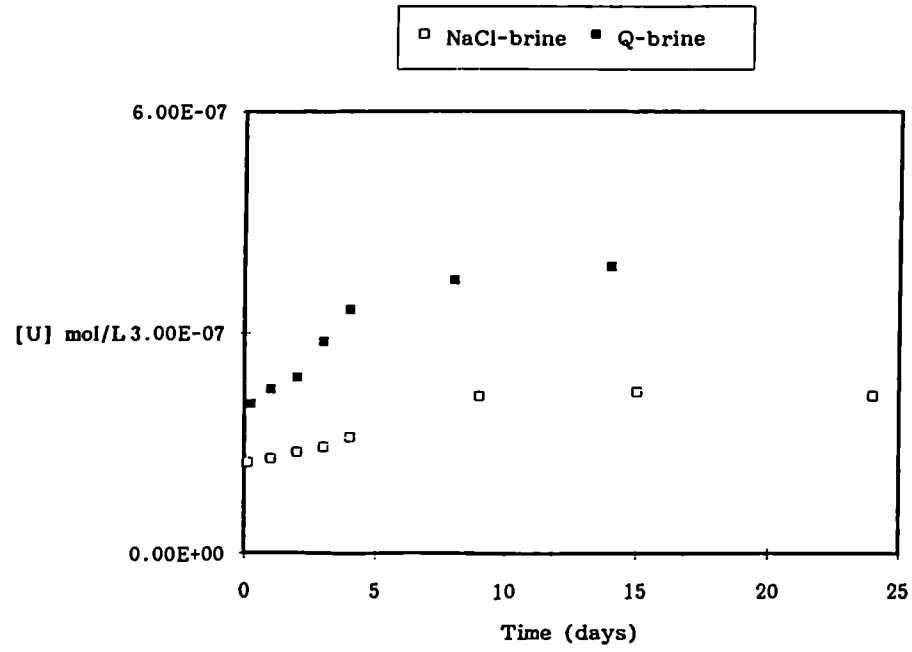


Figure 2: Solubility tests of UO_2 in NaCl and Mg-Cl rich brines at 25°C, 0.21 atm O_2 (1mm particle size), Uranium concentration as a function of time

Title :	Container properties ensuring safety : gas emission, biodegradation, corrosion.
Contractor :	DCC/Dir ÇEA Saclay
Co-contractor :	AEA Technology Harwell
Contract N°:	FI2W-CT90-0077
Contract duration :	October 1991 - October 1994
Period covered :	October 1991- December 1992
Project Leader :	P. LESSART DSD/SEP/SEATN CEA Cadarache

A. OBJECTIVES AND SCOPE

The knowledge of possible evolution of conditionned waste during intermediate storage, handling and deep repository is necessary to warrant the safety of workers and to define the conditions for storage and disposal.

These conditions can depend on production of gases and of chemical compounds able to promote degradation or biodeterioration phenomena.

The origin of gas production can be :

- the waste itself, producing radon and gases from alpha and gamma radiolysis,
- the chemical or microbiological corrosion of embedding matrix and structural material,
- the radiolysis of organic compounds included in the waste.

Living microorganisms can also produce complexing agents and organic or mineral acids able to promote corrosion and to modify the oxydo-reduction conditions and the pH of the repository.

A part of this project is concerned with assessing the effects of alkalitolerant microorganisms on a cementetious matrix.

B. WORK PROGRAMME

Four laboratories are collaborating for this contract, one of them being from AEA Technology Harwell and the others from DSD CEA Cadarache.

Programme 01 : biocorrosion of cement and bitumen used as embedding matrix. Acid and gas production. Physico-chemical modifications of the material.

Programme 02 : gas production by an genuine concrete conditionned waste with high content of radon producers.

Programme 03 : effects of organic complexing agents in concrete, and bitumen conditionned wastes on the gamma radiolysis gas production .

Programme 04 : the aim is to determine the form in which the microbial cells attach to the alkaline surface and the extend to which this change the physical and chemical properties of the cement. This will provide data to assist in setting design criteria for cementitious materials used to condition the pore water chemistry in a radwaste repository.

C. PROGRESS WORK AND OBTAINED RESULTS

Programme 01 : Biocorrosion of cement and bitumen

As a conclusion of a biblographical study, microorganisms exist in a deep repository before man intrusion, and, futhermore, it will be contaminated during excavation processes and waste setting up. All the elements necessary for microbial life exist in a nuclear waste repository. Their origin can be the waste itself, the embedding matrix, or the materials of the near field. Microorganisms have a great adaptation capacity and even if the physico-chemical characteristics of the environment (pH, radiation, temperature, redox potential) are extreme, they cannot bar microbial growth.

During repository evolving after setting-up and sealing, oxygen concentration decreases and even if at the beginning only aerobic microbes may develop, after a long term, anaerobic conditions become probable.

Programme 01 a : Biocorrosion of bitumen

Bitumen is a complex mixture of different heavy hydrocarbons that can be susceptible of biodeterioration because of its organic content. The objective is to study the gas production in anaerobic conditions.

From literature survey, it is known that many microorganisms have the ability to deteriorate petroleum compounds. Although, only a few studies have included the microbial degradation of bitumen.

Literature confirms that aerobic and anaerobic degradation of hydrocarbons involves different mechanisms.

Under aerobic conditions, saturated hydrocarbons are the most attacked by microorganisms.

Under strictly anaerobic conditions, aromatic may be the most biodeteriorated and perhaps, saturated hydrocarbons would not be attacked.

Hydrocarbon biodegradability by sulfate reducing bacteria has never been demonstrated. Denitrifying bacteria are abble to attack hydrocarbons, and especially aromatics. Other bacteria are known to deteriorate hydrocarbons and especially ferri-reducing bacteria. In all cases, mechanisms involved by anaerobic growth do not produce so many free energy as these of aerobic one. Anaerobic bacteria grows slowly compared to their aerobic counterpart and an experiment that requires 2 days with aerobic bacteria can take several weeks or months with anaerobic microorganisms.

First experiments are carried out using a denitrifying bacteria (*Pseudomonas* strain) and "bitumen powder". This is obtained by deposit of bitumen on silicagel (high ratio surface/volume). Hydrocarbons are partly oxidized into CO_2 while Nitrates are reduced into N_2O and N_2.

Other experiments will be carried out using mixed microbial culture. A sampling has been done in june in a soil contaminated by hydrocarbons. Microorganisms selection is investigating in the laboratory by succesive culture on "bitumen powder".

The technic for "bitumen powder" fabrication has been developped. Experimental device are now under operation. An analytical method (gas chromatography using krypton as an internal reference) was developed. First result show that it is possible to inhibit reduction of N_2O into N_2 without modifying the CO_2 production kinetic. This has to be verified. If confirmed, it will be possible to control the biodegradation rate by measuring N_2O production in the gas phasis.

The first results obtained have allowed the choice of the operating conditions for anaerobic bitumen degradation by denitrifying bacteria.

Programme 01a : Biocorrosion of cement

The aim of this work is to study the cement deterioration induced by mineral or organic acids produced by alkalotolerant microorganisms. In France, concretes planned to be used as embedding matrices are based on CPA 45 and CLC 55 cement.

Cement samples, 80mm diameter, 10mm thick, have been manufactured by DSD/SCS Laboratory of CEN Saclay, especialized in concrete studies, according to AFNOR NF P15402. Special devices were built for these experiments.

Cement samples are completly immersed in a mineral media innoculated by :

- a mixed culture of fungi (*Trichoderma viride* and *Aspergillus niger*) using glucose (an intermediate product of cellulose degradation) and producing several organic acids,
- a mixed culture of *Thiobacillus* strains, growing on thiosulfate (a soluble reduced sulfur source) and producing sulfuric acid.

Growth conditions were determined for these two microorganism groups. Both fungi and *Thiobacillus* were adapted step by step to alkaline conditions.

Experiments are carried out for about 270 days.

Chemical analysis of the solution are made every two weeks. From first results, it appears that pH stays quite stable, near 12, in solutions in which CPA is immersed and decreases slightly with CLC based samples. In this later solution, a growth of fungi is observed after 50 days of culture, while *Thiobacillus* growth can be noticed only after more than 100 days.

The pH evolution corresponds to microorganism growth : no evolution (or a slight decrease) appears in sterilized solutions.

A HPLC method was developed in order to determine qualitatively and quantitatively the 14 main organic acids produced by fungi.

Programme 02 : gas production by actual waste package

Among the different kinds of radioactive waste packages likely to be stored in deep repositories, there are the drums containing radifere waste (residues of uranium ores processing) which natural disintegration corresponds to the emission of a number of gases. These gases can be radionuclide, such as radon, or non radioactive gases, induced by the radiolysis of the water or others materials present in the drum. The aim of this study is to make a qualitative and quantitative evaluation of these gases. This needs the knowledge of the chemical and radiochemical composition of the waste, and specific analytical methods.

The inner physical structure of the waste was determined using non-destructive radiometric examination : digital radiography and computerized tomography. A special device was developed in the laboratory : it allows holding and moving the waste in front of a fixed irradiation-detection system and is coupled together with a data acquisition.

The selected radwaste drum has been submitted to accurate tests for its caracterisation : metrological controls, radiography and tomography for determining the waste density (1.4 to 1.0 $g.cm^{-3}$) and heterogeneity (sedimentation of the solid phase), gamma spectrometry for the radiochemical determination.

The ASPRAD system, a device necessary for the study of the radon release was manufactured and checked. The ASPRAD system principle is to put the radon emitter waste into a special container that is coupled with a sampling capacity in which primary vacuum can be realized. A set of valves and fast connectors allows the sampling capacity to be filled with a part of gas contained in the drum. Pressure is monitored in the sampling device. All volumes were determined.

The radwaste drum is in a gaseous products accumulation step since September 1992. One first sampling has been made, the corresponding results are going to be valided.

Programme 03 : effects of organic complexing agents in concrete and bitumen conditioned waste on the gamma radiolysis gas production

The objective of this study is to determine the amount of produced gases by external gamma radiolysis on bitumen containing TBP and cement containing EDTA.

Programme 03a : effects of TBP on gas production from bitumen

Gamma irradiation of bitumen 80/100 containing 0%, 2.5% and 4.2% of TBP is now completed. We chose to study TBP concentration much higher than those possible in actual waste with the objective to enhance its effects.

Conditions of sample fabrication, irradiation and gas analysis were determined. The total irradiation dose corresponds to the cumulated dose after 300 years in a Intermediate Level Waste repository.

Literature reports that :
TBP is an electron scavenger,
radiolysis yield of hydrogen producion from pure TBP is about 4.9 l/kg for 1 MGy total dose.

Both samples containing TBP present a higher gas production rate than pure bitumen. Hydrogen concentration in radiolysis gases is quite constant and near 95%. CO and CO_2 production rate are constant while CH_4 production increases slightly.

For sample containing 4.2% of TBP, gas production results from the added production by pure bitumen and pure TBP (balanced by the fraction by weight, using literature values).
For sample containing only 2.5% of TBP, the yield of hydrogen production is significantly below the predicted value. This result was confirmed. This may be explained by the electron scavenger property of TBP.

A new sample containing only 0.4% of TBP is being studied with the aim to further define this phenomenon.

The physical characteristics of bitumen are greatly modified by high TBP contents : they become softer (flowing effect of TBP) and therefore less apt to swell.

Programme 03b : Effects of EDTA in concrete conditioned waste on gamma radiolysis gas production.

Cement sample containing 0%, 2.5% and 5% EDTA as the acid or as disodium salt were manufactured. After curing 28 days,

they were inserted into gastight stainless steel vessels and underwent gamma external irradiation.

The more concentrated in EDTA the sample is, the greater the hydrogen production or the oxygen consumption. Only a small CO_2 production was noticed.

Hydrogen production by sample containing 5% acid form of EDTA were two times as much as this by sample with the same amount of EDTA disodium salt, or four times as much as cement without any additive.

All results must be confirmed.

Programme 04 : Biodeterioration of concrete

This project is concerned with the growth of microorganisms on and within cementitious matrices typical of those to be used in the disposal of Low and Intermediate Level Waste (ILW/LLW).

The microbial strain was isolated from soil which had been exposed to an alkaline hydrolysate for several years.

Colonisation of cement and plastic surfaces by alkalitolerant organisms in a fed batch reactor were obtained.

Scanning Electron Microscopy is being used to examine the nature of the film of organisms which colonised surfaces. Technics for drying and visualising the organic material were refined so as to minimise the appearance of artifacts.

It is apparent that the long filamentous organisms initially colonise the surface and that the shorter rod type cells then become established in the primary layer. Non-biological material such as the crystals of sodium sulphide also become enmeshed in this framework to give a fully developed biofilm.

Attachment to the smooth surface of plastic appears as robust as to the interconnected porosity of the cementitious matrix.

In a repository situation, the biofilm will be very thin and so methods of detecting very small amounts of cellular material are being evaluated.

A number of physico-chemical methods are being developed to study the changes which occur as the biofilm and associated inorganic precipitates builds up on the surface of concrete.

The hydraulic permeability is expected to changed markedly with the formation of a surface biofilm, but it is not yet clear since the measurement itself will pertub the system by altering the biofilm. Other electrical methods are being developed in order to investigate the biofilm development. These are conductivity (measurement of the cross section area through which conduction can take place), potential measurement between two regions with a chemically

different environment, and electro-osmosis measurement (applying an electric field induces a liquid flow through a fixed bed or a tube). An alternative approach to electro-osmotic flow is to measure the electrical potential induced by applying a hydraulic pressure, nevertheless the first results show that this effect is probably too small to use for monitoring changes on concrete and has the potential disavantage of mechanically pertubing the biofilm.

Cell growth was only noted on the surface of the concrete and not within the pores. This was thought to be the result of either exclusion of cells or nutrient or the fact that the inner pores were a relatively extreme environment compared with the bulk phase (ie the nutrient content was very low and the pH very high). Measurement of effective diffusivity through concrete of nitrates and sorbitol (molecular size similar to ISA) were carried out. Both these solutes were chosen to be stable for long period in the alkaline conditions and to sorb strongly on the matrix.

For a disk of concrete, 10 mm thick, nitrate breakthrough occured after 60 hours and sorbitol breakthrough only began after 60 days.

From effective diffusion coefficient measurement, it would appear that there are a number of well connected pores through which most of the transport occurs, and a substantial number of interconnected but tortuous and narrow pores which contributed little to the through diffusion in this experiment.

The diffusion experiments confirm thar the concrete is porous to solutes typical of the most important nutrients likely to be found in the repository. Thus, there is no reason why organisms in localised niches should not be capable of growing on solutes generated or originating in remoter parts of the repository. In addition, this growth may be possible both at the edges of the blocks and also within the bulk concrete, provided that the nutrients are not scavenged by any intervening biofilm.

Title : **Gas Generation in Supercompacted Waste Products**
Contractor : Forschungszentrum Jülich (KFA)
Contract No: FI2W-CT-91-0094
Duration of contract : 1.10.91 to 31.01.95
Period covered : October 1991 - December 1992
Project leader : R. Odoj

A. OBJECTIVES AND SCOPE

The product control group (PKS) located at the Research Centre Jülich (KFA) has been appointed by the Bundesamt für Strahlenschutz (BfS) to perform quality control of radwaste products prior to disposal in an underground repository. This can be achieved either by qualification of the conditioning processes or by examination of the waste packages. One criterion for acceptance is that adequate low gas release can be guaranteed. In this research program therefore methods to exclude unacceptable gas release by H_2-concentration built up will be investigated as well as possibilities to avoid gas generation/release by vacuum drying of the pellets or adding of materials for absorption/reaction of/with hydrogen.

B. WORK PROGRAMME

B.2.1 Time dependent measurements of gas formation in supercompacted pellets
B.2.1 Gas analyses at inactive pellets with defined composition
B.2.1 Gas analyses at real rad-waste pellets
B.2.1 Gas analyses at a container
B.2.2 Heating of pellets under different conditions (P,T,t)
B.2.3 Gas generation after thermal treatment
B.2.4 Testing filters for hydrogen absorption (physical reaction)
B.2.5 Evaluation and tests of materials reacting with hydrogen (chemical reaction)
B.2.6 Proposal of technical procedures to avoid hydrogen release

C. Progress of work and results

2.1 Measurements of gas formation in supercompacted pellets

Under routine control conditions gas analysis at supercompacted pellets packed in drums/containers as control for acceptable low gas release can practically only be realized by a unique analysis at the drums/container at room temperature (rt). In order to be able to predict the gas release at repository conditions on the basis of this analysis, statistical values concerning the

- long term H_2-formation behaviour and
- increase of gas formation at repository temperature (> 50°C) must be known as well as the
- influence of drum/containers leakage on the relationship between gas release and measured H_2-concentration.

2.1.1 Gas analyses at inactive pellets with known waste composition

As part of the previous program these pellets were supercompacted in March 1989. The average and final gas release rates of the first 15 months after supercompaction were analysed. In the current program the average gas release rate of the last two years and partly the actual rate have been measured.

At 13 of the 23 packages with not dried pellets, the gas release rates measured in 1992 are comparable to the values measured in 1990, at 7 of the packages a decreasing and at 3 an increasing gas release rate has been found.

Fifteen of these drums, filled with one or more pellets were supplied with a heating jacket and time dependent hydrogen release rates at 70°C have been measured. The results show that the release rates proved to be not constant even 2400 h after increase of temperature.
The factors of the release rate at 70°C compared with the rate at rt differ at the tested drums in a range from 10 to > 100 (especially at drums with a low release rate at rt).

2.1.2 Gas analyses at real radioactive waste pellets

For this part of the program 28 drums with pellets supercompacted at KFA in Sept. 1991 have been selected at random.
According to the kind of the primary waste the pellets are divided into 4 groups:

- mixed waste "visibly wet"
- mixed waste
- ashes
- filters.

The average gas release rate since supercompaction and partly the actual rate have been analysed.
On account of the increase of the gas release at repository temperatures (53°C) in comparison to the values analysed at room temperature (rt) the average H_2-release rate of 11 out of 16 drums with mixed waste pellets and of 6 out of 8 drums with ash pellets was found to be higher than 1 ml/h. At 3 out of the 16 drums with supercompacted mixed waste a CO_2 release rate of about 0,5 ml/h at rt and at 5 out of 8 drums with supercompacted ashes a remarkable CH_4 release rate has been detected.

The H_2 and CH_4 release rates measured at 4 inactive drums with ash pellets already controlled in the previous program are comparable to the values measured in 1990.

As a first group, 5 drums containing pellets with mixed waste have been supplied with a heating jacket and prepared for gas release measurement at 70°C.

2.1.3 Influence of drum/container leakage on gas release measurement

Leaks with influence on the gas release measurement have to be expected at a certain percentage of the drums/containers to be controlled. Sealing or overpacking of these drums/containers in order to get better results of measurement would need a lot of time and money. Therefore it should be tried to the gas formation on the basis of a known influence of drum/container leakage on the gas concentration built up. At a

container (filled with drums) the H_2-lost depending on leak rate and the H_2 concentration built up depending on leak rate and H_2 generation (simulated by dosing from a gas bottle) will be measured. Container and H_2-dosing system have been supplied.

2.2/2.3 Vacuum drying of supercompacted pellets

The results of the previous program have shown that gas generation of supercompacted pellets can be avoided by vacuum drying. In the drying experiments of the current program the dewatering behaviour of the pellets under various pressure and temperature conditions is studied in order to get practicable and economic processing parameters which can be controlled in a qualified process. Effectiveness and persistence of the effect of drying will be investigated by controlling the gas generation of the dried products. The program also includes gas analyses at the pellets dried in the previous program and if possible at real rad-waste pellets dried in a commercial facility.

The gas formation of the pellets dried in 1990 (150°C, 30 mbar) has been measured and compared with the values analysed in 1990.
Remarkable gas formation at rt could not be detected. The results of the measurements at 70°C show, that the total gas generation proved to be less than 1000 ml standardized to 80 cm pellet height and the release rate decreased to zero after at most 70 hours.

2.4 Testing filters for hydrogen absorption (physical reaction)

Hydrogen originating from supercompacted waste pellets can be removed by using specifically acting filter cartridges. Two promising principles of operation will be considered in the following:

1. Oxidation of the liberated hydrogen with atmospheric oxygen under formation of water, according to:

   $$1/2\,H_2 + O_2 \longrightarrow H_2O \text{ (absorbed)}$$

   Using a catalyst in adequate form, the reaction rate at room temperature may be high enough to burn all the arising hydrogen. The water produced will be removed by molecular sieves or comparable water absorbing agents.

2. Decomposition of the molecular hydrogen (H_2) to atomic hydrogen (H°)

   $$H_2 \longrightarrow 2H^\circ$$

This reaction may also be induced by a catalyst. Main problem will be the removal of atomic hydrogen by materials forming stable solutions or hydrides with it.

For both cases palladium may be used as catalyst of choice, because it is well known for its ability to decompose molecular hydrogen even at room temperature.
The use of Pd being rather costly it should be supported on granules of a less expensive hydrogen absorbing metal e.g. vanadium. Advantages and disadvantages of the methods proposed were evaluated on the basis of a literature search, briefly summarized in the following sections.

2.4.1 Hydrogen removal by catalytical oxidation

Recombination of H_2 and oxygen under formation of water at ambient temperatures using a precious metal catalyst, preferably Pd has been investigated. The arising water can be absorbed by molecular sieves. A possible technical arrangement is shown in Fig. 1. Following a proposal of KfK Karlsruhe, pressure buildup in waste containers due to hydrogen formation could be governed by using special filter units in the lid. The filters may be filled with water absorbing materials (e.g. molecular sieves) covered with a finely divided precious metal catalyst for cold burning of hydrogen.
To prevent sorption of atmospheric water these filters also should be closed with bursting discs. In case of overpressure the bursting discs will be broken and the hydrogen be reacted to water.

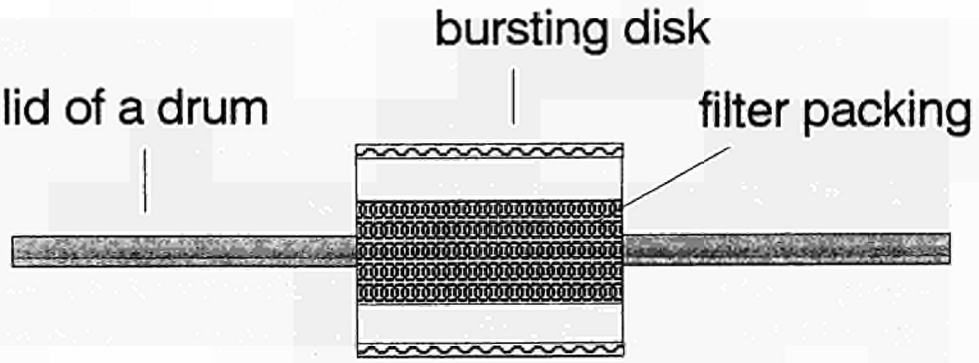


Fig. 1: Schematic drawing of a filter unit for hydrogen removal from waste drums

2.4.2 Hydrogen removal by direct absorption

Dissolution of hydrogen in appropriate metals is well documented in the literature and technical applications have been proposed. At KFA Jülich highly efficient hydrogen absorbers have been developed for the removal of H_2 from nuclear power stations. They mainly consist of Al-foils covered with thin films of the sorption material, vanadium or uranium. The sorption layer itself is tightly covered with palladium of Pd/platinum alloys.
Hydrogen molecules coming into contact with the palladium surface will undergo dissociation and then migrate into the Pd. Following the [H°]-concentration gradient they subsequently will be absorbed by the underlying getter material. The aluminium sheet is to provide the necessary mechanical stability and moreover to dissipate the heat of reaction. Instead of foils, vanadium granules covered with Pd could also be used as sorption material.

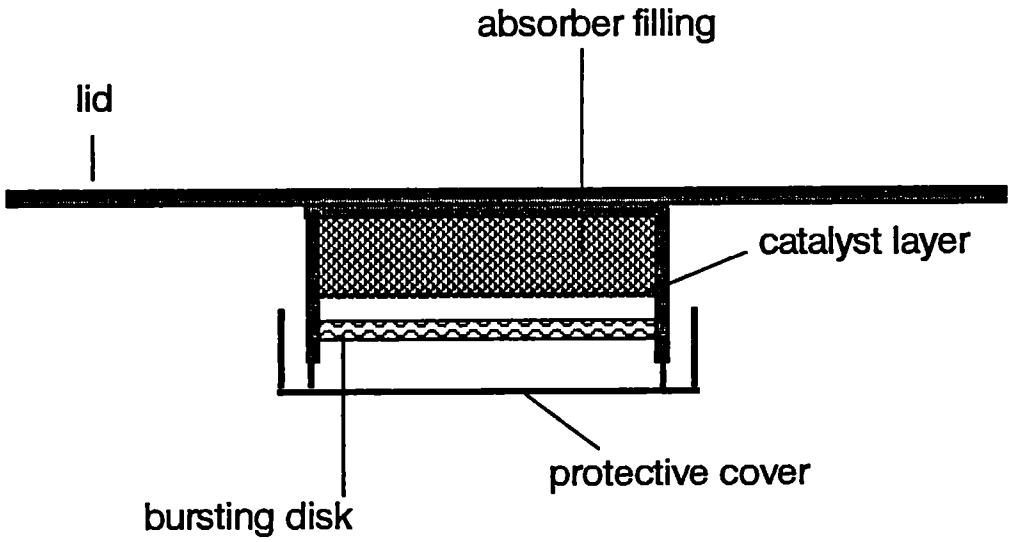


Fig. 2: Schematic drawing of a hydrogen absorption unit to be used in waste drums. The cartridge is filled with a rare gas and tightly closed with a bursting disc.

The proposed hydrogen removal system (fig. 2) essentially consists of a massive can, filled with vanadium granules covered with palladium. The granules are fixed by aid of a metallic net with fine meshes. The can is closed leak tight with a burst disk of a predertermined rupture limit. A punched metallic disc is foreseen to protect the burst disk from being mechanically damaged. This unit could be fixed on the lid inside the drum. In case of overpressure arising in the drum the burst disk will be broken and the H_2 be absorbed.
With respect to solubility data H_2-removal by using hydride formation is a very powerful tool. Under realistic conditions, however, competing and/or inhibiting reactions must be considered.
The rate constant of the dissolution process being rather low at room temperature, optimization of the getter granules diameter will also be a necessary step to get a maximum active surface.
Summarizing the results of the literature direct hydrogen removal from waste drums is not the safest way to overcome the problem. Catalytical oxidation of hydrogen with subsequent absorption of the arising water by molecular sieves seems to be a useful method. Experimental verification of the latter finding is in progress.

2.5 Evaluation and test of materials reacting with hydrogen

General objective of this part of the programme is to demonstrate that the hydrogen carbide, which is formed inside the waste canisters by various chemical processes can be consumed when some suitable oxidative reagent is added to the waste materials.

According to the results of a literature research, two candidate reactions materials for in-drum burning of hydrogen were identified:

1. Battery-grade MnO_2, which is catalytically activated with Ag_2O.

2. $KMnO_4$ dispersed on the surface of a highly porous inert carrier material.

The better material is no longer considered due to possible reactions of $KMnO_4$ with organic waste constituents and metal container materials.

The method of preparation of silver-catalysed MnO_2 was optimized with respect to reaction kinetics and reaction capacity. Best results were obtained when Ag^+ are bound to the surface of MnO_2 particles using the inorganic ion exchange features of MnO_2.

After equilibration the starting material is treated with NaOH in order to obtain small dusters of Ag_2O distributed over the surface ofe the MnO_2 particles. Finally the material is dried by vacuum or at elevated temperatures.

The above mentioned materials were tested for their reactivity with hydrogen. The reaction rate was calculated from the rate of the hydrogen pressure drop in the reaction vessel and the capacity of the material was determined from the H_2 uptake after refilling the apparatus several times with hydrogen.

Fig. 3 shows the reaction rate constant K as a function of the "age" of the material the age of the material is normalized to 100 % for a stochiometric reation according the equation:

$$H_2 + 2\,MnO_2 \longrightarrow Mn_2O_3 + H_2O$$

The capacity of the material is better than 1/2 Mol of H_2 per Mol of MnO_2.

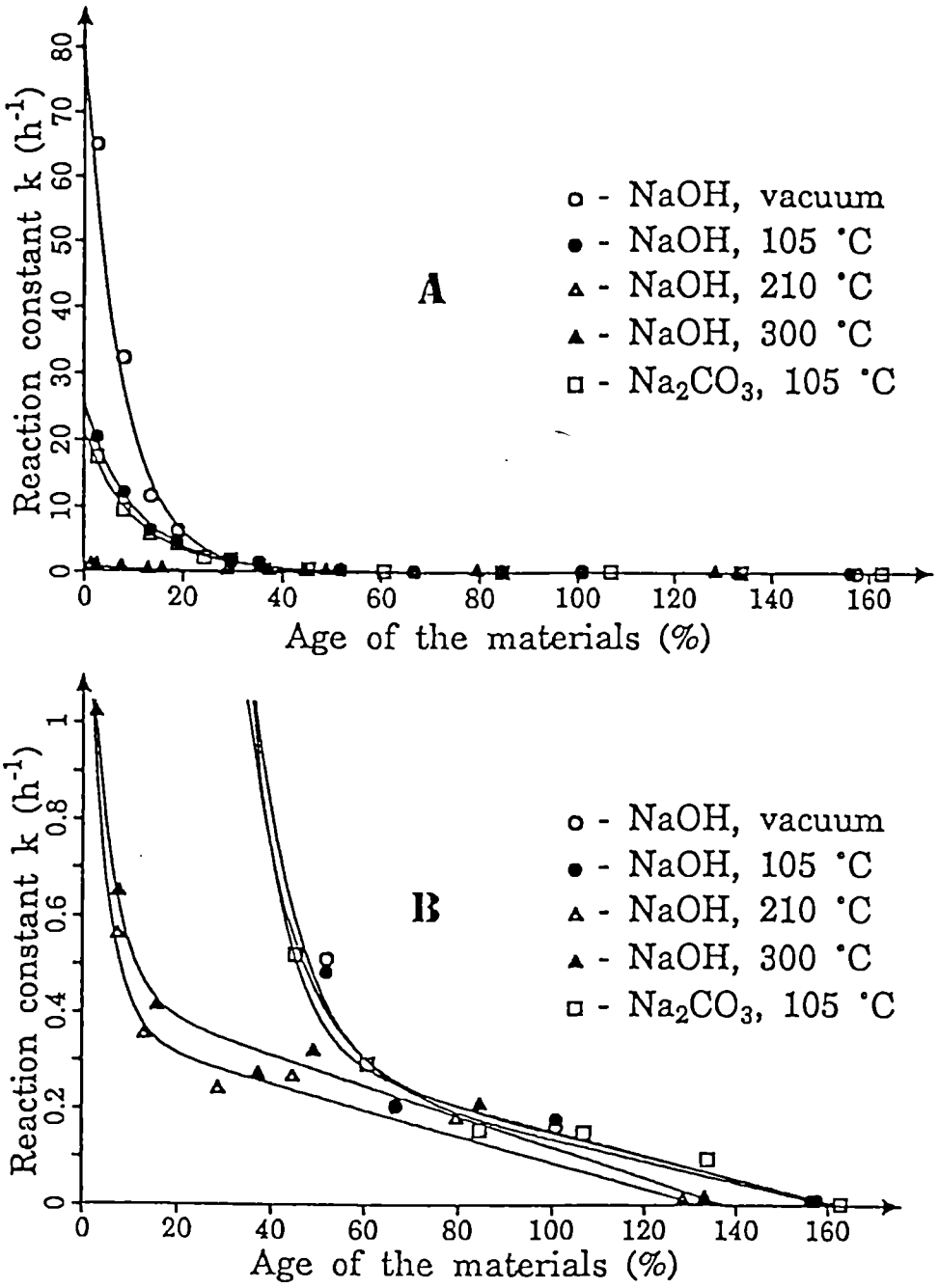


Fig. 3: Reaction rate constant as a function of the material's age. The materials were prepared by ion exchange, chemically treated and dried. Fig. B is the enlarged lower part of fig. A

Title: **Impact of Additives and Waste Stream Constituents on the Immobilisation Potential of Cementitious Materials**

Contractors:	University of Aberdeen / Prof. G. Marx, Free University of Berlin / Dr. M . Angus, AEA Windscale
Contract No.:	F12W/CT90/0099
Duration of contract:	October 1991 - December 1994
Period covered:	January 1992 - December 1992
Project leader:	F.P. Glasser, Univ. of Aberdeen, Scotland.

A. OBJECTIVES AND SCOPE

The objective of this tri-coordinated research programme is to determine the interactions between waste and cementitious materials, in real waste forms, and also to explain the sorption phenomena of transuranics and relate laboratory data to the performance of realistic cemented waste forms within a repository.

The studies will be used to strengthen the links between empirical studies eg. leaching, and more fundamental aspects. They will also be used to determine the impact of the waste itself, both active and non-active, on the properties and performance of the encapsulating cement.

Various techniques will be used in the measurement of aqueous phase and solid phase compositions of cement and blended cement, using inactive controls as well as formulations containing real wastes. Separation factors will be calculated for various isotopes in the above systems. The sorption processes for certain transuranics will be determined on pure cement phases and the role of certain organic complexing agents determined. The impact of selected inorganic ions on cement performance at longer ages will also be measured. The above experiments will be carried out at three isotherms: ambient (~ 22°), 55° and 80°C.

The experimental data gathered will be used to jointly develop models for cement performance.

B. WORK PROGRAMME

B.1 Preparation of blended cements incorporating radioisotopes and process chemicals. (AEA)

B.2 Trial runs at elevated temperatures on modified pore fluid expression device. (AEA)

B.3 Pore fluid extraction of the samples prepared under B.1 and measurement of radioisotope sorption for the various cement blends

and ultimately on real wastes. (AEA)

B.4 Synthesis and characterisation of phase pure cement hydrates for sorption studies. (A.U.)

B.5 Sorption of Eu(III) or Am(III), U(VI), Th(IV), Np(V) and Pu (on a reduced scale) on the above cement hydrates. (F.U.B)

B.6 Study the specific nuclide interactions (Ni, Cl, I and Cs) with cementitious materials. (A.U.)

B.7 Study the impact of chloride, carbonate and sulphate on cement performance. (A.U. & AEA)

B.8 Verification of mineralogy of phase pure cement hydrates used in B.5. (A.U.)

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of Advancement

In the period under review work has begun on all of the above tasks with exception of B.7. The synthesis of the phase pure cement hydrates (B.4) is now complete and they have been handed over to the Free University of Berlin. This task took longer than expected because sources of certain starting materials were no longer in existence and new methods had to be found appropriate to the materials available. Problems also arose in handling large volumes in an inert atmosphere and samples took longer to purify. Work has begun on B.6, concentrating on Ni.

Having first completed the trial runs for the pore fluid expression device (B.3), the measurement of radioisotope sorption on cement pastes is complete. Further studies, about to commence, will investigate the added complexity of the addition of process chemicals and radioactivity.

The Free University of Berlin have begun sorption experiments with europium, uranium and thorium and neptunium on the following cement hydrates; hydrotalcite, ettringite, tobermorite and C-S-H gel.

PROGRESS AND RESULTS

Tasks B.1 - B.3

An important part of this programme is to provide an understanding of the partitioning of radioactive elements between solid and aqueous phases in real cement systems. The work at AEA Windscale provides parallel studies to the sorption work on synthetic phases being carried out at FU Berlin (Task B.5), but uses real cements and ultimately real wastes. In this way it is intended to make a stepwise link between the idealised systems in the batch sorption studies and real cemented wastes.

The partitioning of a radioisotope between cement hydration products and the surrounding pore water is a key factor in determining the near field source term (ie. the concentration of a nuclide in the conditioned ground water at the point at which it leaves the repository). Hydrated cement contains a significant volume of unhydrated water in a continuous pore network and the concentration of isotopes in this water effectively

defines the near field source term.

It is possible to extract the pore fluid from cements under high pressure, and an instrument capable of doing this on radioactive samples has been set up at AEA Windscale. The first stage of this part of the programme, now complete, involved analysing this pore fluid for a series of cements and radioisotopes. Further stages, now commencing, will investigate the added complexity of process chemicals along with the radioactivity in a range of key ILW waste streams, and finally study the pore fluid of cemented real wastes.

Background

Pore fluids have been expressed from a range of cements, and the following variables have been considered;

(a) Radionuclides: chlorine and iodine have been investigated, as they are considered to be poorly sorbed on cement. Plutonium has been studied to ascertain particularly the effect of organic complexing agents on pore fluid concentrations. Thorium has been investigated as a daughter product in the uranium decay chain. Tin has been studied because it may speciate to yield soluble species.

(b) Cement formulations: three formulations have been investigated, two of which are ILW encapsulating matrices (3:1 Blast Furnace Slag/ Ordinary Portland Cement and 3:1 Pulverised Fly Ash/OPC) and one repository backfill (the "Nirex repository vault backfill").

(c) Organics: three organic additives have been studied because of concerns that they may form complexes with certain radionuclides, thereby increasing their solubilities. Sulphonated naphthalene formaldehyde superplasticiser, a solution of degraded cellulose and a synthetic organic compound present in degraded cellulose (iso-saccharinic acid) have been investigated.

(d) Temperature: the work has been carried out either at ambient or at 80°C. The elevated temperature is selected as the highest temperature expected to be reached in a deep repository.

(e) Ground water: pure water and a saline ground water simulant based on the Sellafield site in the U.K. have been used. The saline ground water contains chloride (0.44M) and sulphate as well as other minor components.

Experimental

Cement cylinders (45mm diameter x 90mm high) were individually mixed using mix water pre-dosed with a range of appropriate ingredients. These were cured for 28 days at either ambient or 80°C before the pore fluid was expressed at pressures up to 60 tonnes. When a cylinder was cured at 80°C it was also necessary to carry out the pore fluid expression at 80°C in order to avoid any changes in solution composition due to cooling effects. This was achieved using a temperature controller with wrap-round heating pads. After analysis, results were expressed either as solution concentrations or as separation factors (Rd).

Results and Discussion

A summary of the results is shown in Table 1, it shows the percent of activity sorbed on the solid phase of the various cements used. The results selected are the mean values obtained for the range of conditions considered to be most relevant to a deep underground repository. That is, in the presence of saline ground water and at a curing temperature of 80°C. The results show that in all cases, significant fractions were sorbed.

Although chloride is generally considered to be a "non-sorbing" species, it is clear that even under the most extreme conditions there is considerable sorption, ie. the total initial chloride concentration in the pore water is around 0.5M. The reason for the high sorption is partially the formation of specific chloride phases ("Friedel's salt" $Ca_4Al_2O_6Cl_2 \cdot 10H_2O$), but significant sorption on C-S-H and PFA is also believed to occur.

Iodide sorbs quite strongly on cement under all experimental conditions. The strongest sorption is on the backfill, which is a high lime content formulation. Although the sorption is decreased by competition with chloride and by increased temperature, this does not seriously affect the ability of cements to retain iodide. The main mechanism for the retention is by sorption on the C-S-H phase. The amount sorbed depends on the Ca/Si ratio of the cement. The backfill, which has the highest Ca/Si ratio is the strongest sorber. Some additional sorption capacity is also provided by ettringite, a significant hydration product of the backfill formulation.

The plutonium concentration in the pore fluid was extremely low, in all cases being close to the limit of detection, 7×10^{-11} Moles/L. The organic materials added to the mix water had no effect on the pore water concentration of plutonium. The amounts of organic material added to these blends was realistic in repository terms; yet it had no significant effect on plutonium solubilisation.

Most thorium solubilities were below limits of detection, but at 80°C there were some measurable solubilities. These indicate that virtually all the thorium is sorbed.

Tin was strongly sorbed on all the formulations tested and at both curing temperatures. There was stronger sorption on the backfill than on the two encapsulating matrices, but this additional sorption capacity is sensitive to temperature and salinity. Nevertheless, even under the most extreme experimental condition , virtually all of the tin is sorbed. It is possible that the insoluble tin (IV) oxide, cassiterite, is formed.

Other characterisation work using electron microscopy, x-ray diffractometry and thermal analysis was carried out at Aberdeen University. This provided a useful insight into certain mechanisms of isotope sorption.

Task B.4

In order for the Free University of Berlin to begin their part of the contract, the cement hydrates had to be synthesised. Initially approximately 200g samples of six cement hydrates were prepared. This allowed FU Berlin to carry out some preliminary investigations. Of these six, four were to be used for more extensive studies. They required ~ 2 Kgs of cement hydrates for the sorption studies. The synthesis of the hydrates is described as follows:

Ettringite, (AFt), $C_6AS_3H_{32}$:-

Five batches each of 500g was prepared by the following method. A slurry of $Ca(OH)_2$, w/s = 10, and a solution of 'AnalaR' $Al_2(SO_4)_3 \cdot 16H_2O$ were mixed together at 5°C. The proportions were such that the $Ca:SO_4$ ratio was 2·0. This was stirred for 24 hours, then left to age at 25°C for 14 days. The precipitate was then filtered and analysed by XRD. The batches were then mixed together. The aqueous phase was in close agreement with that of previously measured samples.

Hydrotalcite, (HT), $M_{4-6}AH_{10-13}$:-

Pseudoboehmite ($AlOOH \cdot xH_2O$, BA Chemicals Ltd.) was mixed with freshly calcined MgO in the ratio of 5:1 $MgO:Al_2O_3$. This was dispersed in double distilled degassed water (w/s = ~ 15). The five samples were then aged at 85°C for 1 month. XRD analysis showed the presence of hydrotalcite and a trace amount of $Mg(OH)_2$. A small amount of pseudoboehmite was added and the samples were aged for a further 14 days at 85°C. After this further reaction the product was pure by x-ray. The 5 samples were mixed together, then redispersed in water at 25°C. After 6 dispersions the aqueous phase was similar in composition to other measured samples.

Calcium Silicate Hydrate Gel (C-S-H):-

The C-S-H gel with a Ca/Si = 1·2 was chosen because this reflects the likely composition found in blended cements. It was prepared by mixing appropriate amounts of CaO (from freshly calcined $CaCO_3$) with fumed silica (Aerosil 300, 300m^2/g surface area, Degussa Ltd.) in double distilled, degassed water. The w/s ratio was ~ 20. It was prepared in three batches. The gels were aged for approximately 6 weeks in their mother liquor at 25°C. The aqueous composition is within the limits found previously for gels made from different sources. There has been no dispersion/filtration steps carried out on these gels because any redisperion leads to a depletion in Ca of the solid phase and hence a lowering of the C/S ratio.

Tobermorite, $C_5S_6H_5$:-

After initial problems the following method was used: fumed silica (Aerosil 300, 300m^2/g surface area, Degussa Ltd.) was mixed with CaO and a small amount of basic active alumina (Al:Si = 0.02) which catalyses the reaction. The solids were dispersed in water and then placed in 500ml autoclaves. Due to the size constraint of the autoclave, 50g batches were produced. The reactants were autoclaved at 140°C for 96 hours. Each batch underwent solid and aqueous phase

analysis before being grouped together. X-ray showed the product to be phase pure and quite crystalline. However, the aqueous analysis showed that the calcium concentrations were approximately an order of magnitude too high relative to the K_{sp} for tobermorite. This was probably due to a small amount unreacted $Ca(OH)_2$: The impurity was removed after 5 dispersions.

Task B.5

This part of the programme is designed to complement the work done at AEA Windscale. At AEA Windscale sorption of radioisotopes is being measured on real cements which contain a range of hydrated phases. Pore fluid measurements of radioisotope-doped cements gives a more accurate measurement of isotope sorption. However, the work on this task allows us to quantify which phases within the cement is responsible for the sorption.

The sorption of thorium, uranium, neptunium, americium or europium and also plutonium (on a reduced scale), on ettringite, C-S-H, tobermorite and hydrotalcite is being carried out at the Free University of Berlin. The experiments are being carried out at 25, 55 and 80°C in double distilled water, saturated NaCl solution and Q-brine. The Q-brine is composed mainly of $MgCl_2$ with smaller amounts of NaCl, KCl and $MgSO_4$. Europium is being used as a simulant for americium since it can be handled outside glove boxes. However, some experiments using americium will be undertaken to verify the chemical similarity.

Experimental Details

Blank solutions were prepared by adding one of the four cement hydrates to each of the three aqueous media (1g to 300ml), this gave 12 blank solutions. Stock solutions containing the isotope, were prepared in the following manner: 0.5g of cement hydrate was added to 150ml of each medium. To these solutions soluble salts of the isotope under investigation were added such that a saturated solution was obtained. For analytical reasons the thorium and europium solutions were labelled with ^{228}Th and ^{152}Eu respectively. The batch experiments were then carried out using the relevant filtered stock solution which was diluted with the appropriate blank solution. The following stock solution: blank solution were employed; 0:1, 1:√10, 1:10, 1::√1000 and 1:100. The experiments were carried out on 10mg of cement hydrate and 10ml of solution. After attaining equilibrium the concentrations of the various isotopes were determined.

The europium concentration was measured by gamma spectroscopy; liquid scintillation was used for Th. Uranium was measured by two techniques: time-resolved laser induced fluorescence spectroscopy (TRLIF) and inductively coupled mass spectrometry (ICP-MS).

To date, R_s values, Freundlich and Langmuir isotherms have been obtained for several isotopes at 25°C. Europium adsorption on all four cement hydrates in Q-brine and on ettringite and hydrotalcite in sodium chloride solution and double distilled water is now complete. Uranium has

also been studied for all four cement hydrates in Q-brine. Sorption of thorium on hydrotalcite has been investigated for all three media. Also, experiments on neptunium were performed with hydrotalcite in saturated sodium chloride. The data are listed in Tables 2 - 5.

Task B.6

The interaction of Ni with cementitious materials is being carried out using a combination of the methods described in B.3 and B.5:using pure phases as well as pore fluid expression of cements.

Two phases have been identified as being important 'sinks' for Ni: tobermorite and takovite. Tobermorite is capable of directly substituting up to 20% of its Ca for Ni. Takovite is a naturally occurring mineral $Ni_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, which belongs to the same class of compounds as hydrotalcite (which occurs in cements blended with BFS). This phase, like hydrotalcite, exhibits strong anion sorption. Work is underway to synthesise a phase pure sample which will be used to derive a solubility product and also to study its compatability with other cement hydrates.

The solubility of $Ni(NO_3)_2$ in a saturated $Ca(OH)_2$ (pH = 12.5) is 9 x 10^{-6} M/L. At temperatures above 55°C $Ni(OH)_2$ is formed. However, at 20°C a new, as yet unidentified phase, is produced which has Ca:Ni = ~ 4:1.

Pore fluid expression of an OPC cement mixed with 2500ppm Ni which was cured for 20 days at 20°C yields a solution which a Ni concentration of 0.25 ppm or 4.2 x 10^{-6} M/L. This is in good agreement with the solubility of Ni in $Ca(OH)_2$.

Task B.8

Some preliminary investigations, by x-ray diffraction, into the stability of the cement hydrates in the experimental conditions used in this programme has begun.The hydrates were kept at 25, 55 and 85°C in double distilled water, saturated NaCl and Q-brine solutions for 1 month.

All phases, with the possible exception of ettringite at 85°C, were stable in water over the temperature range studied.

All phases, except hydrotalcite which does not contain Ca,, in contact with Q-brine gave $CaSO_4 \cdot xH_2O$; at 25°C, x = 2 while at 85°C, x = 0.

Hydrotalcite appeared to be stable over the whole range however, there was a decrease in crystallinity with increasing temperature.

Ettringite and hydrogarnet formed Friedel's salt in the presence of NaCl.

C-S-H, tobermorite and gehlenite hydrate were all stable at 25 to 85°C in double distilled water and saturated NaCl. C-S-H in Q-brine showed no crystalline product until 85°C, when $CaSO_4$ was identified.

Table 1. A selection of pore expression results showing per cent of activity sorbed onto solid phase for cements cured at 80°C in saline water.

Isotope	3:1 BFS/OPC	3:1 PFA/OPC	Backfill
Cl-36	57	46	26
I-131	82	80	88
Pu-239	99.95	99.97	99.99
Th-228	99.99	99.99	99.99
Sn-113	99.99	99.90	99.99

Table 2. Europium in Q-brine

dilution	Hydrotalcite		ettringite		Tobermorite		C-S-H	
	C_g [mol/l]	C_s [mol/l]	C_g [mol/l]	C_s [mol/l]	C_g [mol/l]	C_s [mol/l]	C_g [mol/l]	C_s [mol/l]
1:1	6.29E-5 6.55E-5	4.17E-5 3.85E-5	1.08E-6 9.66E-7	2.28E-6 2.39E-6	7.27E-7 8.24E-7	1.03E-5 1.01E-5	7.57E-6	2.80E-5
1: $\sqrt{10}$	2.37E-5 2.22E-5	9.19E-5 1.07E-5	3.69E-7 2.65E-7	6.91E-7 7.94E-7	1.95E-7 2.59E-7	3.28E-6 3.22E-6	2.69E-6 1.95E-6	8.60E-6 9.33E-6
1:10	7.18E-7 7.56E-6	3.22E-6 2.84E-6	6.15E-8 7.43E-8	2.74E-7 2.61E-7	2.07E-8 3.60E-8	1.08E-6 1.06E-6	5.81E-7 7.84E-7	2.99E-6 2.79E-6
1: $\sqrt{1000}$	2.25E-6 2.57E-6	1.04E-6 7.69E-7	5.39E-8 2.20E-8	5.20E-8 8.40E-8	9.96E-7 1.16E-8	3.38E-7 3.36E-7	2.20E-7 3.49E-7	9.09E-7 7.80E-7
1:1000	7.94E-7 9.04E-7	2.46E-7 1.35E-5	1.25E-8 1.66E-8	2.10E-8 1.69E-8	2.80E-9 2.98E-9	1.07E-7 1.07E-7	6.74E-8 5.95E-8	2.90E-7 2.98E-7

C_g = concentration after adsorption
C_s = ratio of nuclide/cement hydrate (mol/g)

Table 3. Uranium in Q-brine

dilution	Hydrotalcite		ettringite		Tobermorite		C-S-H	
	C_g [mol/l]	C_s [mol/l]	C_g [mol/l]	C_s [mol/l]	C_g [mol/l]	C_s [mol/l]	C_g [mol/l]	C_s [mol/l]
1:1	1.2E-6	5.8E-5	5.1E-7	5.5E-6	6.7E-6	2.7E-5	5.4E-6	2.76E-5
1: $\sqrt{10}$	8.3E-7	1.8E-5	1.0E-7	1.8E-6	1.2E-6	9.7E-6	4.1E-7	1.04E-5
1:10	2.2E-7	5.4E-6	7.6E-8	5.1E-7	4.5E-7	2.7E-6	1.1E-8	3.11E-7
1: $\sqrt{1000}$	7.7E-8	2.1E-6	1.8E-8	1.8E-7	9.8E-8	8.7E-7	6.3E-9	9.82E-8
1:1000	9.8E-9	5.4E-7	3.6E-9	4.9E-8	3.0E-8	3.1E-7	1.2E-9	2.98E-8

C_g = concentration after adsorption
C_s = ratio of nuclide/cement hydrate (mol/g)

Table 4. Thorium on Hydrotalcite

dilution	Hydrotalcite in Q-brine		Hydrotalcite in NaCl		Hydrotalcite in water	
	C_g [mol/l]	C_s [mol/g]	C_g [mol/l]	C_s [mol/g]	C_g [mol/l]	C_s [mol/l]
1:1			5.22E-9 5.84E-9	3.86E-9 3.55E-9	1.02E-9 6.8E-10	7.03E-9 7.55E-9
1: $\sqrt{10}$	2.00E-7 1.95E-7	5.36E-7 5.19E-7	1.64E-9 1.65E-9	1.22E-9 2.00E-9	1.2E-10 1.3E-10	2.55E-8 2.38E-8
1:10	5.21E-8 5.45E-8	1.64E-7 1.66E-7	4.4E-10 4.4E-10	3.5E-10 4.0E-10	5.8E-11 5.7E-11	6.88E-9 7.46E-9
1: $\sqrt{1000}$	1.63E-8 1.57E-8	5.89E-8 5.94E-8	1.9E-10 1.7E-10	1.2E-10 1.2E-10	4.9E-11 4.8E-11	2.47E-9 2.04E-9
1:1000	5.65E-9 5.98E-9	1.83E-8 1.71E-8	7.5E-11 7.4E-11	3.3E-11 3.7E-11		

C_g = concentration after adsorption
C_s = ratio of nuclide/cement hydrate (mol/g)

Table 5. Neptunium on Hydrotalcite in NaCl

dilution	Hydrotalcite in Q-brine	
	C_g [mol/l]	C_s [mol/l]
1:1	1.32E-6	6.54E-6
1: $\sqrt{10}$	2.85E-7	2.17E-6
1:10	6.56E-8	6.11E-7
1: $\sqrt{1000}$	2.44E-8	1.92E-7
1:1000	2.47E-9	6.52E-8

C_g = concentration after adsorption
C_s = ratio of nuclide/cement hydrate (mol/g)

Title :	The effect of Microbial Activity on the Near and Far Fields of a Deep Repository
Contractor :	DCC/Dir CEA Saclay
Contract N° :	FI2W-CT90-0022
Duration of Contract :	October 1991- October 1993
Period covered :	January 1992 - December 1992
Project Leader :	M P. LESSART DSD/SEP/SEATN CEA Cadarache
Co-workers :	Mme M.F. LIBERT, M. B. BESNAINOU, MM H. SPOR, M. TRESCINSKI

A. OBJECTIVES AND SCOPE

Microorganims can produce organic or mineral acids that can promote corrosion and complexing agents that can modify the characteristics of the repository. So, radionuclides that have been immobilized by cement or bitumen embedding matrix can be leached either as soluble ions or soluble complexes (effects of the corrosion of the matrix). This leads to an increase of their mobility.

On the other hand, microorganisms can decrease the mobility of initialy soluble species by sorption on the cell membrane or on polymers (especially polysaccharides) produced by cells, and also by bioaccumulation in the cell.

The objective of the present work is to determine the global effect of microbial presence on the mobility of radionuclides supposed immobilized in the near field (clay or cement).

The experiments are realized on pure cement cylindrical samples or on fine mote of clay, containing U (introduced as Uranyl nitrate) or Cs (introduced as Cesium chloride). The organic acid producing microorganisms growth on cellulose, one carbon source that can be found in nuclear waste.

B. WORK PROGRAMME

Litterature survey.

Pilot plant design and realization, hydraulic tests, choice of working conditions.

Metabolism study of cellulolytic microorganisms

Leaching of U and Cs contained in cementitious or clay matrix by the culture medium containing microorganisms.

Study of the different effect of direct and indirect microbial action on radionuclide mobility or retardation.

C. PROGRESS WORK AND OBTAINED RESULTS

Litterature survey
Possibility of microbial action

The bibliographical study was presented in the intermediate report of july 1992. Several studies have already shown that microbial activity (resident microbes) exists in geological formations even under extreme conditions. The geological repository is also contaminated by microbes (introduced microbes) introduced by the excavation process and waste setting up. Some microbial groups can form spores or resting cells if conditions are unfavourable and then germinate when growth conditions become favourable. Most of resident microbes must be in dormant conditions.

Some conditions are necessary for microbial development. Protoplasm synthesis requires an organic or inorganic carbon source, nitrogen, energy, and an amount of mineral compounds such as S, P, K, Ca, Mg, Fe, or oligoelements as Cu, Mn, Co, Zn, Mo, Ni, Se, V... When no phototropic activity can be expected, the biological release of energy requires an electron donor such as an oxidizing organic compound or, in case of chemiolithotrophic microorganisms, oxidizing substances such as ammonia or sulfur compounds. It also requires an electron receiver that can be oxygen, a sulfate, a nitrate, a ferric compound, carbon dioxide or an organic compound. All those chemical exist in a nuclear repository, nevertheless, their bioavailability must be taken into account : the lack of any of them involving a decrease of the growing rate.

Water is essential for microorganism development. Respectively, bacteria and fungi need at least a 20% and 10% water content in their substrata, or if the substratum is more dry, a minimum of 95% or 75% relative humidity. There is a certain amount of water in the embedded waste, and the immediate environment is not absolutely anhydrous as there may be ground water in the geological site area, even in saline rocks (presence of brine). Moreover, although microbial development is inhibited without water, the process involving breathing and energy consumption produce water as a by-product. Once initiated, microbial development is self-perpetuating.

The physical desintegration of radionuclides creates electromagnetic and corpuscular radiation that can dammage cells : nucleic acids can be altered by break of the acid chain, new reticulation, reaction with free radicals... Microorganism resistance to ionizing radiation depends on their ability to repair these alterations. Many microbial groups resist to radiation dose rate much more higher than these expected in a MLW repository, and it is known that microorganisms irradiated by low dose of radiation developp a

higher resistance to radiation due to an increase of their repairing potential.

Many microorganisms resist to the other parameters due to the geological site (temperature and pressure increase with the deepth) or to the repository (pH of water in contact with concrete can increase to 12).

Wathever is the origin of microorganisms, resident or introduced microbes, after a long term corresponding to adaptation and/or selection of microbial population, the ambient microbes will exibit biological tolerance to extreme conditions such as these expected in a deep repository.

Effects of microorganisms on radionuclide transfert

From bibliographical study, microorganisms can modify radionuclide transfert by various mechanisms that are :

* biodegradation of confinement material leading to radionuclide release. The corrosion by microorganisms of materials such as concrete or iron alloys is well known.
* local modifications of the redox and pH conditions of the system that can affect chemical species (oxydation or reduction) and therefore modify the solubility of the considered element.
* modification of the sorption properties of the matrix by microbial adsorption and by site saturation. This can lead to a reduction in the adsorption of radionuclide by decrease of the free adsorption sites... or to an increase by formation of new sites on the bacterial surfaces : Biosorption can take place on cell wall sites such as phosphate, sulfate groups.
* production of surface factors or excreted polymers such as polysaccharides that remain on the external surface of the microbial cells, increasing the radionuclide immobilisation on the microbial cells. The high ionic concentration in these polymers allows the cell to grow in demineralized water.
* Adsorption can be followed by accumulation into the cell. Assimilation of metals that can lead to accumulation into the cell (mobility decrease) or to the formation of soluble or volatile complexes (by biomethylation for example), increasing the mobility.
* production of chelating agents (by-products of microbial metabolism) that can increase or decrease the mobility of certain radionuclides.
* gas production that can contribute to modify the mechanical characteristics of the repository.

Direct action of microorganisms on radionuclide mobility supposes that biomass is in contact with radionuclide.

The microorganism accumulates essential elements or toxic metals in the cells by the means of active, passive or facilited transport. Most toxic metals penetrate into the cell by a passive diffusion phenomenum : intracellular accumulation corresponds to an increase of membrane permeability and can be

considered as result of toxic interaction. With many metals such as Lead, Uranium or Thorium, for most microorganisms, accumulation takes place on the microbial biomass with little or no intracellular accumulation except by diffusion. However, with some other metals like Cadmium or Aluminium, processes involving active transport by means of phosphatase enzymes have been described.

Indirect microbial action can also takes place. Microorganisms produce various chemical that can change the pH and, by this way, contributes to increase radionuclide mobility. Ferrous compounds can be oxydized into ferric ones by microorganisms, that can lead to oxydation of U^{IV} to U^{VI} and thus increase Uranium solubility... The same result can be obtained by chemicals producing soluble radionuclide complexes. On the other hand, some chemical produced by microorganisms can decrease the metal solubility leading to precipitate (sulfides, insoluble complexes like these of humic acids).

Microorganisms can interact by various mechanisms which effects can be an increase or a decrease of the radionuclide mobility either on aerobic or on anaerobic growth conditions.

Metabolisms study of a cellulolytic microorganism

Trichoderma viride is a common cellulolytic fungus. It grows either under aerobic conditions either with only a low oxygen content in the atmosphere. In aerobic conditions, it grows very rapidly but produces only small amounts of organic acids. Oxygen limiting conditions lead to fermentative growth mechanism. Growth rate decreases, but total organic acids production increases in the medium. After some adaptation time, they can become a nutrient and are consummed (two main possibilities : selection of heterotrophic microorganisms abble to use the intermediate metabolites, or adaptation of *Trichoderma viride* to the new carbon source by development of enzymatic system). A HPLC method for identify qualitatively and quantitatively 14 various organic acids has been developped.

In anaerobic conditions, in a low mineral content medium, after a 97 days culture period, the total organic acid concentration rises 0.6 g/l. The 3 main organic acids (about 97% of the total) produced by this fungus are butyric acid (up to 65%), gluconic acid (up to 18%) and acetic acid (14%), the other acids being isobutyric, succinic, lactic and isovaleric one. In small amount, other acids have been identified : citric, malonic, fumaric, formic, propionic, valeric and isocaproic ones. But the ratio of these various acids is continuously varying and depends mainly on the growth conditions.

The acid accumulation is mainly observed when culture conditions change from aerobic to anaerobic. In those

condition , pH of the solution (6.5 initialy) can decrease to 4.5 and then stabilizes.

Pilot plant design and realization, hydraulic tests, choice of working conditions

The pilot plant has been described in the annual report on january 1992. Hydraulic tests lead to minor adaptations. As cellulose can be found in nuclear waste, we chose to study the effects of a cellulolytic fungus, *Trichoderma viride*, growing at 30°C (a temperature that can be found in a repository) in a low mineral content medium (similar to some deep ground water), using cellulose as the only carbon source. Conditions are aero-anaerobic (no feeding with air, conditions close to these expected in a deep repository after sealing). A 2 days residence time is realized around the cement or the clay samples.

Leaching of U and Cs contained in cementitious or clay matrix by the culture medium containing microorganisms

The cement samples have been manufactured by a CEA Laboratory specialized on cement and concrete studies at Saclay. To realize clay samples, clay is mixed in a water solution containing U or Cs, then recovered by centrifugation dried and pounded. Granulates are obtained that can be introduced in a column that stays porous to water flow. Uranium has been incorporated as Uranyl nitrate and Cesium as Cesium chloride. Manufacturing is described in the detailed annual report.

Pilot plant is now under experiment for 6 months.

Defined culture conditions are not favorable for cell growth and, after some weeks, it is possible to notice spores formation and accumulation at the bottom of the culture vessel.

Study of the different effects of direct and indirect microbial action on radionuclide mobility

For better understanding of the various possible action of microorganisms on Uranium, we developp two different experimental apparatus to measure respectively direct and indirect effects. They are described in the detailed annual report.

To measure the direct effects, the cells grow under aerobic conditions in a medium containing Uranyl nitrate and glucose (that is an intermediate product of cellulose degradation and allows a more rapid growth than cellulose). These experiments will allow to quantify the sorption capacity of cells.

Indirect effects have been measured using a 2 compartment device separated by a microporous membrane allowing the free diffusion of ions and molecules. Cells are grown in one compartment while Uranium, included in the matrix, is in the other. Contact between microbial cells and metal is impossible : solubilization of Uranium is in relation with the diffusion of metabolites produced by microbial cells.

Title: Corrosion of Selected Packaging Materials for Disposal of Heat-Generating Radioactive Wastes

Contractors: KfK Karlsruhe, ENRESA Madrid
Contract No.: FI 2W-CT-90-0030
Duration of contract: January 1991 - December 1994
Period covered: January 1992 - December 1992
Project Leader: E. Smailos, KfK-Karlsruhe, Germany

A. OBJECTIVES AND SCOPE

In previous corrosion studies, carbon steels and the alloy Ti 99.8-Pd were identified as promising materials for heat-generating nuclear waste packagings acting as a barrier in a rock-salt repository. To characterize the corrosion behaviour of these materials in more detail, a research programme including laboratory-scale and in-situ corrosion studies has been undertaken jointly by KfK and ENRESA/INASMET. Besides carbon steels and Ti 99.8-Pd, also Hastelloy C4 and some Fe-base materials will be examined in order to complete the results available to date.

The research programme has two objectives:

- Investigation of the influence of essential parameters on the corrosion behaviour of the materials in disposal relevant salt brines. These parameters are: temperature, gamma radiation and selected characteristics of packaging manufacturing (KfK).
- Investigation of the resistance of carbon steels to stress corrosion cracking in an $MgCl_2$-rich brine at various temperatures and strain rates by means of the slow strain rate technique (ENRESA).

B. WORK PROGRAMME

B.2.1 Corrosion studies on the unalloyed fine-grained steel in three salt brines (two $MgCl_2$-rich, one NaCl-rich) at 150°C and gamma dose rates of 1 Gy/h and 10 Gy/h (laboratory-scale immersion tests, KfK).

B.2.2 Corrosion studies of two low-alloyed steels (TSt E 460, 15 MnNi 6.3) in three salt brines at 150°C (laboratory-scale immersion tests, KfK).

B.2.3 In-situ corrosion studies on specimens of Fe-base materials, Ti 99.8-Pd and Hastelloy C4 in rock salt at rock temperature (reference experiments, KfK).

B.2.4 In-situ corrosion studies on tubes of carbon steel, Ti 99.8-Pd and Hastelloy C4 provided with selected container manufacturing characteristics in rock salt/brines at 90°C-200°C (KfK).

B.2.5 Statistical analysis of corrosion data (KfK).

B.2.6 Stress corrosion cracking studies on unalloyed and low-alloyed steels (fine-grained steel, TSt E 460, 15 MnNi 6.3) in an $MgCl_2$-rich brine at various temperatures (25°C, 90°C, 170°C) and slow strain rates (10^{-4} - 10^{-7} s^{-1}) (ENRESA / INASMET).

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

In the period under review, the long-term immersion tests lasting 18 months and the stress corrosion cracking studies (slow strain rate tests) on three preselected carbon steels in disposal-relevant salt brines at 150°C-170°C have been completed. Moreover, first irradiation-corrosion studies have been performed on the unalloyed carbon steel TStE 355 in salt brines at 150°C and a gamma dose rate of 10 Gy/h (10^3rad/h).

PROGRESS AND RESULTS

B.2.1 Corrosion studies on the unalloyed steel TStE 355 in brines under gamma irradiation (KfK contribution)

First corrosion studies lasting 100 days were performed on the hot-rolled unalloyed steel TStE 355 (0.17 wt.% C; 0.44 wt.% Si; 1.49 wt.% Mn; bal. Fe) in three disposal-relevant brines at 150°C and a gamma dose rate of 10 Gy/h (10^3rad/h). The compositions, pH-values and O_2-contents of the brines are given in Table I. Two of them (brines 1 and 2) are highly concentrated in $MgCl_2$, the third one (brine 3) has a high concentration of NaCl.

The integral corrosion rates of the specimens calculated from the weight losses and the material density are compiled in Table II. All values are average of three specimens. In the $MgCl_2$-rich brines 1 and 2, significantly higher general corrosion rates of 173 µm/a and 208 µm/a, respectively, were determined than in the NaCl-rich brine 3 (21 µm/a), as in previous investigations without irradiation [1]. The higher corrosivity of the $MgCl_2$-rich brines compared to the NaCl-rich brine is attributed to their higher HCl-concentration. This could be explained by the higher Cl^--concentration and the hydrolysis of the Mg^{2+}.

Surface profiles and metallographic examinations of corroded specimens have shown that the steel was resistant to pitting corrosion in all irradiated brines. After the test time of 100 days, a non-uniform general corrosion was observed in the $MgCl_2$-rich brines, as for the specimens without irradiation. However, the measured maximum penetration depth of this uneven corrosion corresponded to the value of the average thickness reduction. In case of the NaCl-rich brine, the corrosion attack of the steel specimens was fairly uniform. Figure 1 shows optical micrographs of steel specimens after 100 days exposure to the test brines at 150°C and 10 Gy/h.

In general, it can be stated that the corrosion rates determined so far for the steel under gamma irradiation imply corrosion allowances technically acceptable for the thick-walled containers discussed. For a final statement about the influence of gamma radiation on the corrosion of carbon steels in brines at the high temperature of 150°C, the results of the ongoing long-term experiments are necessary.

B.2.2 Corrosion studies on low-alloyed steels in salt brines (KfK contribution)

The long-term general and local corrosion studies on the two low-alloyed steels TStE 460 and 15 MnNi 6.3 were completed by examination on the 18-month specimens. Both steels were tested in the three brines (two $MgCl_2$-rich, one NaCl-rich) given in Table I at 150°C. The steel TStE 460 was examined in the hot-rolled and annealed condition, the steel 15 MnNi 6.3 in the forged and annealed condition. The steels, which are discussed in Germany as container materials for the disposal of spent fuel in the galleries of a rock salt repository, had the following compositions in wt.%:

TSt E 460 : 0.18 C; 0.34 Si; 1.5 Mn; 0.51 Ni; 0.15 V; bal. Fe
15MnNi6.3 : 0.17 C; 0.22 Si; 1.59 Mn; 0.79 Ni; bal. Fe.

Besides specimens of the parent materials, also submerged-arc welded (SAW) specimens were investigated in order to examine the influence of this

welding technique discussed for the spent fuel container closure on the corrosion. All specimens were examined for general and local corrosion in the brines by gravimetry, microscopic evaluation, measurements of pit depths, surface profilometry and metallography.

The general corrosion of the unwelded 18-month steel specimens (parent materials) at 150°C in the three brines, expressed as the thickness reduction, is plotted in Fig. 2. For comparison, also the results of previous studies [2] up to 12 months duration have been entered. The corrosion results obtained for the 18-month specimens made of TStE 460 and 15 MnNi 6.3 agree well with those of up to 12 months. They confirm that the thickness reduction of the steels linearly increases with exposure time, i.e. the linear corrosion rate is time independent. The values of the linear corrosion rates of the steels are compiled in Table III. The lowest corrosion rates occurred in the NaCl-rich brine 3 with values of 56 µm/a (TStE 460) and 71 µm/a (15 MnNi 6.3), respectively. In the $MgCl_2$-rich brines 1 (Q-brine) and 2, higher corrosion rates (65-203 µm/a for TStE 460, 94-117 µm/a for 15 MNi 6.3) were obtained compared to the values of the NaCl-rich brine. The higher corrosivity of the $MgCl_2$-rich brines compared to the NaCl-rich brine is attributed to their higher HCl-concentration, as already discussed in Session B.2.1. The acceleration of the steel corrosion in brines containing high amounts of $MgCl_2$ is in line with the results reported by Westerman et al. [3].

It is evident from the metallographic examinations and the surface profiles that the unwelded 18-month specimens were resistant to pitting corrosion in all three brines. A non-uniform corrosion was observed for both steels in the test brines which is attributed to inhomogeneities of the steel composition. However, the maximum penetration depth of this uneven corrosion attack corresponded to the values of the average thickness reduction.

Welding did not influence noticeably the corrosion behaviour of the steels in the NaCl-rich brine 3. The SAW specimens underwent a non-uniform corrosion attack as did the unwelded specimens, and the general corrosion rates corresponded to the values obtained for the parent materials. In the $MgCl_2$-rich brines, however, considerable local corrosion attacks were detected for both steels in the heat-affected zone. The depth of these corrosion attacks increased with exposure time to the brines and reached after 18 months values between 2 mm and 4 mm, depending on the steel and the brine (Table IV).

The corrosion products formed on the surface of the steel specimens were analysed by X-ray diffraction. For specimens exposed to the NaCl-rich brine 3, Fe_3O_4 (magnetite) and γ-Fe_2O_3 (maghemite) were identified. In the $MgCl_2$-rich brines, $(Fe,Mg)(OH)_2$ of the amakinite structure and β-FeOOH (akaganeite) were found, with no evidence of oxides. The formation of Fe_3O_4 and $(Fe,Mg)(OH)_2$ at high temperatures in NaCl-rich and $MgCl_2$-rich brines, respectively, is also reported by Westerman et al. [3].

In general, it can be stated that the corrosion rates obtained for the parent materials imply corrosion allowances technically acceptable for the thick-walled carbon steel containers discussed. However, submerged-arc welding strongly reduces the corrosion resistance of the steels in highly concentrated $MgCl_2$-brines. Therefore, other welding techniques, e.g. Metal Active Gas (MAG) welding, for the container closure should be examined.

B.2.6 Stress corrosion cracking studies on carbon steels (ENRESA / INASMET contribution)

The stress corrosion cracking studies on the steels TStE 355, TStE 460 and 15 MnNi 6.3 in the $MgCl_2$-rich brine 1 (Q-brine) at 170°C and slow strain rates were completed by examination of the specimens at a rate of $10^{-7}s^{-1}$. In order to be able to interpret the results obtained in the brine, additional comparative investigations were carried out in argon as an inert medium. For the tests round specimens of 6 mm diameter, finished with 1000 grade emery paper were used. In addition to the parent materials, also MAG (Metal Active

Gas) welded materials simulating an alternative container closure technique to submerged-arc welding (SAW) were examined. SAW-specimens were not investigated because the results obtained from the general and local corrosion studies (see Session B.2.2) indicated that this welding technique significantly reduces the corrosion resistance of the steels in $MgCl_2$-rich brines.

The experiments at 150°C were conducted in Hastelloy C-276 autoclaves at an argon pressure of 13 MPa. Load, position, time and temperature data were continuously logged by the microprocessor that controls the testing machine. After each test, the elongation (E), reduction of area (R.A.), energy, yield strength (Y.S.) maximum load, and true stress at fracture were calculated. To evaluate the resistance of the steels to stress corrosion cracking, metallographic and scanning electron microscopic (SEM) examinations of the fracture specimen surfaces were performed in addition to the tensile experiments.

The results of the slow strain rate tests for the three steels in argon and Q-brine at 170°C and a strain rate of $10^{-7}s^{-1}$ are given in Figs. 3 and 4. For comparison, also the values at strain rates of $10^{-4}s^{-1}$, $10^{-5}s^{-1}$ and $10^{-6}s^{-1}$ obtained in previous work [2] are plotted. Compared to the values in argon, a clear diminishing of the elongation, reduction of area, energy and true stress at fracture occurred for all steels in the brine. The values for the yield strength and maximum load in Q-brine, however, are closed to those obtained in argon.

In the metallographic examinations of specimens made of the hot-rolled steels TStE 355 and TStE 460, a non-uniform general corrosion was observed. Secondary cracks typical for stress corrosion were not observed. For this reason, the reduction in ductility of these steels in Q-brine compared to argon cannot be attributed to stress corrosion cracking. For the loss in ductility in this brine another mechanism such as embrittlement could be responsible.

In the SEM examinations of TStE 355 and TStE 460 specimens tested in argon, a ductile fracture was observed at all strain rates. In Q-brine, the morphology of the fracture specimen surface depended on the strain rate. At $10^{-4}s^{-1}$ a beginning embrittlement, at $10^{-5}s^{-1}$ and $10^{-6}s^{-1}$ small brittle features at the specimen edges, and at $10^{-7}s^{-1}$ an embrittlement of larger specimen areas was observed.

In the metallographic examinations of the forged steel 15 Mn Ni 6.3 tested in Q-brine at strain rates of $10^{-4}s^{-1}$ and $10^{-7}s^{-1}$, no secondary cracks indicating stress corrosion cracking were observed. On the contrary, at strain rates of 10^{-6} s^{-1} and particularly $10^{-5}s^{-1}$, a clear susceptibility to stress corrosion was observed. Besides a non-uniform corrosion, extensive lateral secondary cracks were identified. The results of the SEM examinations are very similar to those for the steels TStE 355 and TStE 460. In Q-brine at $10^{-4}s^{-1}$ only negligible embrittlement, and at $10^{-5}s^{-1}$-$10^{-7}s^{-1}$ a brittle fracture of larger specimen areas was observed. In argon the fracture surface was ductile.

The embrittlement of the steels in Q-brine at 170°C and slow strain rates is likely due to the hydrogen produced during corrosion which enters the materials in atomic form, predominantly in zones of high stress level, causing a loss in ductility. However, this effect does not appear to be serious because the residual reduction of area and elongation at fracture of the steels after testing in the brine environment are still relative high.

The examinations of MAG welded steel specimens in argon and in Q-brine at 170°C and strain rates of 10^{-4}-$10^{-7}s^{-1}$ show only a slight decrease in the elongation, reduction of area and energy compared to the values of the parent materials. As for the unwelded specimens, a loss in ductility was observed for the steels in Q-brine in comparison to argon. Metallographic and fractographic studies on welded specimens are under way. Furthermore, stress corrosion cracking studies on the steels at lower temperatures of 25°C and 90°C have been started.

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[2] E. Smailos, "Corrosion of Selected Packaging Materials for Disposal of Heat-Generating Radioactive Wastes in Rock-Salt Formations," Annual Progress Report 1991, CEC-Report EUR 14418 EN (1992) p. 257.
[3] R.E. Westerman, J.H. Haberman et al., "Corrosion and Environmental-Mechanical Characterization of Iron-Base Nuclear Waste Package Structural Barrier Materials, "PNL Report 5426 (1986).

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W. Schwarzkopf, E. Smailos, R. Köster, "In-situ Corrosion Studies on Cast-Steel High-Level Waste Packagings Plated with Titanium/Nickel Alloys", Proc. of the XV Int. Symp. on the Scientific Basis for Nuclear Waste Management, November 4-7, 1991, Strasbourg, France, Vol. 257, p. 423, 1992.

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Table I: Compositions, pH -values and O_2 -contents of the salt brines used in the laboratory - scale corrosion experiments

Brine	Composition (wt.%)							
	NaCl	KCl	$MgCl_2$	$MgSO_4$	$CaCl_2$	$CaSO_4$	K_2SO_4	H_2O
1	1.4	4.7	26.8	1.4	---	---	---	65.7
2	0.31	0.11	33.03	---	2.25	0.005	---	64.3
3	25.9	---	---	0.16	---	0.21	0.23	73.5

pH (25°C): 4.6 for brine 1; 4.1 for brine 2; 6.5 for brine 3
O_2(55°C): 0.8 mg/l for brine 1; 0.6 mg/l for brine 2; 1.2mg/l for brine 3

Table II: Integral corrosion rates of the unalloyed steel TStE 355 after 100 days exposure to the test brines at 150°C and a gamma dose rate of 10 Gy/h

Brine	Corrosion rate (µm/a)
1	173.0
2	208.3
3	21.0

brine 1 and 2: $MgCl_2$-rich; brine 3: NaCl-rich

Table III: Linear corrosion rates of the unwelded steels TST E 460 and 15 MnNi 6.3 in the test brines at 150°C

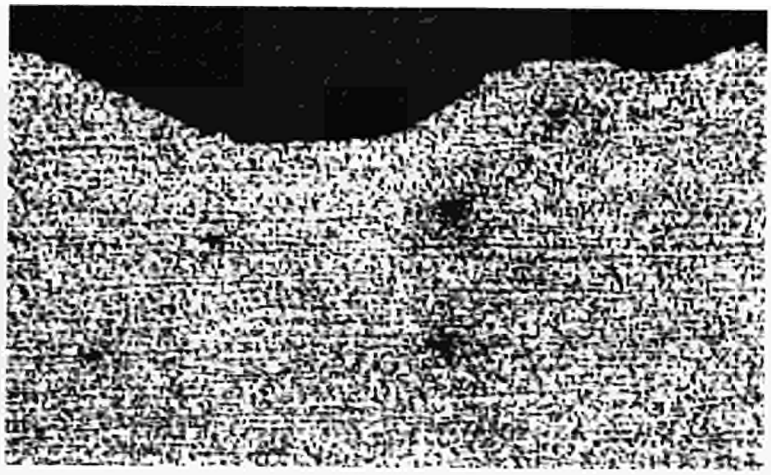
Material	Corrosion rate (µm/a)		
	Brine 1	Brine 2	Brine 3
TStE 460	203.5	65.4	56.3
15 MnNi 6.3	117.3	94.0	71.3

brines 1 and 2: $MgCl_2$ - rich; brine 3: NaCl - rich
test duration: 4 - 18 months

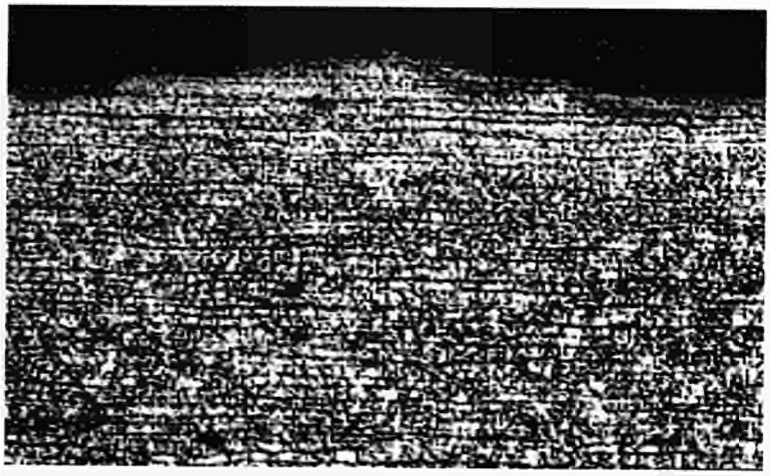
Table IV: Maximum penetration depth of corrosion in the HAZ[+)] of the submerged arc welded steels TStE460 and 15 MnNi 6.3 after 18 months exposure to brines at 150°C

Material	Maximum penetration depth (mm)		
	Brine 1	Brine 2	Brine 3
TStE 460	2.0	2.5	0.04
15 MnNi 6.3	1.9	4.0	0.05

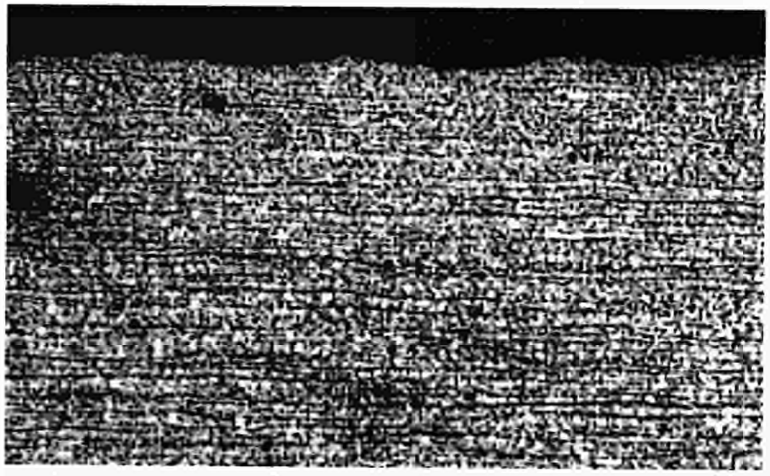
[+)] heat - affected zone



Brine 1 ($MgCl_2$-rich) X 100



Brine 2 ($MgCl_2$-rich) X 100



Brine 3 (NaCl-rich) X 100

Fig.1: Optical micrographs of the steel TSt E 355 after 100 days exposure to brines at 150°C and 10 Gy/h

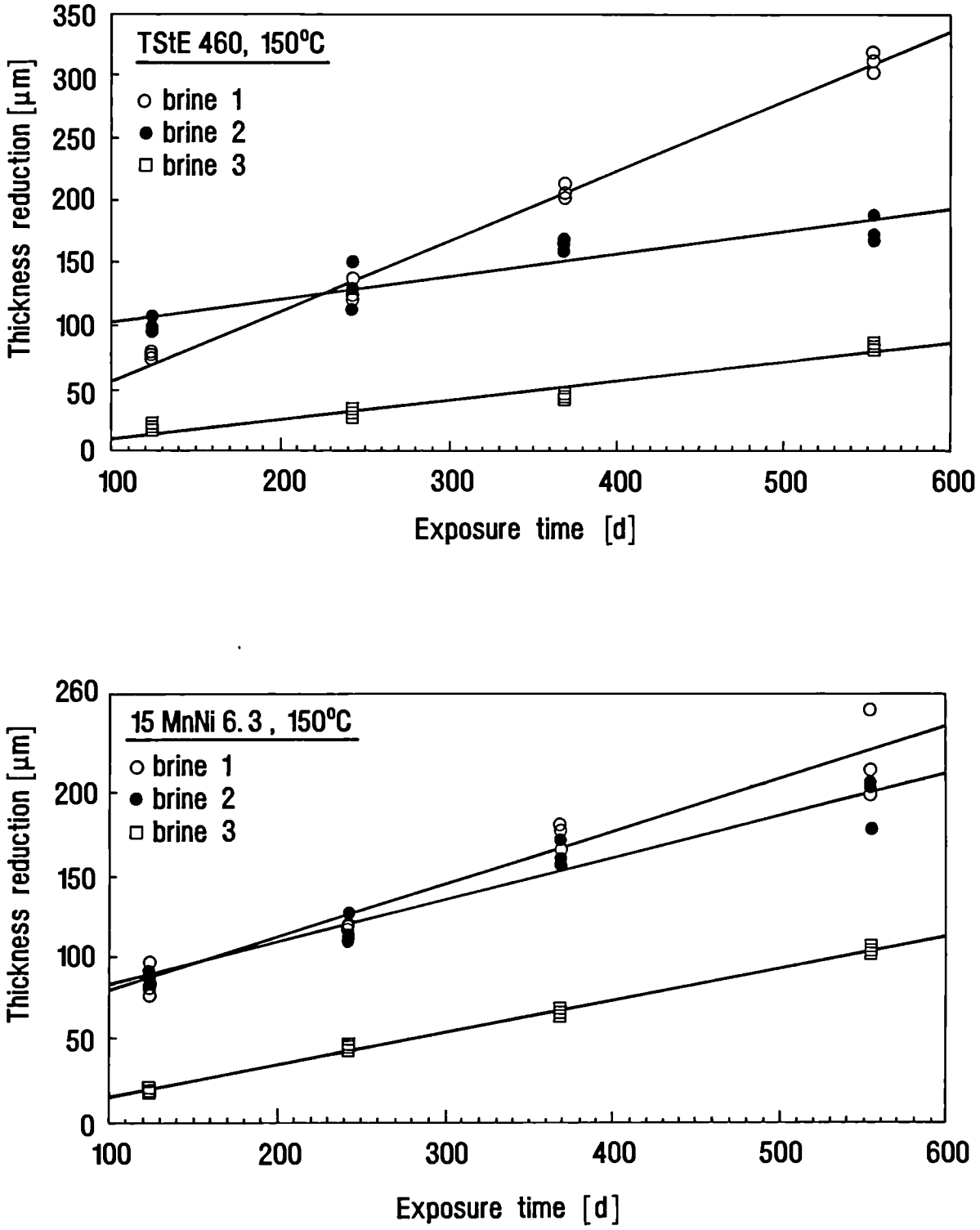


Fig.2: Thickness reduction of the steels TStE 460 and 15 MnNi 6.3 in salt brines at 150°C

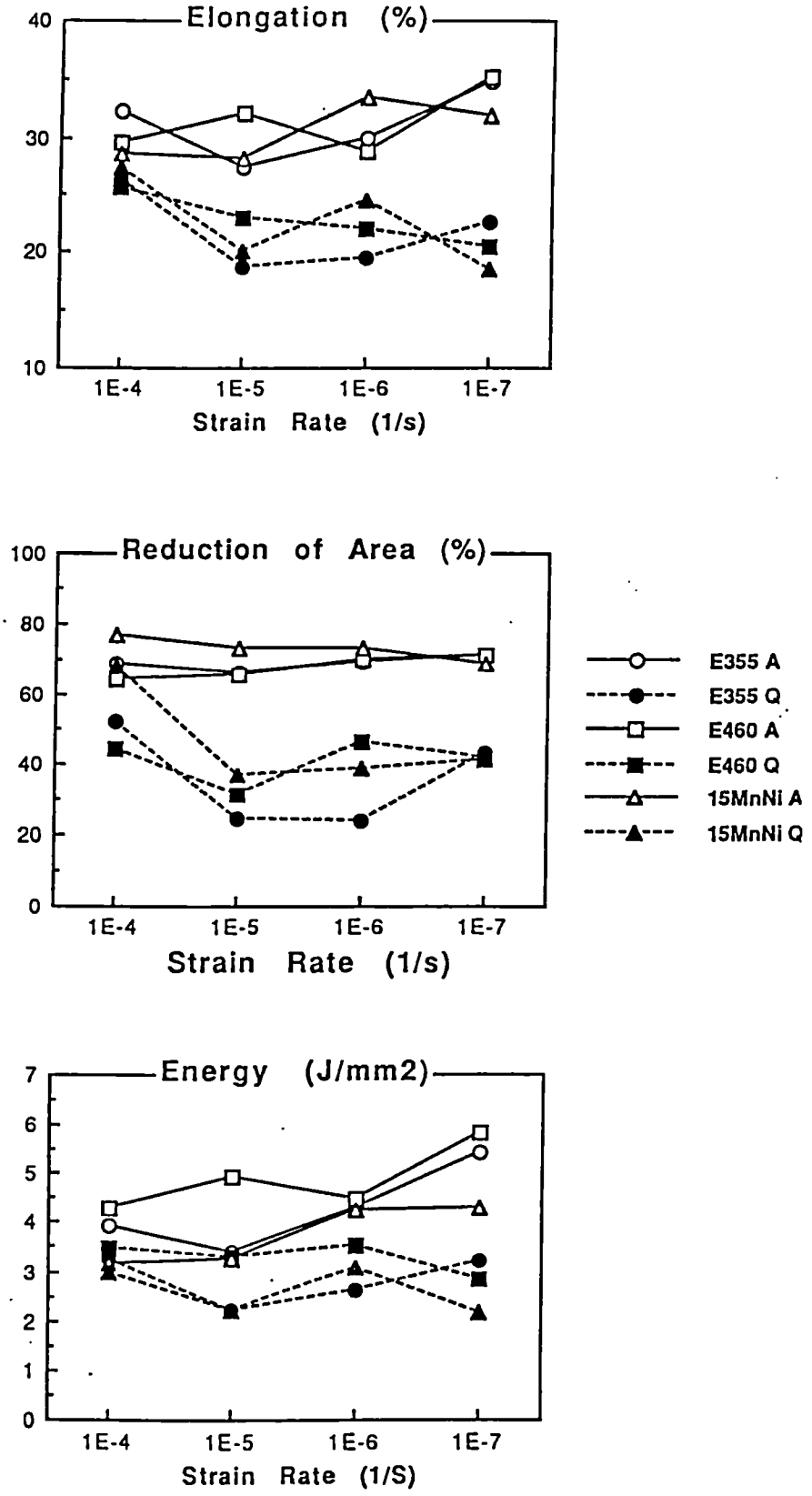
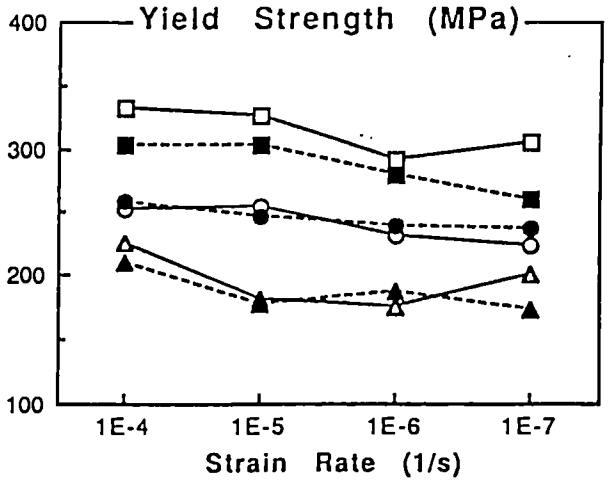
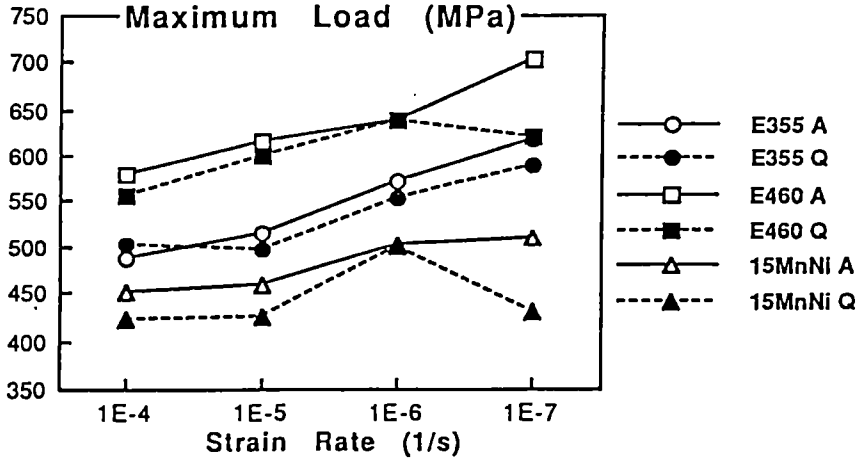


Fig.3: Elongation, reduction of area and energy versus strain rate for the steels TSt E 355, TSt E 460 and 15 MnNi 6.3 tested at 170°C and 13 MPa in argon and Q-brine





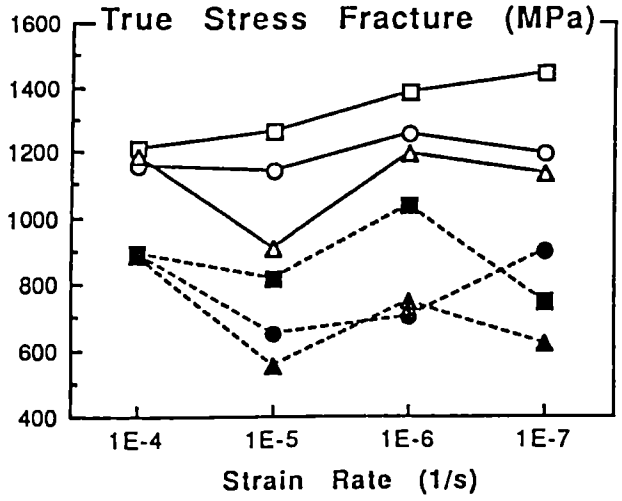


Fig.4: Yield strength, maximum load and true stress fracture versus strain rate for the steels TSt E 355, TSt E 460 and 15 MnNi 6.3 tested at 170°C and 13 MPa in argon and Q-brine

THEORETICAL AND EXPERIMENTAL STUDY OF DEGRADATION MECHANISMS OF CEMENT IN THE REPOSITORY ENVIRONMENT

Contractor :	Commissariat à l'Energie Atomique/CE.Saclay/DCC/DSD/SCS
Contract :	F12W-CT.90-0035
Duration of contract :	January 1991 - December 1994
Period covered :	February 1992 - December 1992
Project leader :	Mme REVERTEGAT, CEA/CE.Saclay/DCC/DSD/SCS

A. Objectives and Scope

The object of the research program supported by CEC contract number F12W-CT90.0035 is to estimate the long-term corrosion of concrete used for waste disposal and to determine the mechanisms involved. Therefore we are developing a corrosion model based on the different mechanisms involved, in which it will be possible to introduce storage conditions specific to each site (type of corrosive solution, cement composition, storage temperature...).

B. Work programme

1. Investigation about degradation mechanisms involved when the cement paste is corroded by a solution including aggressive ions :
   - study of phase diagrams to determine which phase may coexist and acquisition of the thermodynamic data necessary to solve the model in the different possible cases (study of equilibria as functions of aggressive ions and temperature)
   - study of degradation processes of cement pastes submitted to various aggressive environments (chlorides, sulfates, carbonates)

2. Testing of the local equilibrium hypothesis (by checking that the kinetics is effectively governed by diffusion)

3. Modelling of cement paste degradation :
   - mathematic writing of the model equations built on physico-chemical laws
   - numerical resolution of the model by a microcomputer program : in a first step, a simplified algorithm is developed in order to validate the model equations
   - model validation
   - algorithm extension to resolve any case (modelling of Cl^-, SO_4^{2-} and carbonates attack and taking into account the main reactions of precipitations and dissolutions occuring)

4. Application to cement clay interaction : resolution of the generalized model and comparison with experimental results

C. Progress of work and obtained results

To understand the mechanisms of cement paste attack, on the one hand, we study the phase diagrams to determine which phases may coexist and acquire the thermodynamic data necessary to solve the model in the different possible cases. We pay attention to the CaO-Al_2O_3-$CaSO_4$-H_2O, CaO-Al_2O_3-$CaCl_2$-H_2O and CaO-Al_2O_3-$CaCO_3$-H_2O systems.

For the CaO-Al_2O_3-$CaSO_4$-H_2O system, two mains factors have been investigated : first the variations due to an increase of temperature and secondly the influence of potassium.
Compared to the phase diagram at 25°C, the existence of a stability domain for monosulphoaluminate at 50°C adds two segments and alters the nature and sequence of invariant points at low sulphate concentrations. The stability domain of monosulphoaluminate, even if small, appears clearly in the three dimensional drawing of the phase diagram (figure 1). A temperature increase (from 50 to 85°C) increases the stability of monosulphoaluminate and modifies the sequence of invariant points relative to their sulphate concentration.

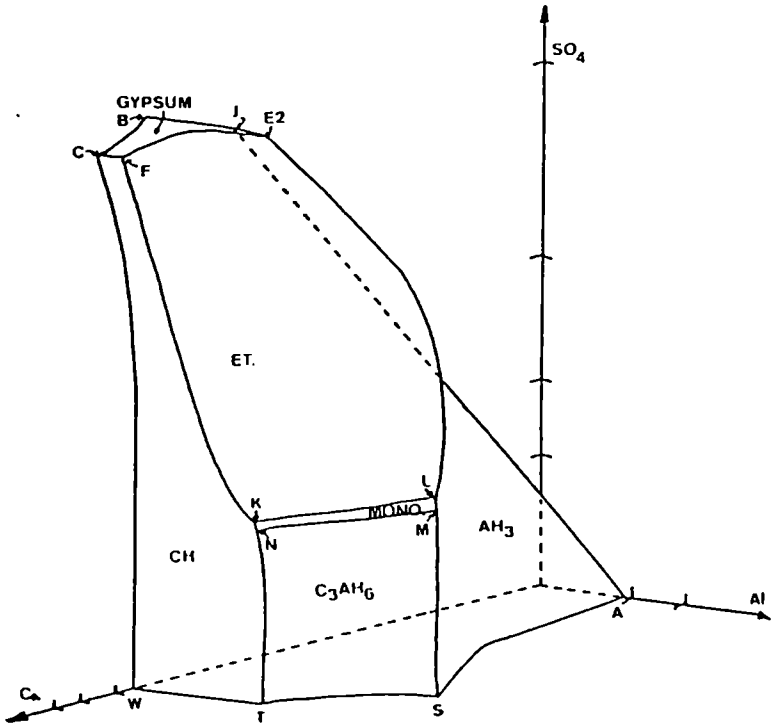


Figure 1. Three dimensional representation of the CaO-Al_2O_3-$CaSO_4$-H_2O system at 50°C.

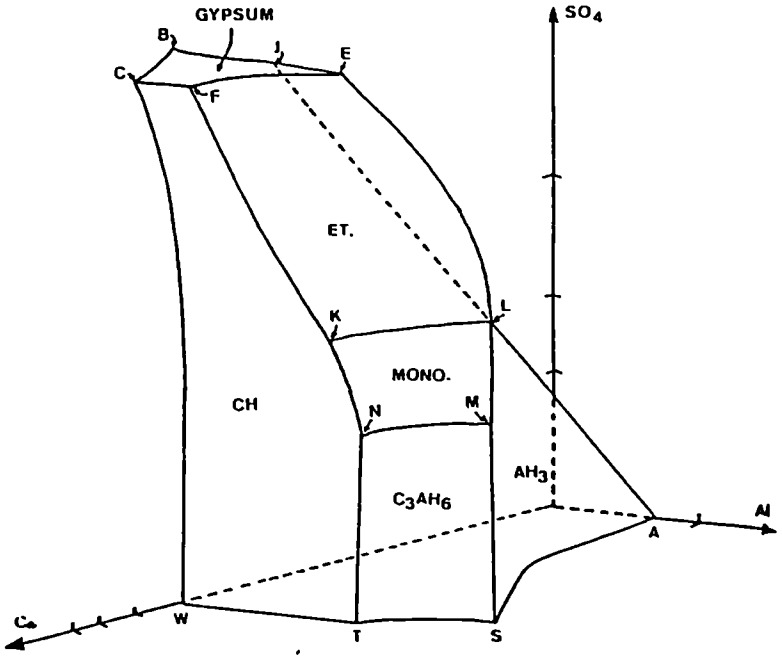


Figure 2. Three dimensional representation of the $CaO-Al_2O_3-CaSO_4-H_20$ system at 85°C.

TABLE 1

Solution Compositions for the Main Points in the $CaO-CaSO_4-K_2O-H_2O$ System at 25°C (concentrations are given in molality 10^{-3})

Point	Solids in equilibrium	[Ca]	[K]	[SO_4]	pH
W	CH	21.90	0	0	12.48
C	CH-gypsum	33.58	0	12.44	12.43
B	gypsum	15.52	0	15.52	7.05
K1	CH-gypsum-syngenite	12.25	434.1	168.8	12.87
K2	gypsum-syngenite	8.23	395.1	205.8	7.25
K3	K_2SO_4-syngenite	0.485	1223.6	612.2	7.30
K4	CH-syngenite-K_2SO_4	1.15	1427.5	432.2	13.51
K5	K_2SO_4	0	1223.6	611.8	7.30
K6	K_2SO_4-KOH	0	15300	2	
K7	K_2SO_4-KOH-CH	0.0001	15300	2	
K8	KOH-CH	0.0001	15300	0	
K9	KOH	0	15300	0	

The $CaO-Al_2O_3-CaSO_4-H_2O$ equilibrium diagram at 85°C (figure 2) resembles the diagram obtained at 50°C (figure 1); the main differences concern the greater extent of the equilibrium surface of monosulphoaluminate which confirms an increase in stability of this hydrate. However ettringite still remains as the hydrate which is stable over the widest range of sulphate concentration.
The hydrate sequence encountered for the $CaO-Al_2O_3-CaSO_4-K_2O-H_2O$ system at 25°C is shown in table 1 .

At temperatures higher than 25°C, the system becomes more complex for two main reasons: (i) the appearance of pentasalt and (ii) monosulphoaluminate becomes stable for temperatures higher than 50°C. It is not yet known if the formation of syngenite in a cement paste is destructive but it is a possible subject for investigations.

The $CaO-Al_2O_3-CaCl_2-H_2O$ system, has not been completely investigated as it was the case for the $CaO-Al_2O_3-CaSO_4-H_2O$ system /1/, /2/. Some solubility experiments have been carried out at Aberdeen for both monochloroaluminate and chloro-ettringite. Experiments on the latter have been less successful and some work is still necessary on this hydrate. To calculate of the $CaO-Al_2O_3-CaCl_2-H_2O$ system, the $CaO-Al_2O_3-H_2O$ and $CaO-CaCl_2-H_2O$ sub-systems have to be investigated first: the sub-system $CaO-Al_2O_3-H_2O$ system has been investigated as part of the $CaO-Al_2O_3-CaSO_4-H_2O$. Thus our first task will be to calculate the $CaO-CaCl_2-H_2O$ sub-systems and compare the results with the experiments of Milikan /3/. However the very high ionic strengths that occur in this system might make precise calculations difficult.

The $CaO-Al_2O_3-CaCO_3-H_2O$ system appears to be complex: the carbo-ettringite ($3CaO.Al_2O_3.\ 3CaCO_3.30H_2O$) and monocarbonate hydrate ($3CaO.Al_2O_3.CaCO_3.10H_2O$) exist. Moreover these hydrates are likely to be substituted, as reported in figures 5 and 6. Some solubility data exist for the monocarbonate /4/ but these have to be used with caution: the carbonate concentration of the solution is not reported and the solubility product is defined with a calculated carbonate concentration. Thus all these hydrates have been synthesised in order to determine their solubility.

To investigate further about degradation mechanisms, on the other hand, we studied in Saclay the degradation processes of CPA and CLC samples exposed to corrosive solutions at pH 8.5 too. In particular, we chose to study the action of solutions with $[Cl^-] = 20$ g/l or with $[SO_4^{2-}] = 10$ g/l in comparison with a solution without aggressive ions.
After 6 and 12 months leaching, we established the zonality in solid phase by X-ray diffraction. This zonality greatly depends on the quality of the procedure used to separate physically the zones before the analysis. It is worth checking these results by microprobe.

Nevertheless, the following comments can be made :

- the zonalities observed are characteristic of local equilibria.
- the depth of the corroded layer is greater in the CPA paste than in the CLC paste (this is probably due to a finer porosity in the CLC, leading to lower diffusion factors).
- X-ray diffraction analysis does not show significant differences in the zones sequence between CPA and CLC.
- chlorides in the corrosive solution seem to speed up the corrosion.

- sulphates in the corrosive solution give rise to gypsum in the sample but the corrosion is slower than in the presence of chorides. It is noteworthy that our previous results, obtained for samples in contact with a solution with pH = 11.5, $[SO_4^{2-}]$, showed that there was no formation of gypsum inside the CLC structure during a 3 year experiment.

To verify the assumption of local equilibrium, we determined precisely the leaching kinetics of hydroxyls from Portland cement (CPA) with 0.4 or 0.65 water to cement ratio and slag and fly ash cement (CLC) with 0.4 water to cement ratio. The results obtained show that in all cases the leaching kinetics is a function of the square root of time, which is characteristic of a diffusion process and of local equilibrium. For CPA with W/C = 0.4, analyses are performed on the solid samples after leaching. They confirm the local equilibrium : we have noticed an uncorroded core, dissolution fronts and a progressive decalcification zone between the uncorroded core and the sample surface. The corroded layer after 3 months is 1.5 mm deep.

Considering these experimental results, we have established a theorical corrosion model to depict physicochemical phenomena and developed a simplified algorithm to solve this model. Figure [3] gives the calcium experimental concentrations profiles in solid phase after 3 months leaching. The depth of the corroded layer, the succession of zones together with their mineral composition and the variation of the C/S ratio for CSH, as calculated by the model (fig 3-4), are in harmony with those measured experimentally. The model is thus validated in an ordinary case (cement paste with deionized water as the corrosive solution).

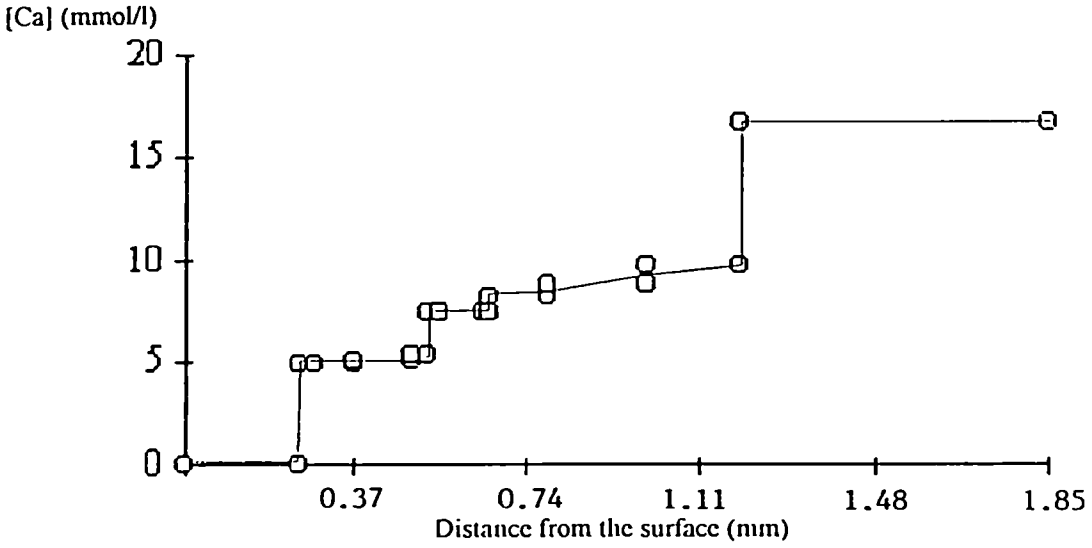


Figure [3] : Evolution of [Ca] in solid phase at 3 months

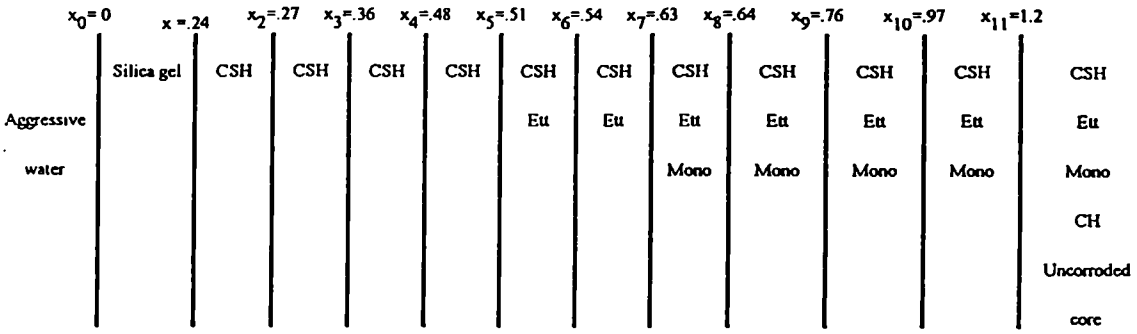


Figure [4]: "zoning" of the CPA cement paste,
consisting of an assemblage of multi-mineral domains separated by boundaries
(x in mm)

References :

/1/ F.E. Jones, J. Phys. Chem. ,48(6), 356-378 (1944)
/2/ J. D'Ans and H.Eick, Zem.-Kalk-Gips,6,302 (1953)
/3/ H.J. Kuzel, N. Jahr. f. Mineralogie Monat.,31,477-491 (1971)
/4/ F. Zhang, Z. Zhou and Z. Lou, 7th Int. Symp. on the Chemistry of Cement, Paris,2,88-93

Completion of the corrosion programme in Boom clay (in situ experiments)

Contractor : ONDRAF/NIRAS, Brussels, Belgium

Contract N° : FI2W/0096

Duration of contract : July 1991 - December 1994

Period covered : January 1992 - December 1992

Project leader : J. Van Miegroet

A. OBJECTIVES AND SCOPE

The in situ corrosion experiments in the Boom clay underground laboratory (Mol, Belgium) were initiated during the 1985-1989 five-year plan to obtain realistic corrosion rates for a large range of metallic and non-metallic materials (glasses, bitumen, concrete, and container- and overpack-materials). Different corrosion tubes were installed in the period 1985-1991 or will be installed in the near future. The aim of the present research programme is the completion of the corrosion experiments initiated in the previous programme and the beginning and completion of the operation of two additional corrosion tubes. The experimental work is performed by CEN/SCK.

B. WORK PROGRAMME

1. Monitoring and controlling the ongoing corrosion experiments.
2. Design, construction and installation of the new corrosion loops.
3. Overcoring and retrieval of the different tubes in due time.
4. Analysis of the metallic and waste form samples and of the surrounding clay-core.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Surface and cross sectional analyses of both the overpack and waste glass samples from the overcored tubes 1 (5 years, 170 °C) and 4 (5 years, 16 °C) were started and some important results were obtained.

The main experimental results of the in situ corrosion experiments to date have been synthesized and, whenever possible, an interpretation of the observed corrosion behaviour was put forward.

The preparation of two new tubes (5b at 90 °C and 10 at 16 °C) and the samples to be studied was finished. An automatic He gas-outflow system, designed to remove the accumulated clay water in the type II and III tubes, was successfully tested. This outflow system will be installed on tubes 8 and 9 (already running) and tubes 5b and 10 (to be installed). The extensive testing of this prototype outflow system has delayed the installation and start up of the tubes 5b and 10 till 1993.

Progress and results

Main experimental efforts were devoted to the surface and cross sectional analyses of the overpack samples (Carbon-steel, Hastelloy C4, Ti/0.2 Pd) and the waste glass samples (SON68, SON58, SM58 and SM513).

For the corrosion-resistant metals (Hastelloy-C4, Ti/0.2 Pd) all surface analyses confirm the absence of any measurable form of corrosion, as previously demonstrated by the negligible mass losses of the weighed samples. Surface analysis techniques used were optical microscopy, metallography and scanning electron microscopy.

For the corrosion-allowance steel, both pitting and homogeneous corrosion were found. Surprisingly, pits of 100 to 120 um depth were detected on the 16 °C samples (tube 4), while the 170 °C samples (tube 1) showed areas of very large but undeep pits.

Given the experimental results presently available for C-steel corrosion at 16 °C (tube 4), 90 °C (tube 2) and 170 °C (tube 1), the observed corroded surface morphology can be explained as follows (B. Cornélis et al., 1992). In the initial aerobic phase of the experiment, lasting a few months at most as evidenced by in situ E_h monitoring, the main corrosion mechanism would be a temperature dependent pitting corrosion. When anaerobic conditions return, corrosion would proceed uniformly and consequently a progressive erosion or levelling out of the pits would take place.

Preliminary XRD analysis results of the corrosion layer of C-steel at the three temperature (16 °C, 90 °C and 170 °C) are summarized in Table 1. It seems that the exact mineralogical nature of the corrosion products is only marginally affected by temperature.

The corrosion behaviour of a small number of glass samples (SON68, SON58, SAN60, SM58, SM518) of importance for Belgium was studied by SEM-EDXA and SIMS analysis (secondary ion mass spectrometry) (Van Iseghem and Chen, 1992 ; Lodding et al, 1992).
An overview of the surface analyses on the waste glass samples is given in Table 2. A typical SIMS elemental profile is shown in Figure 1. The main conclusions from these SIMS analyses are :

- mixed mechanisms of leaching are found. In the early corrosion phase selective leaching seems to predominate. Mobile elements as B, Li and Cs are strongly depleted in the interaction layer (β-layer, see Figure 1). The thickness of the interaction layer was found to range between 20 and several hundreds of µm at 170 °C but was less then ± 0.5 µm at 16 °C. An influx of elements initially absent in the glass (e.g. H, K, Mg) was demonstrated. A third group of elements seems to be inert and remains nearly undepleted (e.g. Al, Si, Ti, Cr, Zr, Fe, Th). At more prolonged interaction times congruent dissolution seems to become the dominating corrosion mechanism.
- The leaching resistance of the Pamela type glasses (SAN60, SM58, SM513) is found to be slightly better than that of the Cogema type glasses (SON58 and SON68).

The installation of the new test tubes 5b (type II, to be operated at 90 °C) and 10 (type III, 16 °C) has been delayed due to technical problems during the testing of the automatic He gas outflow system, which will be connected to the new tubes 5b and 10 to avoid an accumulation of inflowing clay water in the bottom end of the tubes. The same system will also be installed on the existing tube 8. As the connection of the outflow system to the tube implies an anoxic He atmosphere, the current samples on tube 8, which was running under oxic conditions, have been retrieved for surface analysis and new samples will be placed.

List of publications

- Cornélis B. and Van Iseghem P., 1992
  "In situ tests of canister and overpack materials in Boom clay : results after five years".
  Paper presented at the Corsendonk workshop "In-situ testing of radioactive waste forms and engineered barriers" October 13th-16th, 1992.

- Lodding A., Odelius H. and Van Iseghem P., 1992
  "Belgian HLW glasses after burial in Boom clay : elemental trends in leaching".
  Paper presented at the Corsendonk workshop.

- Van Iseghem P. and Chen H., 1992
  "In-situ interaction between waste glass and Boom clay - results after five years testing".
  Paper presented at the Corsendonk workshop.

- Van Iseghem P., Labat S. and Cornélis B., 1992
  "In situ tests on waste package materials in clay : concept and performance".
  Paper presented at the Corsendonk workshop.

Table 1 : Results of XRD analyses on corroded carbon steel samples ("x" = certain ; "?" = likely ; "??" = possible).

Phases		"Blank"	16 °C	90 °C	170 °C
magnetite	Fe_3O_4	x	x	x	x
hematite	αFe_2O_3	x	?	?	?
lepidocrocite	$Fe_2O_3.H_2O$	??	??	?	-
maghemite	Fe_2O_3	-	-	?	x
goethite	$\alpha FeOOH$	-	??	?	?
quartz	SiO_2	-	x	x	x
calcite	$CaCO_3$	-	-	-	?
pyrrhotite	$Fe_{(1-x)}S$	-	-	-	?

Table 2 : Overview of surface analyses on waste glass samples

	Cogéma type		DWK/Pamela type		
	SON58	SON68	SAN60	SM58	SM513
90 °C in-situ (2 y) (Tube 2)	SIMS	SEM EMPA SIMS	SEM EMPA SIMS	SEM EMPA	SIMS
170 °C in-situ (5 y) (Tube 1)	SIMS	SEM EMPA SIMS	SEM EMPA SIMS	SEM	SEM EMPA SIMS
16 °C in-situ (5 y) (Tube 4)	SIMS	SEM SIMS	SEM SIMS		SEM SIMS

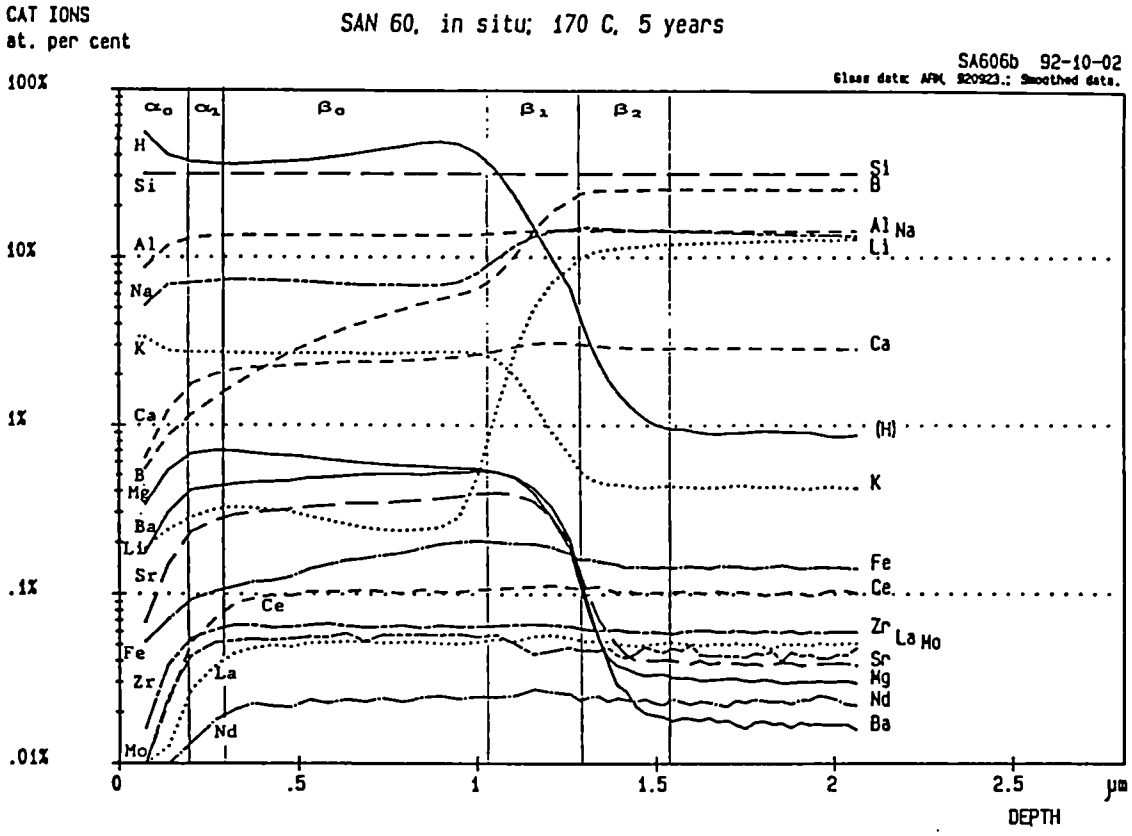


Figure 1 : SIMS in-depth profiles of element concentrations (Si-normalized), selectively leached Pamela-type glass.

Title	The Performance of Cementitious Barriers in Repositories
Contractor(s)	AEA Technology (co-ordinator)
	Riso National Laboratory
	Bundesanstalt fur Material Forschung und Prufung
Contract N°	FI2W-0040
Duration of Contract	from 1 May 1991 to 30 April 1994
Period covered	1 January 1992 to 31 December 1992
Project Leader	Dr A.W. Harris (AEA Technology)

OBJECTIVES AND SCOPE

Cementitious materials are likely to be used in waste disposal facilities to help retain radionuclides by acting as chemical and physical barriers to migration. Current source term calculations are based on the homogeneous repository assumption. This is unlikely to be true in reality since cementitious materials will crack, leading to inhomogeneities in mass transport and chemistry. The impact of these inhomogeneities will depend upon reactions with groundwater that can lead to the healing of cracks, to the benefit of the physical barrier performance, and sealing of concrete surfaces, to the detriment of chemical performance.

Validated models and supporting data for the physical and chemical barrier performance of cementitious materials will be developed and used to examinethe simpler models employed in safety assessments. The mechanisms of crack healing within cementitious materials under repository conditions will be investigated. An assessment of the impact of cracks and inhomogeneities on the source term will be made. The reference repository will be based on the designs provided by Nirex and hence will be realistic.

WORK PROGRAMME

Task 1 - Healing of Cracks by Cementitious Materials

Sub-task 1.1 - Experiments on crack healing
Sub-task 1.2 - Modelling of crack healing

Task 2 - Cement-groundwater interactions

Sub-task 2.1 - Diffusive cement-groundwater interactions
Sub-task 2.2 - Perfusive cement-groundwater interactions
Sub-task 2.3 - Modelling cement-groundwater interactions

Task 3 - Barrier Properties of the Inhomogeneous Repository

Sub-task 3.1 - Chemistry varying with position and time
Sub-task 3.2 - Effect of fissures on the source term
Sub-task 3.3 - Validation of source term model

PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

In the period under review, the study on the effects of cement-groundwater interactions on the diffusion of significant species were commenced and the work on perfusive interactions were extended to include simulated groundwaters, as opposed to pure water. Some problems were encountered due to the unexpected reduction in material permeability during interaction with groundwater (caused by the formation of magnesium hydroxide). This has extended the timescales necessary for individual experiments considerably and has necessitated a reduction in the number of experiments which will be performed. In order to compensate for this, additional work will be carried to characterise the specimens which have been used in experiments.

The computer simulation of the perfusion experiments has been extended to incorporate the effect of groundwater. Comparison of experimental data with the predicted results indicates that equilibrium may not be achieved. This is also indicated by some analyses of the specimens on completion of the experiments. The effects of perfusion will be studied in more detail using additional materials prepared during the period under review.

Progress and results

Task 1 - Crack Healing

Sub-task 1.1 - Experiments on crack healing

A calcium bicarbonate solution, flowing slowly through a crack in concrete, precipitates calcium carbonate by reaction with hydroxyl ions from the cementitious material. For narrow cracks, those less than 0.1 mm wide, the result is often that the crack is "healed" and the flow diminished or ceased. For wider cracks, those greater than 0.2 mm wide, a more typical result seems to be the formation of a protective layer on the inner surface of the crack. This layer prevents an efficient contact between the solution and the bulk of the cementitious material.

Eight new experiments with crack filling were performed and gave results confirming previous experience. Somewhat surprisingly, a crushed specimen with a relatively coarse crack structure also gave indications of crack closure. The layer of precipitate was shown to be an efficient barrier to the out-diffusion of hydroxyl ions. The precipitates were examined using scanning electron microscopy (SEM). In some cases the crack was also characterised by micro-tomography at BAM in Berlin. Even narrow cracks could easily be distinguished using the tomography technique but the layers of precipitate could not be as readily identified.

In two of the experiments de-ionised water was used instead of the calcium bicarbonate solution. With water the result was expected to be simple leaching of the cementitious material leading to a coarsening of the crack. However, closure of narrow cracks was also observed in this experiment. It is proposed that the reason for this is the re-distribution of some of the components of the cementitious material, although the inclusion of a minor amount of carbon dioxide in the water cannot be excluded.

The leaching of caesium-134 radiotracer from two specimens exposed to a flow of either calcium bicarbonate solution or water alone has been investigated. The leaching curves show that the caesium leaching is only slightly influenced by the formation of a carbonate layer during the flow of the bicarbonate solution. A similar effect has been observed for the leaching of alkali metals, sodium and potassium, from the cementitious material. It appears that the small quantity of hydroxyl ions leached from the cementitious material through the

precipitate layer is dependent on the leaching of an equivalent quantity of alkali metal cations.

Sub-task 1.2 - Modelling of Crack Healing

A model of the crack filling process is under development but is still at a relatively early stage. The out-diffusion of calcium, sodium and hydroxyl ions from the cementitious material and the in-diffusion of $(HCO_3)^-$ and $(CO_3)^{2-}$ ions are modelled using a numerical technique. It is important that the diffusion of the various major ions are treated simultaneously. Due to the high mobility of the hydroxyl ion, this species will dominate the migration process and will influence the diffusion of the other ions via the electro-neutrality requirement. The precipitation reactions in the surface layer result in very steep concentration gradients and the reactions function as an efficient barrier to the release of calcium hydroxide from the cementitious material.

Task 2 - Cement-groundwater Interactions

Sub-task 2.1 - Diffusive Cement-groundwater Interactions

In the case of a repository designed to provide containment of radionuclides through the provision of highly alkaline conditions, the chemistry of water flowing in cracks be a significant factor in determining the performance of the repository. The formation of reaction layers on the surfaces of cementitious materials adjacent to cracks will influence the interaction between the material and the water flowing in the crack. The principal types of mineral which might contribute to the formation of reaction layers have been identified as calcium carbonate, formed through the effect of dissolved carbon dioxide gas, and magnesium hydroxide, precipitated from magnesium-bearing groundwater. The former process is known as carbonation.

The impact of the reaction layers formed by interaction with reactive groundwaters on the diffusion and sorption properties of cementitious materials is being assessed. Initial work has concentrated on the reactions of the Nirex reference backfill. A series of specimens have been carbonated by exposure to carbon dioxide saturated water. The formation of magnesium-bearing layers is being studied both by exposure to magnesium chloride solution and to similar solutions saturated with carbon dioxide. It has been observed previously that a duplex layer is formed if both carbon dioxide and magnesium ions are present. The impact of the formation of reaction layers on the migration of species into the aqueous phase has been determined by measuring the uptake (sorption and diffusion) of tin and caesium radiotracer species from solution.

Carbonation for a period of 50 days gave rise to an increase in the rate at which tin was removed from the solution. Continued carbonation to give an accumulated exposure of 120 days did not change the rate of tin uptake. In contrast, the rate of uptake of caesium was reduced after carbonation. It has been observed previously that caesium is only poorly sorbed by cementitious materials and the reduction in the uptake of this species can be attributed to a reduced diffusion coefficient in the reaction layer compared to the pristine reference backfill. This seems to be inconsistent with the observed increase for tin. It has been proposed that the uptake of tin has been enhanced due to additional sorption capacity in the reaction layer.

Sub-task 2.2 - Perfusive Cement-groundwater Interactions

The interaction between groundwater and cementitious material during the flow of the solution through the pore structure of the material may lead to the deposition of reaction products within the pore structure and the preferential dissolution of certain minerals, in

particular portlandite (calcium hydroxide). This may give rise to preferential flow pathways within the material and consequently reduce the effective sorption and pH buffering capacities of the backfill.

Initial experiments were performed using the reference backfill grout and pure water. Typical results are illustrated in Figure 1, including the predictions derived from the modelling work described under sub-task 2.3. The pH was initially buffered to a value of 12.5 by the dissolution of calcium hydroxide and subsequently decreased as the CSH phase was leached. The permeability of the material was observed to increase by a factor of about five during the perfusion of 12 l of water. This volume of water corresponds to about 300 times the volume of the specimen and simulates long periods of leaching by groundwater flow. The increase in permeability was accompanied by a decrease in strength and it is obvious that such excess leaching gives rise to an increase in the fractional porosity of the material through the dissolution of the solid material.

Subsequent accelerated leaching experiments have been performed using a saline groundwater simulant. In contrast to the case of pure water, the permeability was observed to decrease by an order of magnitude after approximately 2 l of solution had been perfused. Examination of the specimens indicated that magnesium hydroxide had precipitated and it was assumed that this material had significantly occluded the specimen surface. Continued leaching gave rise to a decrease in compressive strength which was accompanied by an increase in the fractional porosity of the material.

The pH of the simulated groundwater was buffered to a value of about 12.4 and the observed calcium concentration in the eluate was consistent with the dissolution of calcium hydroxide. The variation in eluate chemistry with volume perfused is illustrated in Figure 2, including the predictions derived from the modelling work described under sub-task 2.3. The measured calcium concentration is increased above that expected for the dissolution of calcium hydroxide by the additional contribution from the calcium in the groundwater. The magnesium initially present in the groundwater was completely removed by the precipitation of magnesium hydroxide. Examination of the specimens using differential scanning calorimetry demonstrated that calcium hydroxide was present in the material when the eluate chemistry was no longer being buffered by the dissolution of this phase. This has been attributed to either preferential leaching (flow being effectively excluded from some of the specimen volume) or a limitation in the migration of calcium through some of the other mineral phases which might surround particles of calcium hydroxide.

Leached specimens have been examined using scanning electron microscopy. When a comparison with unleached material is been made, very little difference can be detected. It was not possible to definitely demonstrate the presence of calcium hydroxide in the leached material. Additional materials are being prepared to further the investigation of the leaching of calcium hydroxide.

Sub-task 2.3 - Modelling cement-groundwater interactions

The interaction of groundwater and cement mineral phases during flow within the pore structure is being modelled. The initial models have been set up to simulate the through-flow experiments carried out under Sub-task 2.2. The models will be used to interpret the experimental data. In particular, it is expected that the groundwater-cement interaction will at some stage become limited by the formation of depleted-layers around mineral phases and the formation of reaction products. At this stage the pH buffering and calcium dissolution into the solution will deviate from expectations based on the absolute calcium content and calcium-silicon ratio of the material. It is hoped that this will lead to an assessment of the true buffering capacity of the material and the potential for the formation of preferential pathways.

Typical groundwaters will contain significant quantities of a number of species which can play a part in the formation of imhomogeneities, in particular dissolved carbon dioxide, which will form calcium carbonate, as considered in Tasks 1 and 2.1. In addition, the concentration of magnesium may be significant since the substitution of magnesium for calcium in the portlandite phase gives brucite. This is a relatively insoluble mineral which buffers the pH at a value significantly less than those given by calcium-bearing phases.

For the demineralised water case, the model predicts a similar amount of buffering to that observed experimentally; a predicted value of 0.14 mol of calcium leached as compared with a measured value of 0.16 mol. The predicted variation in calcium concentration in the eluate with perfused volume is broadly similar to that observed but falls more steeply - the calcium is released more slowly than is predicted, as is shown in Figure 1. It is suggested that this is due to a dis-equilibrium between the solution and the solid phase, perhaps caused by a retardation of calcium by a rim of CSH gel around calcium hydroxide particles.

The modelling of the leaching of cement by groundwater predicts a complex series of mineral dissolution and precipitation reactions. Despite this complication, a general agreement between observation and prediction can be achieved, as shown in Figure 2. The model tends to over predict the calcium concentration in solution compared with the experiments. Similar reasons to those proposed for the discrepancies in the demineralised water case probably apply. The model also predicts the precipitation of calcium carbonate (calcite) throughout the experiment. This has not been confirmed by observation due to the difficulty of distinguishing precipitated calcite from the aggregate in the material.

Task 3 - Barrier Properties of the Inhomogeneous Repository

Sub-task 3.1 - Chemistry varying with position and time

The large-scale development of inhomogeneities within a repository may result in groundwater flow being substantially or completely confined to cracks. A simple model of the interaction of the interaction between the water flowing in the crack and surrounding backfill was developed as part of the work carried out during 1991 /1/. This model was simplified to the extent that only a single chemical process was considered; the dissolution of calcium hydroxide. The analytical model is not able to simulate the potential of reaction layers on crack surfaces to hinder the interchange of aqueous species between the water flowing in the crack and the backfill.

This simple analytical model has shown that cracks may exert a significant influence on the evolution of pH of the groundwater exiting a repository and hence may affect the retention of radionuclides. During the current year the development of a more advanced model capable of dealing with this situation has commenced.

The advanced model of the behaviour of cracked media is essentially a two-dimensional version of the CHEQMATE code also used in a one-dimensional form in Task 2.3. This model will allow the incorporation of a full set of chemical reactions including the dissolution of the various cement minerals as well as the dissolution and precipitation of other minerals. The model is currently undergoing verification and validation tests.

Sub-task 3.2 - Effect of fissures on the source term

The results of the experimental and modelling work undertaken thus far indicate that significant differences may arise between a repository source term based on the assumption of homogeneous chemistry and one which incorporates the effects of inhomogeneities. For

example, the time evolution of the repository chemistry is significantly different if a proportion of the groundwater flow is confined to cracks. It is intended that the interaction with source term modelling will be extended and suggestions will be made as which effects should be incorporated and how this might be achieved.

References

/1/ ATKINSON, A., Nirex Safety Study Report NSS/R287 (1991) (draft).

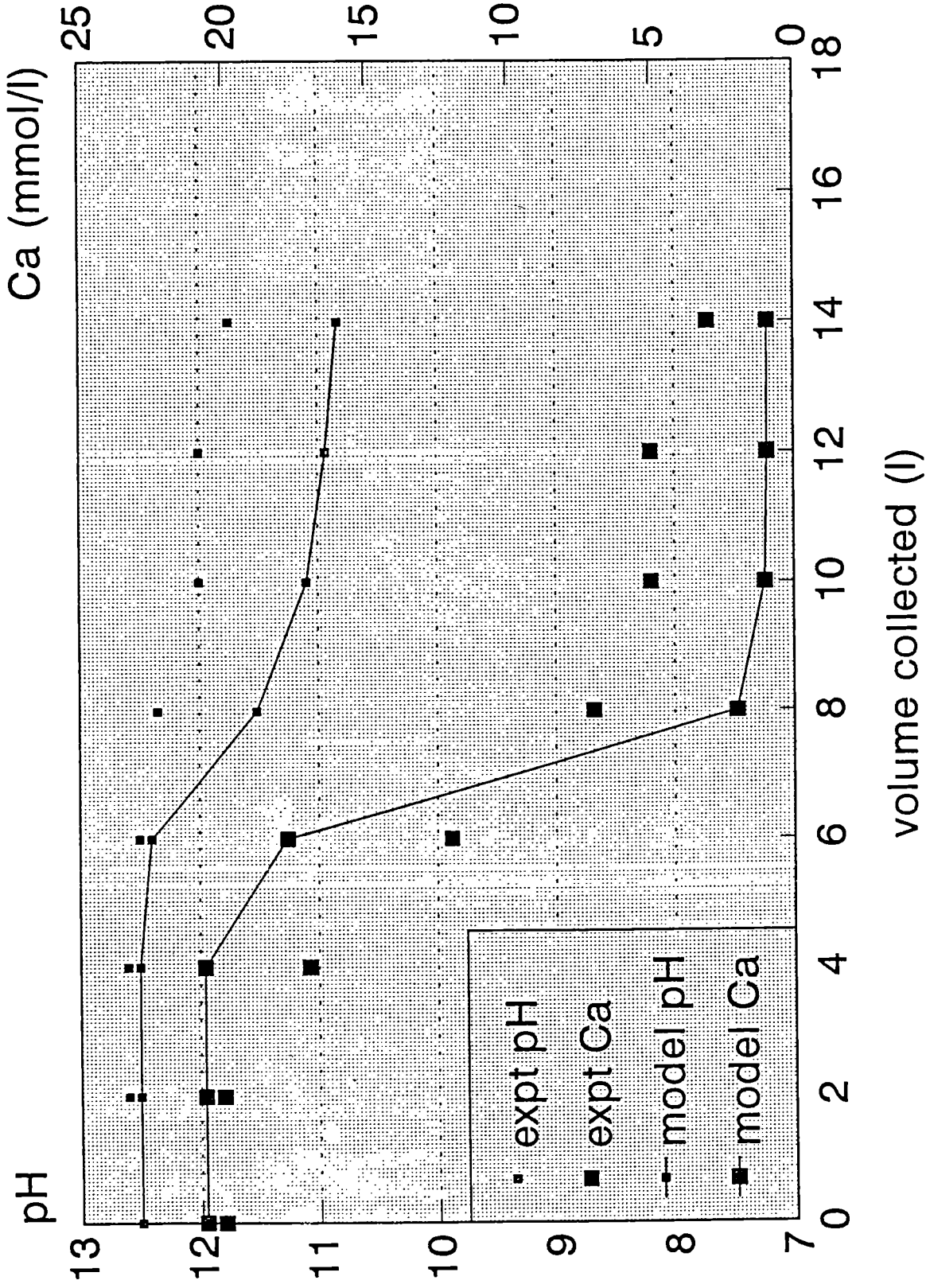


Figure 1 Comparison of predicted and measured eluate calcium concentration for the perfusion of demineralised water through reference backfill.

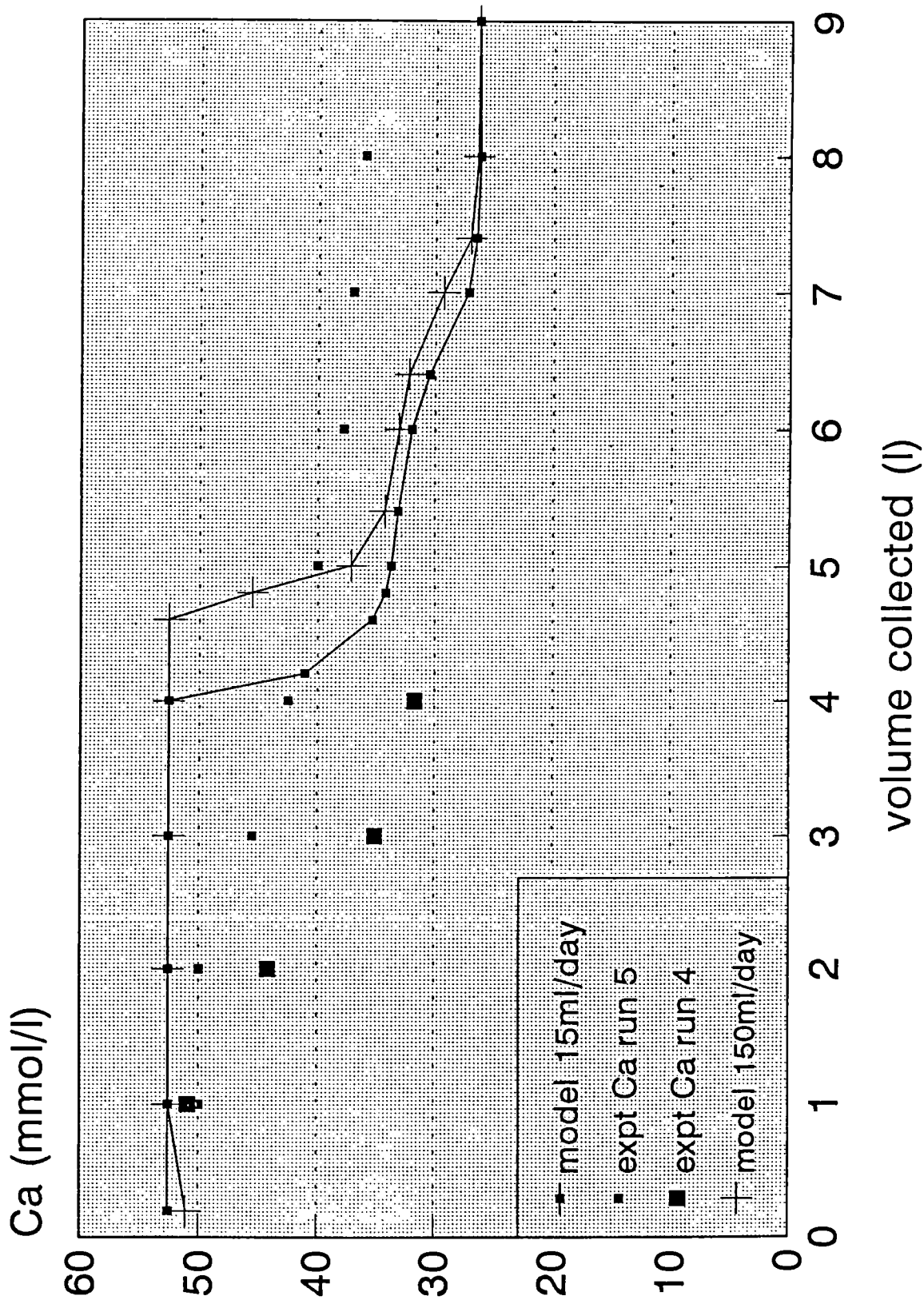


Figure 2 Comparison of predicted and measured eluate calcium concentration for the perfusion of simulated groundwater through reference backfill. The initial concentration in the groundwater is about 25 mM.

Title : **Determination of Fissile Material by Neutron Transport Interrogation**
Contractors : Forschungszentrum Jülich (KFA)
SCK/CEN Mol
Contract No: FI2W/0010
Duration of contract : 1 November 1991 to 31 October 1995
Period covered : 1 January 1992 to 31 December 1992
Project leader : Dr. R. Odoj

A. OBJECTIVES AND SCOPE

This research is concerned with non-destructive assay techniques for fissile material determination in waste material mainly in waste drums. The starting point for development work was an assay system at the KFA for fissile material determination by active neutron interrogation with an Sb-Be neutron source. In this assay system the fission neutrons were discriminated from the source neutrons by their transport properties in hydrogenous material. The neutron count rate was composed of a source term and a second term proportional to the fissile material content of the investigated sample. The system directly determines all the fissionable nuclides U-233, U-235, Pu-239, Pu-241. It required shieldings due to the approx. 2 E12 Bq Sb-124 and had detection limits between 1 mg and 1 g fissionable material depending on sample size and matrix composition.
Neutron transport calculations at CEN/SCK Mol are intended to achieve a theoretical understanding and an improvement of the assay system with different neutron sources by modelling the neutron transport properties in the waste drum and the assay system. A replacement of the Sb-Be neutron source by other low energy neutron sources, such as Am-Li, will lead to an assay system with minimum shielding requirements and constant source strength (Am-241, t1/2 = 432.6a, Sb-124, t1/2 = 60.3d). As an additional advantage there is no need for a reactor to reactivate the Sb. The replacement of the Sb-Be neutron source by Am-Li is therefore an important objective of this research. Passive neutron emission mainly results from spontaneous fission in Pu-238, Pu-240, Cm and Cf isotopes.
Counting these neutrons gives additional information on the presence of transuranic elements in the waste matrix. Effective recording and evaluating of these neutrons is another objective of this research. The aim of the final assay system is an easy-to-use and reliable instrument for the estimation or determination of the fissile material content of various packages, mainly waste drums.

B. WORK PROGRAMME

B.1. Checking and optimization of the Sb-Be system by comparison with neutron transport calculations.

B.2. Active neutron interrogation with other neutron sources, in particular Am-Li and comparison with neutron transport calculations.

B.3. Modification of the system for passive neutron counting capabilities.

B.4. Test and performance of the active/passive neutron assay system with actual samples, mainly waste drums from the nuclear fuel cycle.

C Progress of work and important results

C1 The Sb-Be system

The original system (Fig. 1) is based on transmission geometry. The neutron source, the drum and the neutron detector are placed in a straight line. The one-dimensional transport calculation (Fig. 3) shows a strong decrease in the interrogating neutron flux over 2 to 3 decades when it penetrates the drum, especially for the low-energy Sb-Be and Am-Li neutron fluxes. The number of induced fission neutrons from those parts of the drum which are close to the detector is accordingly low. This strong degree of attenuation is in principle confirmed by various attenuation measurements as compiled in Fig. 4. It is greatly influenced by the hydrogen content of the drum coming e.g. from water in the case of a cement waste form. An improvement was therefore expected from a setup as shown in Fig. 2. The source and the detector are close to each other. Fission neutrons with a high probability of detection arise in a region of high source neutron field. Various parts of the drum surface are accessible by rotating the drum. More details are reported for the Am-Li system (C2). Experimental work with the Sb-Be system is not possible at present since the research reactor DIDO is not ready for activation of Sb-124. The calculation of two-dimensional neutron fields as relevant in Fig. 2 is in preparation.

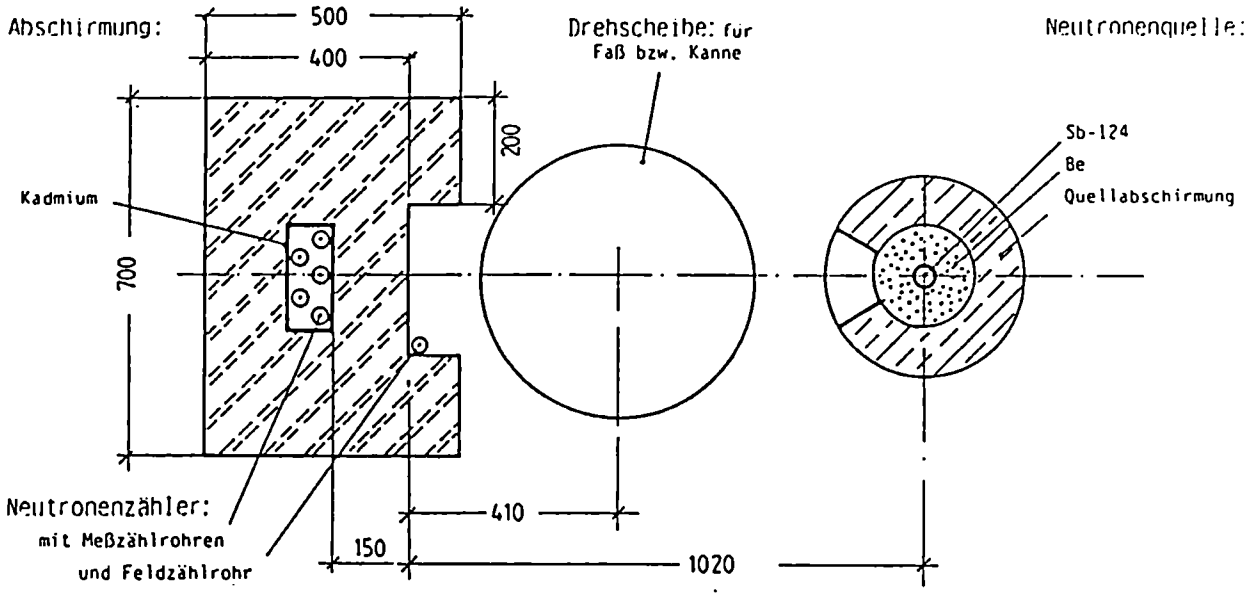


Fig. 1: Active neutron system with Sb-Be source for waste drums and transmission geometry

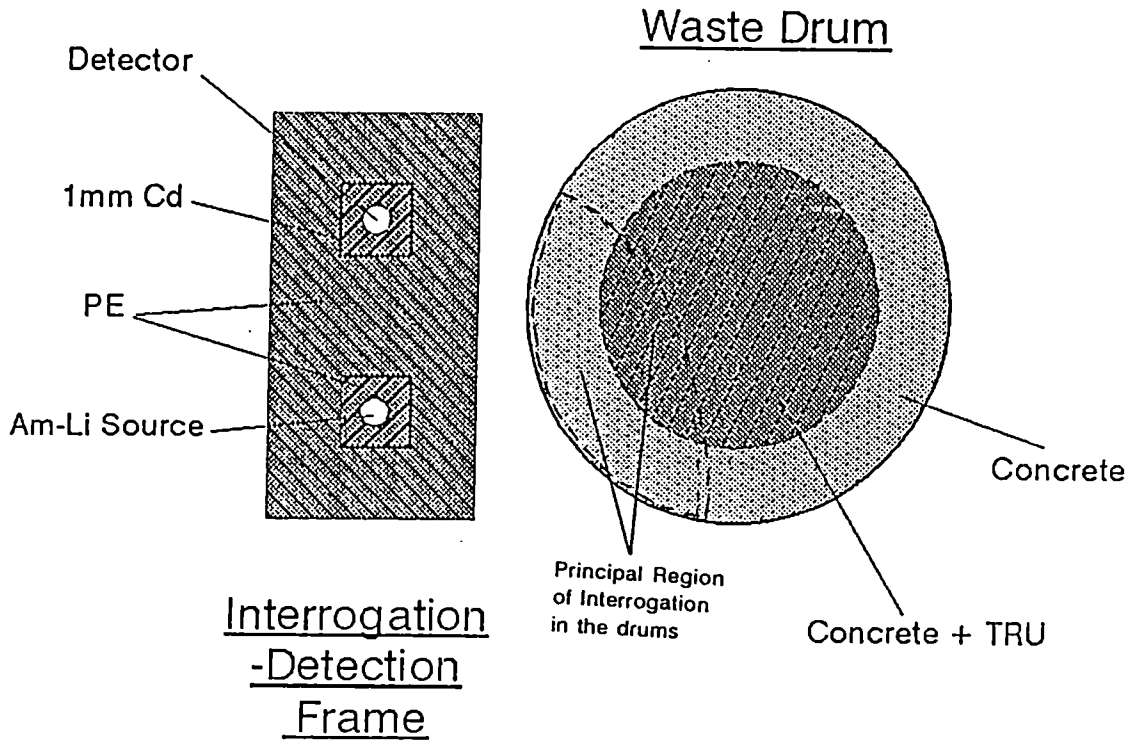


Fig. 2: Active neutron system (with Am-Li source) for waste drums with two-dimensional configuration

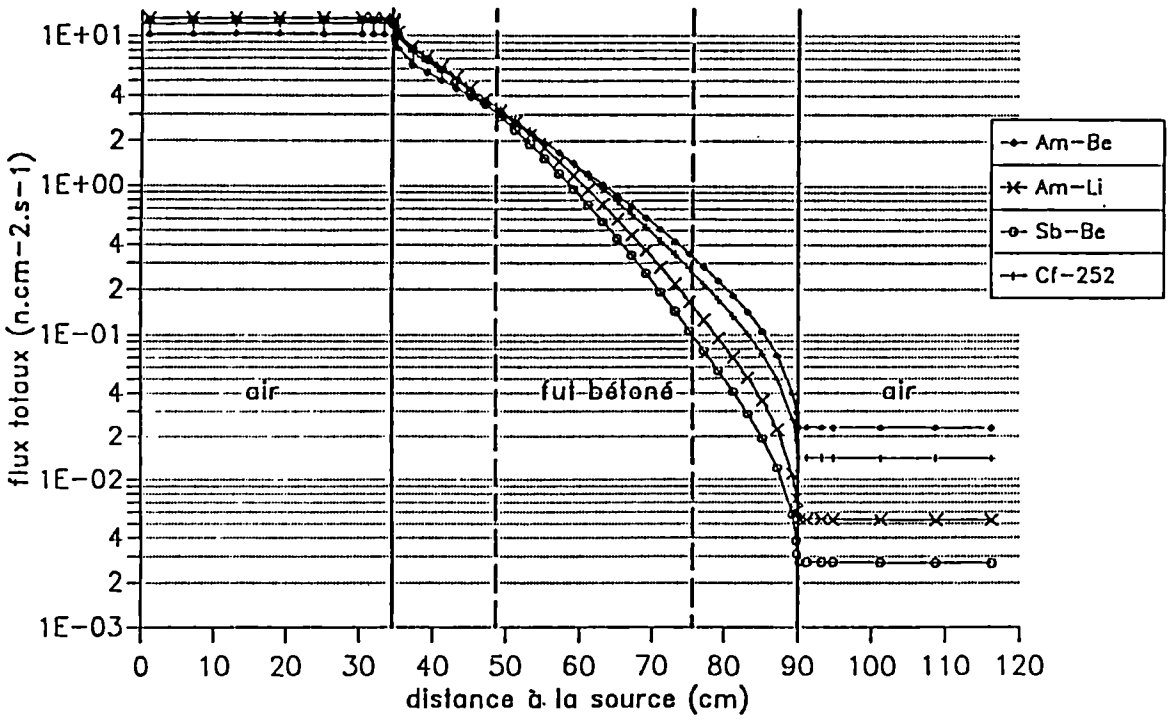


Fig. 3: Variation of the total neutron flux of different neutron sources over the diameter of the waste drum

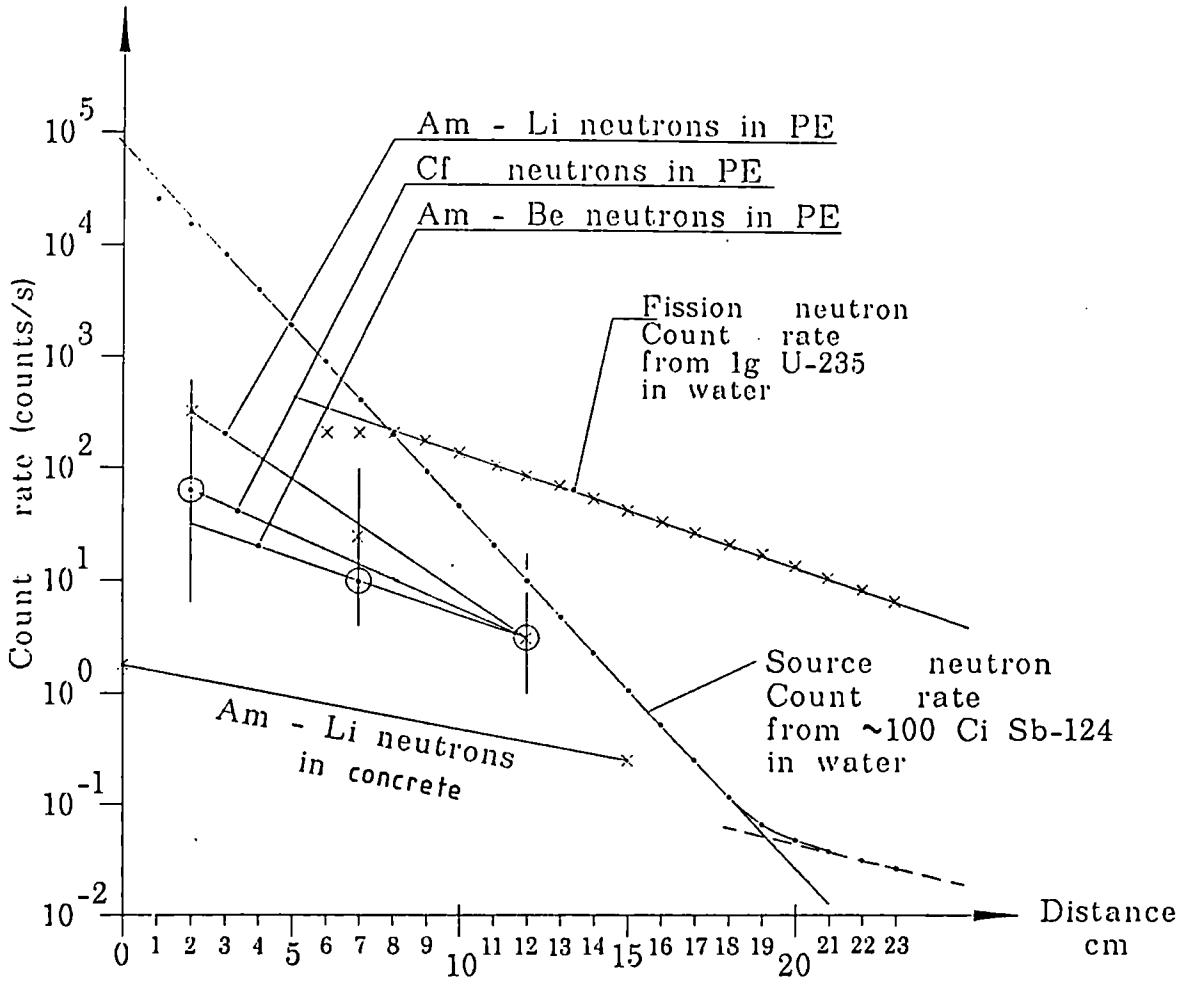


Fig. 4: Variation of neutron count rate (proportional to the thermal neutron flux) in different media and for different sources

C2 The Am-Li system

The average neutron energy of the Am-Li source of 0.5 MeV is clearly below the average energy of fission neutrons (2.5 MeV) but far above 0.025 MeV, the energy of Sb-Be neutrons. The use of the Am-Li source together with a fast neutron detection system, as used with Sb-Be neutrons and mentioned in C1, needs appropriate tailoring of the source neutron field with the following aims:

- minimize the number of source neutrons at the detector position
- maximize the thermal neutron flux and the induced fission neutrons in the sample.

Detailed experiments with different scattering and moderating materials led to the present layout shown in Fig. 5.

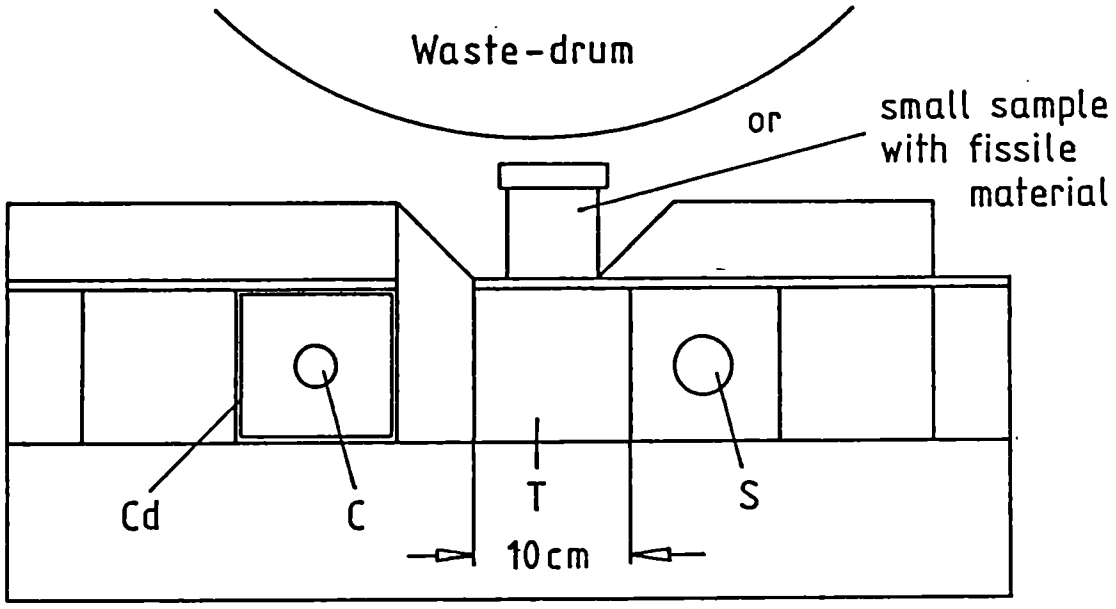


Fig. 5: Active assay system with an Am-Li neutron source

C = He-3 neutron counter (10 bar)
Cd = 1 mm Cd shield
S = Am-Li neutron source (3 Ci Am-241, 1.4 E5 N/s)
T = exchangeable transport layer (PE or Al)
All other material except the sample or waste drum = PE

The use of aluminium (Al) as a transport medium at the location marked T in Fig. 5 provides higher neutron fluxes than polyethylene (PE). On the other hand, the fast neutron contribution from the source neutrons is relatively high. Table I shows significant count rates from typical sample types for transport layers T of PE or Al.

Table I

Neutron count rates in fissile material interrogation with two different transport layers T (Al or PE) for a slightly modified set up as shown in Fig. 5

Am-Li source	Count rate with	
Type of sample	PE transport layer	Al transport layer
no sample	0.70 s^{-1}	3.17 s^{-1}
200 g graphite	0.71 s^{-1}	3.16 s^{-1}
200 g graphite + 1 g U-235	0.82 s^{-1}	3.43 s^{-1}

The neutron fluxes were calculated by the one-dimensional neutron transport code DTF IV. The results are shown in Table II.

They indeed show PE and Al as the most promising transport media. The thermal fluxes (detector values) are relatively high with the Al transport layer. On the other hand the fast flux is less attenuated as with the PE transport layer where the thermal fluxes are lower as well.

As a whole the results of the measurement and the transport calculation are considered to be in good agreement. Some further investigation on the mixing of Al and PE for a more efficient assay system is still planned.

The following Table III gives results with the present layout (Fig. 5) and U-235 or Pu as the fissile material in small samples

Table II: Flux attenuation between source and detector, calculation by transport code

Total discrimination layer between source and detector					
Configuration	21 cm PE	18 Cm PE + 1 mm Cd + 3 cm PE	3 cm PE + 10 cm Fe + 8 cm PE	3 cm PE + 10 cm Al + 8 cm PE	3 cm PE + 10 cm graphite + 8 cm PE
Source values*					
Total flux	1.000	1.000	1.001	0.973	1.118
Thermal flux	0.55	0.55	0.55	0.53	0.59
Fast flux	0.26	0,26	0,27	0,27	0.23
Detector values*					
Total flux	8.3 E-04	5.8 E-04	7.3 E-03	1.0 E-02	3.4 E-03
Thermal flux	7.1 E-04	4.5 E-04	6.3 E-03	9.0 E-03	3.0 E-03
Fast flux	3.8 E-05	3.9 E-05	2.8 E-04	2.8 E-04	8.4 E-05
Flux attenuation					
Total flux	1203	1728	136	98	298
Thermal flux	774	1208	86	58	197
Fast flux	6657	6526	935.8	941	2753

* The fluxes are given in $n.cm^{-2} . s^{-1}$

Table III

Active assay of 1 g U-235 and 1 g Pu in small samples containing graphite

Type of sample	Without neutron source	with Am-Li neutron source
No sample	0.03 s^{-1}	1.71 s^{-1}
200 g graphite		1.78 s^{-1}
200 g graphite + 1 g U-235		2.03 s^{-1}
approx. 10 g graphite + 1 g Pu*	1.20 s^{-1}	3.13 s^{-1} = 1.20 s^{-1} + 1.93 s^{-1}

* Pu: 78 % Pu-239, 19 % Pu-240, 1.4 % Pu-241, 1.6 % Am-241

Table III shows that U-235 and Pu lead to approximately the same increase in the active neutron count rate. As a first approximation, the active system actually determines the total fissile content. According to its Pu-240 content, the Pu-sample gives rise to a significant increase in the passive neutron count rate, which is slightly less than but in the same order as the increase in the active count rate. According to the much lower background count rate, as compared with the source count rate, the detection limit is better in passive counting. The passive count rate can also be measured separately as is reported in the following section.

C3 Passive neutron counter for the detection of spontaneous neutron emitters

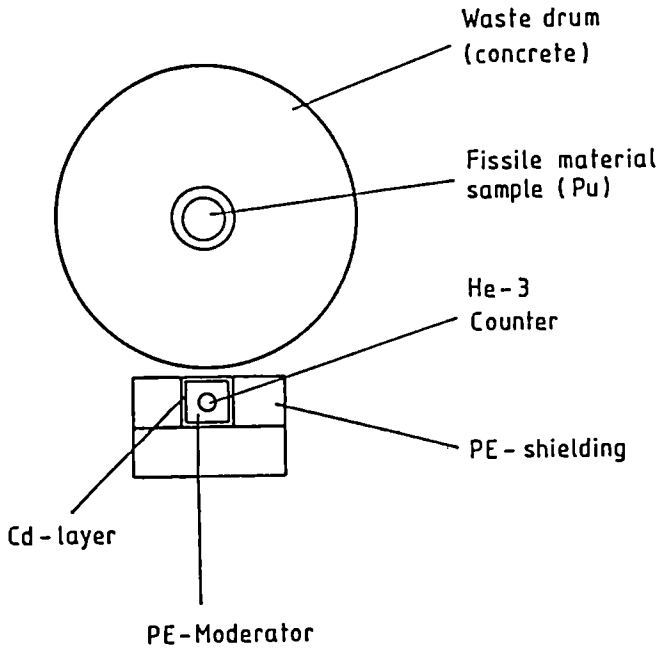


Fig. 6: Passive neutron counter for fissile material detection

The passive neutron counter shown in Fig. 6 is a reliable instrument for efficient neutron detection. Depending on the neutron background of the measuring site, lateral PE shielding (usually 5 cm PE) is necessary. Table IV shows the performance of this instrument and its shielding capabilities in a hot cell laboratory site (outside the cell).

Table IV
Neutron detection from 1 g reactor Pu (777 mg Pu-239, 193 mg Pu-240, 14 mg Pu-241, 16 mg Am-241) in the axis of a 200 l drum filled with concrete (ρ = 2 g/cm^3) with an assay system according to Fig. 6

Sample Description		Neutron Count Rate
Background of the counter	PE shielding 0 cm PE shielding 5 cm PE shielding 10 cm	180/1000 s 120/1000 s 100/1000 s
1 g Pu in the centre of the drum		663/1000 s = 0.56 s^{-1} + 0.1 s^{-1}
3 · σ of background		30/1000 s
54 mg Pu		Quantity of pure Pu equivalent to 3 · σ

A detection limit of 54 mg Pu (reactor-grade) in a waste drum is reached with this counting system in typically 1000 s measuring time.
This type of neutron counter cannot discriminate between fission neutrons and (α, n) neutrons. In view of the fact that reactor waste may emit up to 100 times as many fission neutrons from Cm than from Pu, the contribution of (α, n) neutrons is considered to be less important. If the composition and contribution of different neutron emitters is known, a detection limit of 1 mg Pu seems possible for waste material.
Passive neutron counting is therefore considered to be a very promising characterization method for reactor waste. The quantitative evaluation of the measured count rate with respect to the Pu-content requires knowledge of the isotope vector of the fissile content. Experiments with this type of neutron counter will be continued.

D Conclusion

Research is stimulated by intensive cooperation and exchange of results between the experimental and the theoretical working group. It is in good agreement with the proposed time schedule. The possible layout of the final assay system can already be envisaged.

Title: **Inventory and Characterization of Important Radionuclides for Safety of Storage and Disposal. Correlation with Key Nuclides that are Easy to Measure in Typical Waste Streams.**

Contractors: CEA Cadarache, GRS-Cologne, ONDRAF/NIRAS, ENEA-Saluggia, ENRESA, AEA-Dounreay.
Contracts No: FI2W-CT90-0034 and FI2W-CT91-0109
Duration of contracts: 01.05.91 - 30.04.95
Period covered: January 1992 - December 1992
Project leaders: A. Raymond, CEA-Cadarache (co-ordinator for contract no FI2W-CT90-0034) - W. Müller, GRS-Cologne (co-ordinator for contract no FI2W-CT91-0109) - R. Gens, ONDRAF/NIRAS - M. Gili, ENEA-Saluggia - A. Morales, ENRESA - A. Yates, AEA-Dounreay.

A. OBJECTIVES AND SCOPE

This contribution to the characterization of the inventory of radionuclides important for the safety of storage and disposal includes a study of the main radioactive waste streams produced in each participating country.

This programme has three main objectives:

- checking and standardisation of operational analytical methods for application to real samples of the main waste streams,
- development of some alternative analytical methods for long-lived radionuclides,
- computation of correlation factors for critical radionuclides to easily measurable key nuclides, through the analysis of the main waste streams of the contractors.

Only low- or intermediate-level wastes originating from both power plants or reprocessing plants will be considered in the framework of these contracts.

Samples of each selected waste stream will be analysed for both easy-to-measure key nuclides and critical isotopes as determined by the national safety assessment of each contractor.

B. WORK PROGRAMME

B.1: Organization - Coordination

- review of the initial situation of the participants
- list of information to be collected and studied
- final choice of the list of samples and of radionuclides to be analysed
- setting up of a working organization

B.2: Development of analytical methods

- improvement of the current procedures for long-lived radionuclides
- search for alternative methods as compared to those based on radiation detection
- development of special procedures for the recovery of radionuclides from solid, low-level technological wastes

- drafting of some common analytical methods

B.3: Measurement of wastes from nuclear power plants (CEA, ONDRAF/NIRAS, ENRESA, GRS)
- collection of available results from previous measurements
- waste sampling and analysis for the radioactive content
- collection of the necessary relevant information
- transfer of the corresponding results into the data bank
- assessment of the results and discussion of possible further improvements concerning the number and the representativity of samples

B.4: measurement of wastes from fuel reprocessing plants (ENEA, AEA)
- construction of a non-destructive measurement system for gamma-emitters (ENEA)
- preparation of simulated waste drums
- tests of the measuring equipments with simulated wastes
- intercomparison of the tests results (AEA and ENEA)
- destructive and non-destructive measurement campaigns on reprocessing wastes
- assessment of the results and discussion of possible further improvements

B.5: data evaluation and processing (GRS)
- evaluation of available results from previous measurements
- continuous evaluation of the results relevant to this programme
- implementation of data banks for wastes from both reprocessing and nuclear power plants
- development of statistical tools for evaluation of results
- development of individual evaluation codes for each participant
- testing and optimisation of codes for routine applications

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

AEA-Dounreay and ENRESA-Madrid, which have been taking part to this programme since the beginning, have been officially incorporated early in 1992 in the framework of a new contract (n° FI2W-0109) with GRS as the co-ordinator.
According to schedule, in 1992 the first experimental results were obtained from France, Spain, Belgium and U.K. The relevant data have been transfered to the data bank and a first evaluation by GRS has been initiated.
The measurement work has been supported by the development or the improvement of analytical methods for some long-lived, hard-to-measure radionuclides so as to have more reliable and more sensitive techniques.
Two workshops have been organized and were attended by all the contractors so as to harmonize and to coordinate this work.

Progress and results

CEA-Cadarache

Development of analytical methods

CEA focused its development work on the analysis of Cs-135 and I-129 and of the mineralization of solid waste samples.
Cs-135, a pure beta-emitting fission product, was successfully analysed in ion-exchange resins from the primary circuit of a P.W.R. In a first step, a specific extraction of caesium isotopes was achieved by liquid-liquid extraction with a crown-ether associated with Na-tetraphenylborate. Then the Cs135/Cs-137 ratio was determined by thermal-ionization mass-spectrometry. The lower limit of detection was around 6 Bq/l in liquid samples and 0.12 Bq/g in solid samples. A significative Cs-135 activity of 1 Bq/g, giving a Cs-135 to Cs-137 activity ratio of $3.4*10^{-6}$, was obtained on one of these samples.

For the measurement of I-129, the procedure which was developed relies on the preconcentration of this radionuclide as silver iodide prior to its measurement by accelerator mass spectrometry (AMS). Indeed, very low activities were expected in waste samples from N.P.P. and this technique is several orders of magnitude more sensitive than classical radiation detection methods.
This procedure was applied to the analyses of two primary coolant and of one evaporator concentrate samples from CRUAS N.P.P. As expected, very low activities (around $2*10^{-3}$ Bq/l) were found in primary coolant samples.

For the solubilization of solid samples, micro-waves techniques offer an interesting alternative toward acidolysis with conventional heating because they are safer, faster, more reproducible and more efficient.
The CEA procedure, which involves the use of an open-type micro-waves digester, has been applied to the solubilization of ion-exchange resins, of filter cartridges and of evaporator bottom sludges. With this system, a quantitative recovery of the volatile radionuclides is achieved by connecting a series of acid and alkaline bubblers to the digestion flasks.

Analyses of waste samples

In 1992, CEA-Cadarache carried out the radiochemical determination of over 30 radionuclides on seven waste samples from Cruas N.P.P.: two primary coolants, three ion-exchange resins, one evaporator concentrate and one filter cartridge. The corresponding results were transfered to the GRS data bank. This represents about 20 % of the CEA scheduled analyses.

ENEA-Saluggia

Gamma scanning system

1992 has been dedicated to the construction of a gamma scanning system that ended in November. The first tests illustrated the necessity of improvement in two directions:
- to avoid vibration problems of the HPGe detector,
- to correct the vertical speed of the detector as a function of the dead time.

Analytical techniques

In order to validate the results obtained with the gamma scanning system from the measurement of technological waste drums, a comparison with destructive analyses is required. In this respect, the radioactive content has to be put into solution and the initial method (complete dissolution of the material) in sulfuric acid was found to be inadequate. Preliminary experiments have shown than an other approach - leaching of the waste by nitric acid - should be more adequate, as long as the subsequent analysis of radionuclides is concerned.
A method for the measurement of Tc-99 has been developed. It relies on a selective chromatographic extraction of Tc followed by its measurement by liquid scintillation counting.

Correlated activities

Ventilation filters of the EUREX plant were placed inside 220l. drums. During these manipulations, representative samples were taken and analysed for total alpha, total beta and gamma content. The results will be compared to those obtained with the gamma scanning system.
The radiochemical analyses of reprocessing liquid wastes corresponding to 4 different campaigns were initiated. The results will be used as a comparison test with those resulting from destructive analyses of technological waste drums.

ENRESA

Development of analytical methods

ENRESA/CIEMAT focused their development work on the analyses of I-129, Tc-99, Ni-59, H-3, C-14, Pu-241, Sr-89/Sr-90 and on the dissolution of ion-exchange resins.
For the analysis of Tc-99, it was verified that there is no significative loss of this radionuclide during the dissolution step of solid wastes. On the contrary, any subsequent concentration step by evaporation was found to be responsible for the loss of as much as 89% of Tc-99, bringing to the conclusion that this radionuclide must be analysed directly in the mineralization solution.

The same observation was made concerning I-129. For the determination of this radionuclide, CIEMAT tested a direct procedure by low-energy gamma-ray spectrometry, without any previous chemical separation. A detection limit around 20 Bq/g was calculated for used ion-exchange resins doped with I-129, after mineralization.
For the analysis of Ni-59, CIEMAT tested a conventional method based on a selective extraction with dimethylglyoxime and on a measurement by low-energy gamma-ray spectrometry. A detection limit around 50 Bq/g was calculated for ion-exchange resins after mineralization.
For the determination of H-3 and C-14 in I.E.R. and evaporator concentrates, CIEMAT tested the applicability of a combustion method in comparison with acidolysis. The combustion method was found satisfactory in that it is fast (6 minutes per sample), efficient (chemical yield above 90% for both radionuclides) and selective (separation ratio for H-3/C-14 above 99%).
For the analysis of Pu-241, the procedure that was developed relies on the isolation of Pu by an anion exchange method followed by a measurement by liquid-scintillation counting, the chemical yield being determined through the alpha-ray spectrometric measurement of a Pu-236 or Pu-238 tracer.
For the determination of Sr-89/90, CIEMAT tested a liquid-chromatographic separation method based on the use of commercially-available columns filled with a 18 crown-6 derivative as the stationary phase. In comparison with more conventional precipitation methods, this procedure showed comparable chemical yields and decontamination factors but was found much faster and much simpler to use.
For the solubilization of IER , CIEMAT tested a closed-type micro-waves digester. This instrument was not found to be as effective as the open-type model used by CEA-Cadarache (see above) and this technique was thus abandoned to the profit of conventional heating methods.

Analyses of waste samples

ENRESA/CIEMAT completed the analysis of over 20 radionuclides in seven ion-exchange resins from Cofrentes N.P.P. and of eight evaporator concentrates from Cofrentes and Garona N.P.P. All the corresponding results were transfered to the GRS data bank. This represents about 40% of the ENRESA/CIEMAT scheduled analyses.

ONDRAF/NIRAS

Development of analytical methods

ONDRAF/NIRAS-CEN/Mol focused their development work on the analyses of I-129, Tc-99, Nb-94, Sr-90, H-3, U and Pu isotopes.
For I-129, the method that was tested on dissolved wastes samples involved a separation on an anion-exchange column followed by a purification step using a redox adjustment and liquid-liquid extraction. A total recovery yield around 60% was obtained. Further improvements are in progress.

For Tc-99 also, the tested method relies on anion-exchange chromatography and on liquid-liquid extraction. Here, a total recovery yield around 83% was obtained. Further improvements are in progress.
A combined procedure for the radiochemical separation of Tc-99 and I-129 was also evaluated at CEN-Mol. Involving the same principles as the separate methods but with different conditions and reagents, this procedure gave recovery yields around 96% for Tc-99 and 90% for I-129, and detection limits of 5 Bq/l in primary coolant samples for both isotopes. The implementation of this method is now being investigated for acid samples resulting from the dissolution of solid wastes.
For Nb-94, the developed procedure is based on liquid-liquid extraction with tributyl phosphate and of a measurement by gamma-ray spectrometry. The experimental detection limit in liquid samples was around 50 Bq/l.
For Sr-90, the developed procedure is based on a concentration step with an oxalate salt, on a liquid-liquid extraction with dicyclohexano-18-crown-6 and on a measurement by liquid scintillation counting. As this procedure was found tedious and not fully satisfactory, further improvements are in progress.
For the Uranium and Plutonium isotopes, two isotope-dilution mass-spectrometric methods after a chemical separation were investigated. Detection limits were found to be in the range between 10^{-2} and 10^{-6} Bq/l for the Uranium isotopes, and between 3 and 10 Bq/l for Pu-239 and Pu-240.
For Tritium, the procedure investigated by CEN-Mol on waste solubilization solutions is based on the dissociation of tritiated water with calcium followed by an oxidation back to water of the produced hydrogen. The detection limit was found to be 30 Bq/l when a 5 ml sample aliquot is used.

Analyses of waste samples

Nine samples of evaporator concentrates and six samples of ion-exchange resins have been transfered to CEN-Mol. The dissolution and the gamma-ray spectrometric analysis has been completed on eight samples of evaporator concentrates and on one sample of ion-exchange resins. The specific measurements of C-14, Ni-63, Cs-135 and U isotopes have also been completed on four samples of evaporator concentrates.

AEA TECHNOLOGY-Dounreay

Waste drums data

During 1992 results have been collected from the Dounreay segmented gamma scanner. Data sheets from 85 scans have been submitted to GRS for the data base. These drums all contain technological wastes from a fast reactor reprocessing plant. The in-house computer code "FISPIN" has been run to calculate the total activity of radioisotopes for each reprocessing campaign. For a particular drum, the FISPIN data is normalised to the measured Cs-137 and the relative activity calculated for 32 other isotopes and entered on a data sheet.

Destructive analysis

A method for opening and analysing selected 220 l. drums has been prepared. The drums will be opened in a tented facility and the contents loaded into 4 l. containers. After sorting into low and high activity, the contents of the high activity containers will be leached in 3M HNO_3 and the resulting liquid will then be analysed using various radioactive counting techniques.

GRS-Cologne

Although the results achieved so far in this programme are of intermediate nature, the following conclusions can be drawn:
The main causes for differences in the evaluated correlations are due to:

- lack of data
- different materials
- different activity concentrations
- different physical and chemical conditions
- different operating histories
- different physical and chemical behaviour of individual nuclides

These causes will be further investigated.
Differences due to different materials were minor for different plant designs. They often were observed in combination with changes in chemical treatment of the primary coolant. In these cases, a separation of these two parameters had to be postponed due to a lack of further information. For individual plants, however, marked differences in single correlations appeared that were attributable to either material differences or chemical treatment.
For individual nuclides a separate evaluation has to be performed between liquid waste streams (concentrates, resins) and solid waste streams (ashes, compacted wastes).
Additional investigations will be directed in future to identify the influence of fuel defects on the correlations.

Title: Construction and Testing of a Computer Tomography Assembly for Routine Operation

Constractors:	Forschungszentrum Jülich (KFA)
Constract No.:	FI2W-CT90-0009
Duration of contract:	from September 1991 - August 1995
Period covered:	01.01.1992 - 31.12.1992
Project Leader:	Dr. Reinhard Odoj
Executant:	Dr. Rainer Duwe

A. OBJECTIVES AND SCOPE

The product control office (PKS) of the BfS located at KFA has been appointed to perform quality control of rad-waste packages for the licensing authorities prior to disposal in an underground repository. This can either be achieved by nondestructive and/or by destructive analysis of the waste packages. The decisive criterion for acceptance is the knowledge of the specific activity of the conditioned waste and the total activity of the waste package. Determination of the specific activity and total activity is straightforward in the case of a homogeneous waste matrix of densities between 0.1 and 3 g/cm^3. It is strongly dependent on the μ/ρ values of the transmitting matrix for the registered gammarays. In the case of shielded structures or inhomogeneous fillings, the calculation must include shielding factors which range from 1 for homogeneous filling to 20. A better estimation of the shielding properties by computer tomography is the aim of this contract. The objective is a direct measurement of the distribution of and μ/ρ or μ in shielded structures and heterogeneous fillings of waste drums by attenuation measurement and computer tomography. The application of computer tomography (CT) the the γ-scanner "GERNOD" will be done in close cooperation with groups in KFA and BAM.

B. WORK PROGRAMME

B.1 Modified scanner with active gamma ray screening capability
- addition of a gamma source
- addition of count rate measurement/evaluation for CT application

B.2 Computer tomography for samples of uncommon composition and density distribution
- design of technical equipment
- suitable isotopic source
- software adjustment

B.3 Comparative test measurements

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The project started in the second half of 1991 with
- considerations for an extension of the existing gamma scanner for inclusion of computer tomography
- tests for the application of existing software programs on this computer.

The computertomography-program developed in KFA is using the arithmetic reconstruction technic (ART). The horizontal measuring slice is divided in a rast of up to 10.000 (100 x 100) quadratic fields (PIXEL), in which for each pixel the characteristic absorption coefficient μ is calculated.

The calculation is performed iteratively and corresponds a solution of a strongly underestimated equation system. Even after several iteration steps there is resulting only one approximation solution. The advantage of the algebraic methode in relation to the analytical reconstruction methode seems to need less projections (e.g. 16 angles) to get a satisfying picture.

Nevertheless a comparison between both reconstruction methods will be performed.

PROGRESS AND RESULTS

To measure the local resolution a test dummy was used (Fig. 1). The test dummy, fabricated from aluminium had different boreholes varying from 2 - 50 mm. The dummy was fabricated at DORNIER. The measurements were perfomed with an Ir-192 source in order to get some knowledges in the different kev regions at 300 keV, 470 keV and 600 keV (Fig. 2). The activity of the Iridium source was 3,7 TBq. The dead time of the AD-Converter in the multi-channel-analysator was about 50 %, caused by the high pulse rate.

As an example for the kind of registrated measurements the absorption curves of the test dummy at 8 angle positions were measured (measuring time 20 s and step with of 1 mm).

The interpretation of these measurements with 8 angle positions (Fig. 3) makes it possible to get to know the rough structure of the measuring object. Under the same measuring conditions measurements and interpretation were performed with 16 (Fig. 4) and 32 (Fig. 5) angle positions.

Concluding from these figures it is evident that an optimization of the resolution will be obtained with increasing angle amounts. For the measurements the peak sequence of Ir-192 at 296 - 316,5 keV were evaluated, as they produce the highest pulse rates.

For comparison, the peak sequences of Ir-192 at 468 keV and 588,6 - 612,5 keV were evaluated. Although the pulse rates are 3,4 resp. 8,8-times lower, the resulting reproduced picture gave good informations.

As result of these measurements it can be resumed:
- clefts of width < 5 mm
- holes of a diameter < 6 mm

can be clearly identified.

To demonstrate, that by mathematical treatment of the measuring datas with digital filtering methods, improvements concerning the reproduced pictures are possible, the measured absorption curves of the 32 angle measurements (peak sequence at 300 keV) were smoothed and after that the density distribution of the measuring body was calculated by the tomography-programme. The resulting plotting shows a more homogeneous picture (Fig. 6).

After finishing this basic investigations concerning the effectivity of our measuring- and mathematical system, the transfering to the mobile γ-scanning device "GERNOD" has to be performed. For this reson a sliding carriage was constructed and fabricated at MEC-company. On this sliding carriage (Fig. 7) the turn table of the γ-scanning device will be installed.

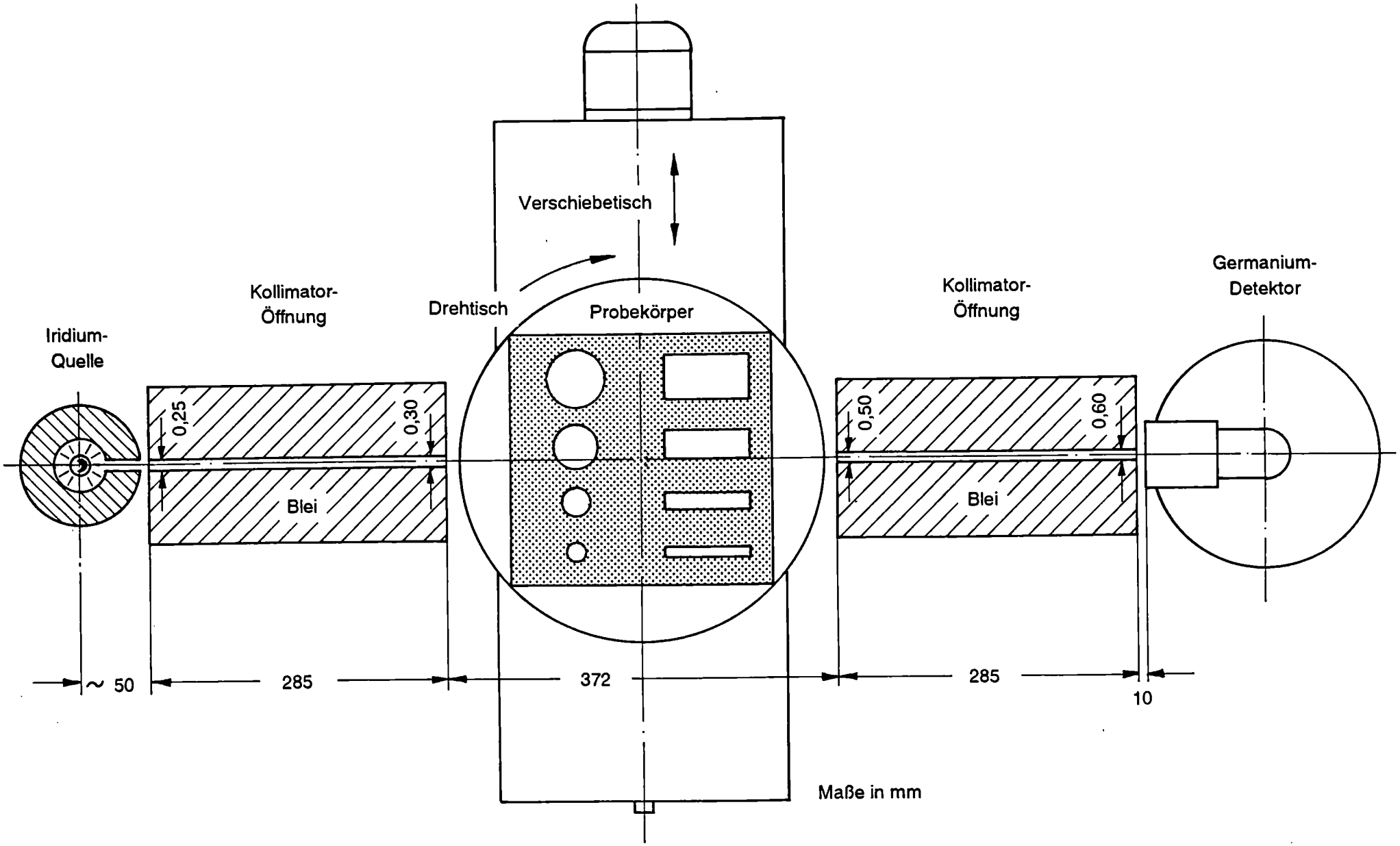


Fig. 1 : **Meßanordnung zur Transmissions-Computer-Tomografie**

(Blick von oben auf den Versuchsstand)

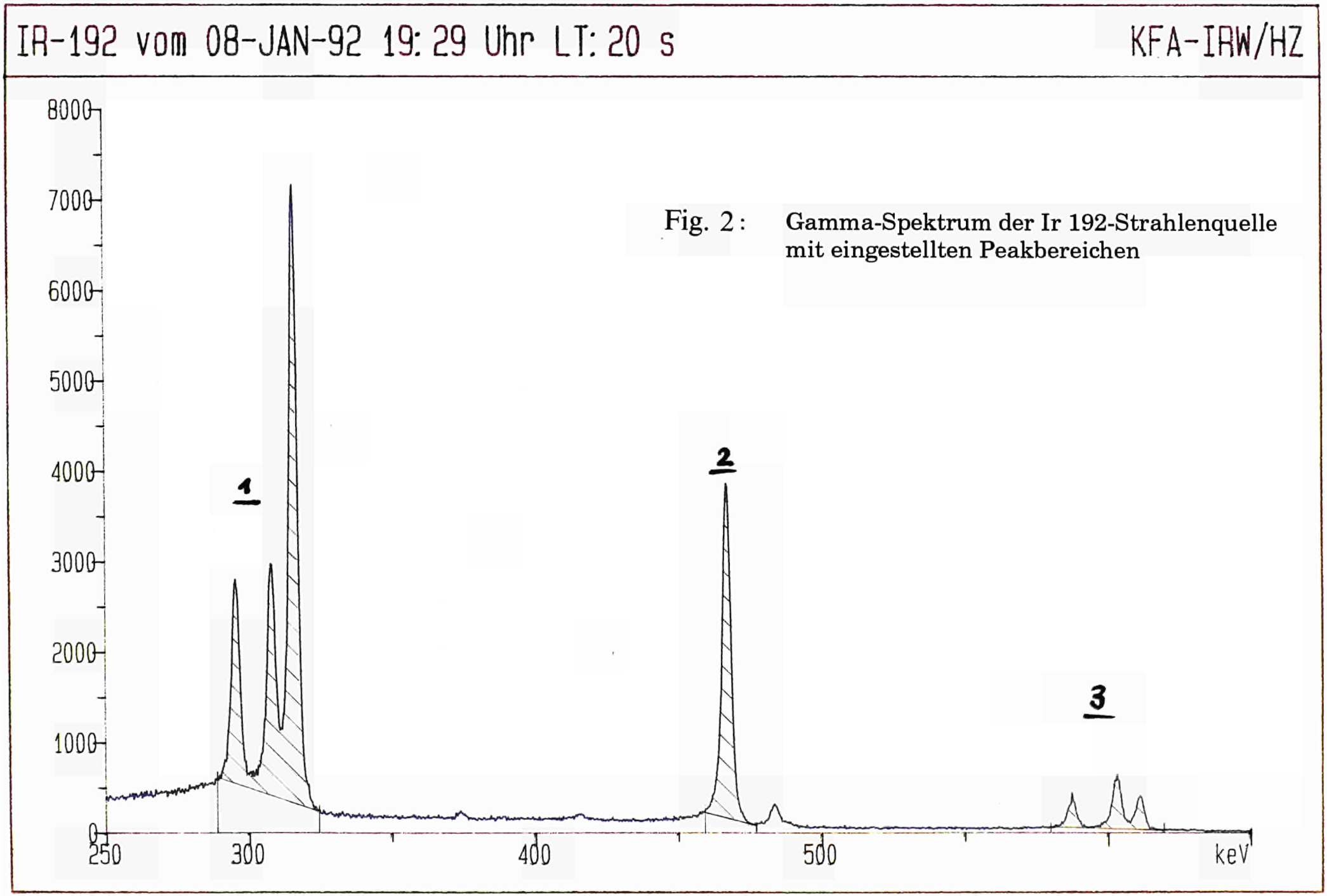


Fig. 2 : Gamma-Spektrum der Ir 192-Strahlenquelle mit eingestellten Peakbereichen

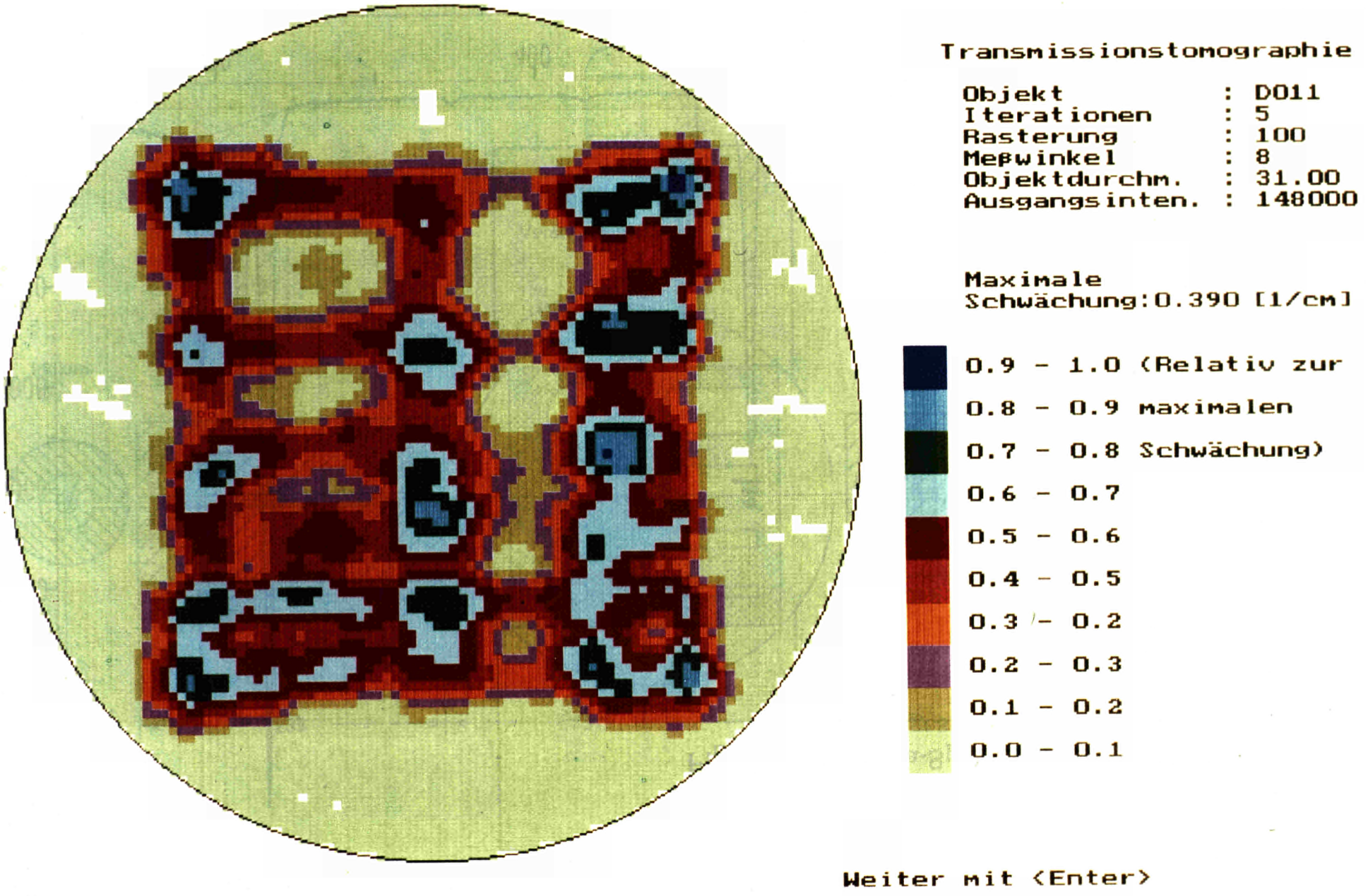


Fig. 3 : Dichteverteilung des Probekörpers Dummy_2 bei 300keV
8 Meßwinkeln - Schrittweite von 1mm

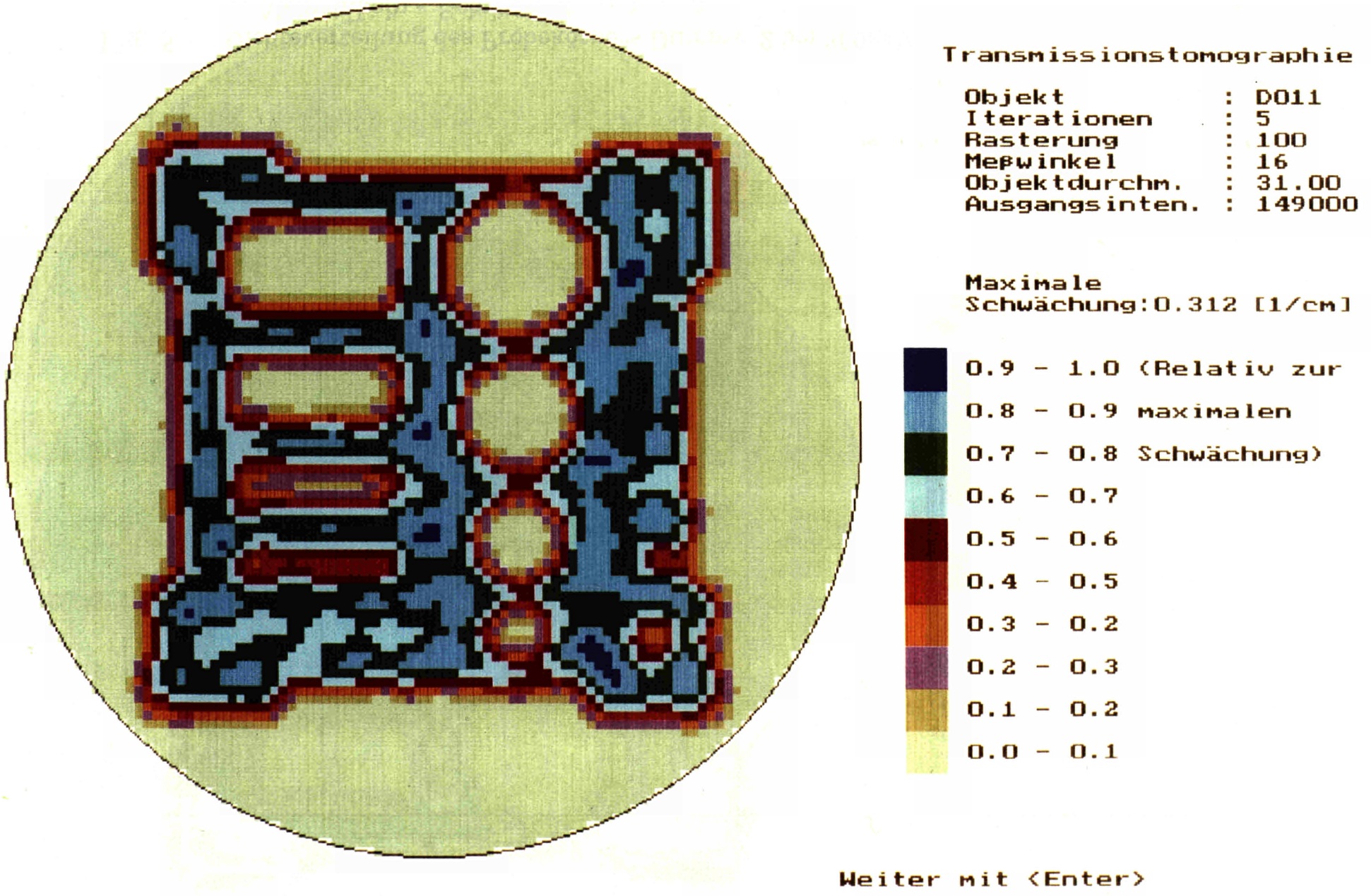


Fig. 4 : Dichteverteilung des Probekörpers Dummy_2 bei 300keV
16 Meßwinkeln - Schrittweite von 1mm

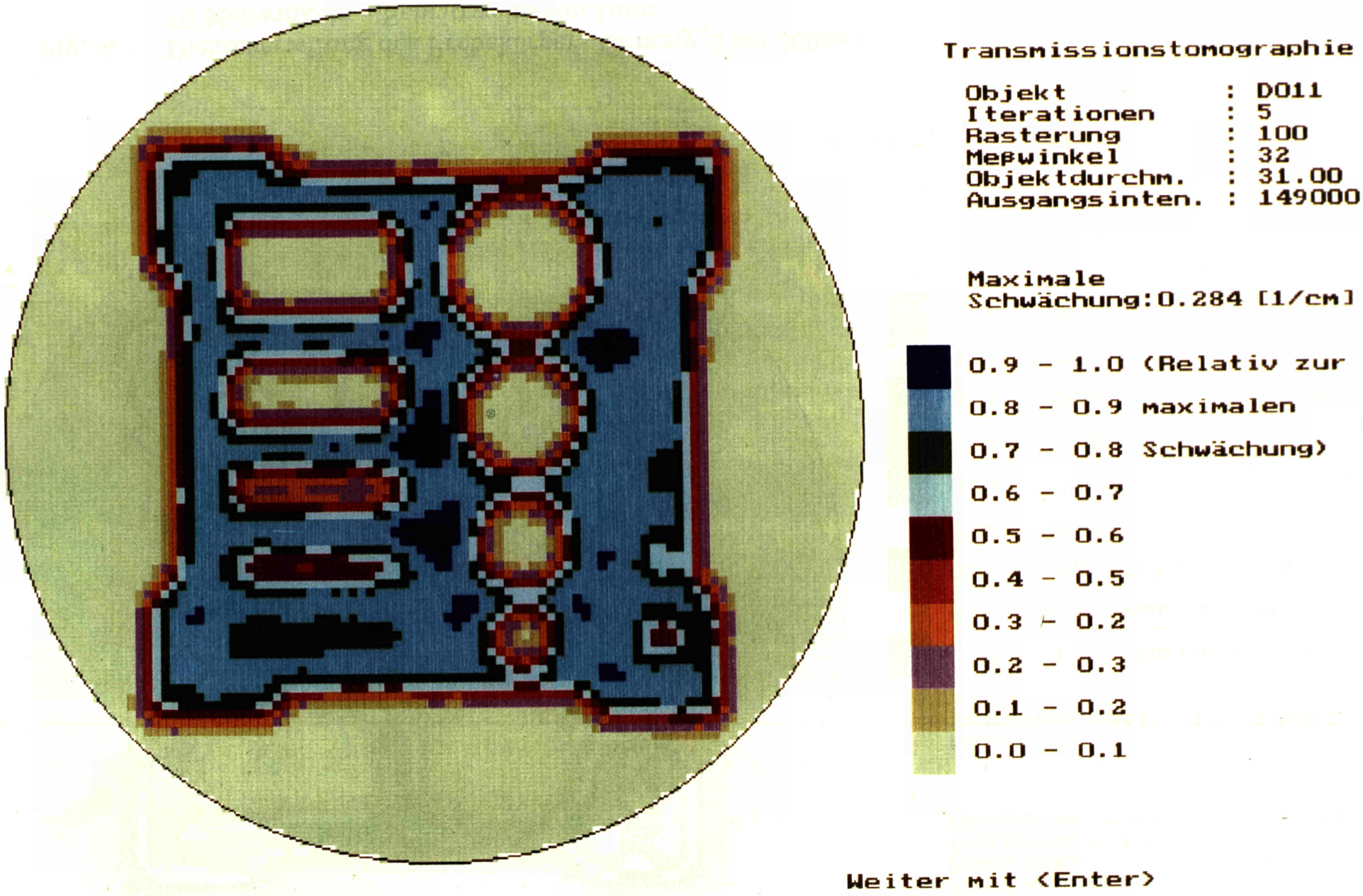


Fig. 5 : Dichteverteilung des Probekörpers Dummy_2 bei 300keV
32 Meßwinkeln - Schrittweite von 1mm

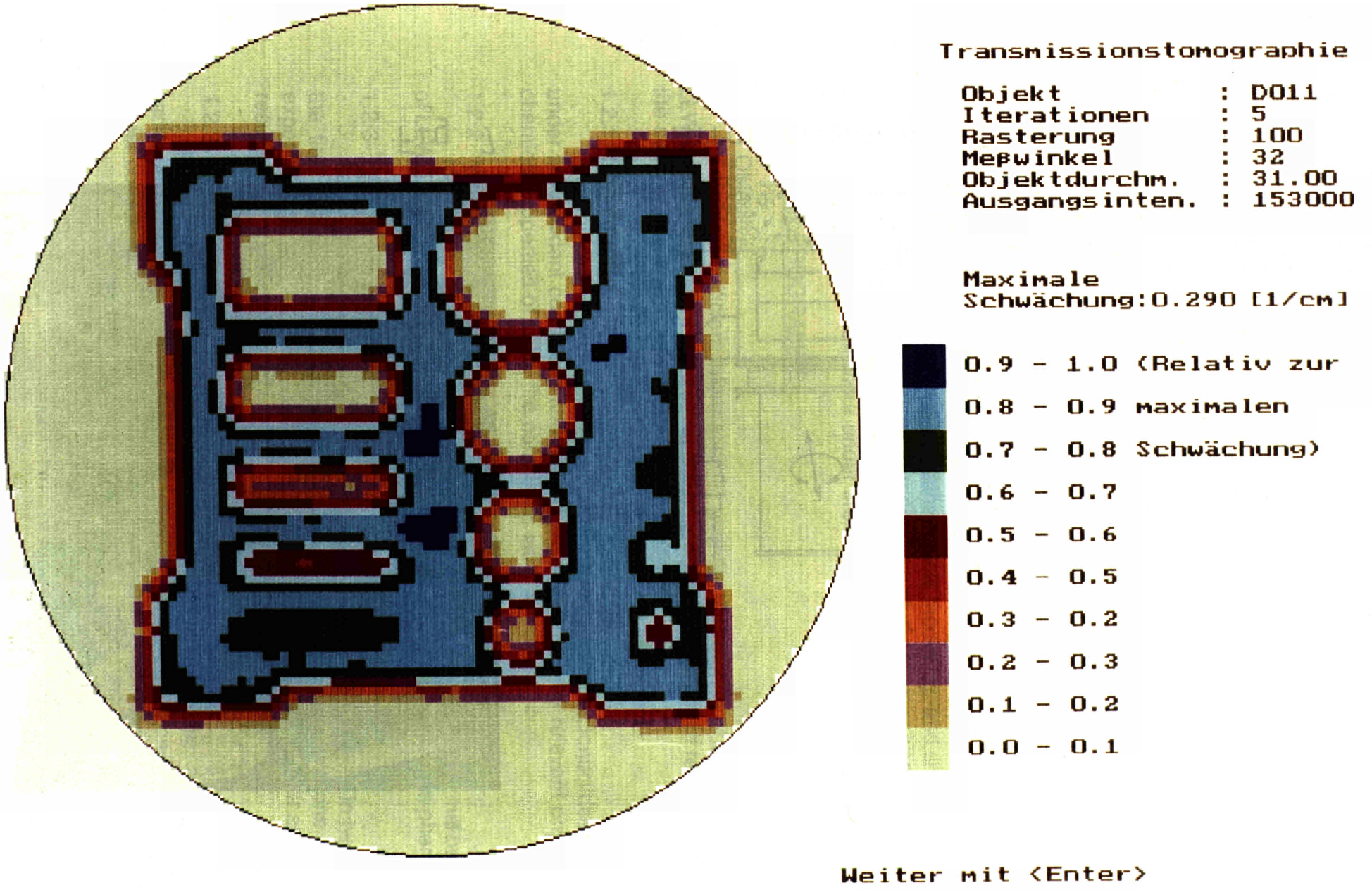
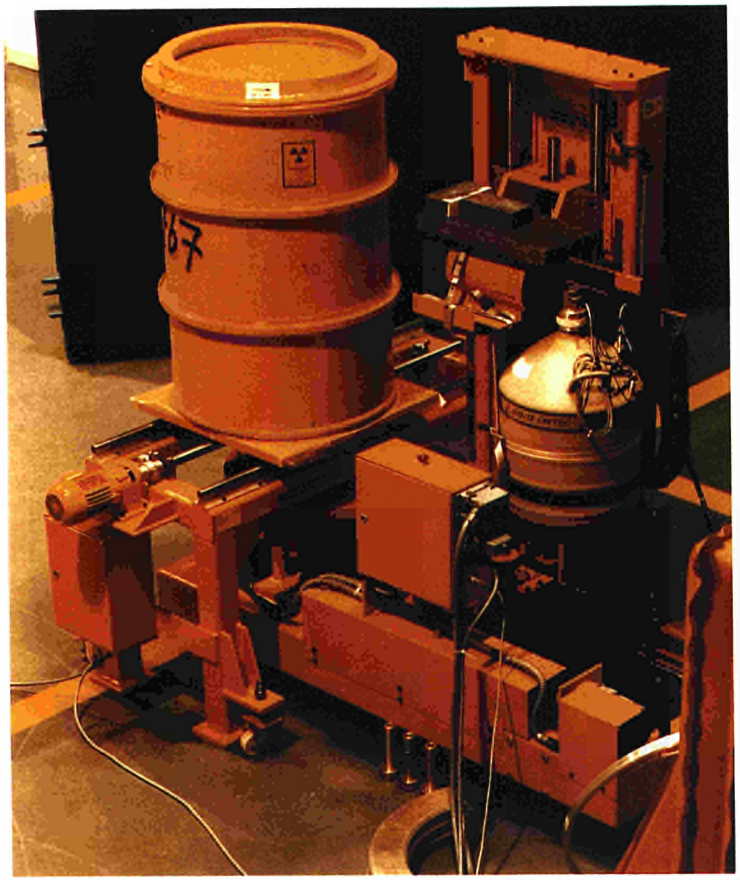


Fig. 6 : Dichteverteilung des Probekörpers Dummy_2 bei 300keV nach Glättung der Absorptionskurven 32 Meßwinkeln - Schrittweite von 1mm



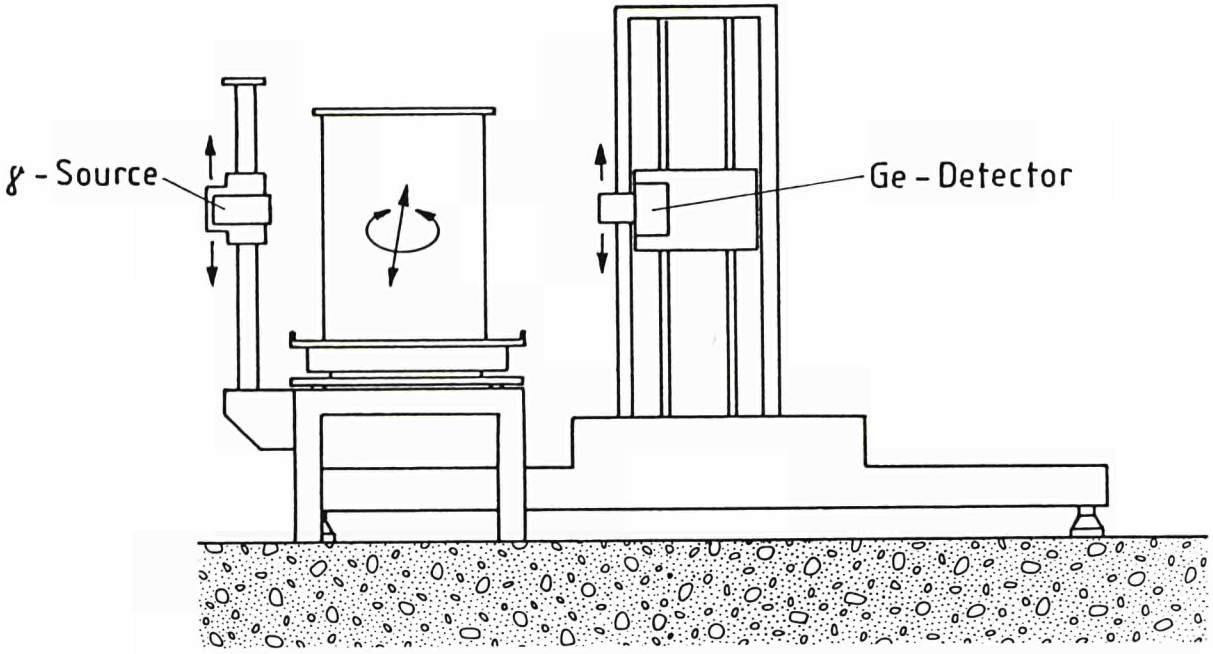


Fig. 7 : Arrangement for CT - Measurement

Title: Behaviour of Low Level Radioactive Waste Under Fire Accident Conditions

Contractor:	AEA Technology
Contract No:	FI2W/0014
Duration of Contract:	from 1st October 1991 to 30th September 1993
Period Covered:	1st January 1992 to 31st December 1992

A. OBJECTIVES AND SCOPE

The objective of the work to be undertaken within this project is to provide information on the release of radionuclides from low level waste (LLW) under fire accident conditions and to understand how these releases depend on the severity and characteristics of the fire accident. Mathematical models will be used to enable the response of packaged LLW under various conditions to be predicted.

Little information relevant to this topic is available. The approach to the project (based on large-scale inactive tests, mathematical modelling, and small-scale active experiments) is similar to that used in a previous study of immobilised intermediate level waste, but will take account of the special properties of LLW and its constituents that are relevant to its behaviour under fire conditions.

B. WORK PROGRAMME

1.1 Objective

To obtain sufficient information to quantify the release of radionuclides from LLW under fire accident conditions, and to understand how these releases vary with the severity and characteristics of the fire accident.

1.2.1 Literature Review

A literature review will be carried out on the release of radionuclides from LLW under fire accident conditions and related areas, such as the relevant physical and chemical properties of LLW, fire conditions etc.

1.2.2 Modelling Studies

Mathematical models will be developed and validated for the thermal behaviour of LLW, including heat and mass transfer, gas diffusion and combustion phenomena.

1.2.3 Large-Scale Testing

Large-scale thermal tests will be carried out on simulated LLW in two stages: the first to provide a basis for the modelling and to define conditions for active experiments; and second, to validate the models and provide a basis for applying the results to a range of situations.

1.2.3 Small-Scale Thermal Tests

Small-scale thermal tests will be made to determine the releases of radionuclides from radioactive samples of individual LLW components and mixtures, under conditions to be defined from the modelling work and large-scale tests.

C. PROGRESS OF WORK AND RESULTS OBTAINED

1. State of Advancement

The literature review has been completed. Mathematical modelling of the important situation where an unbreached box containing LLW pucks is exposed to an external fire is at an advanced stage. Codes are available for the study of single pucks directly exposed to fire, and relevant physical property measurements to provide data for the calculations have been made. The first tranche of large-scale thermal tests on supercompacted 200ℓ pucks of simulated LLW have been completed. Detailed plans have been formulated for small-scale active experiments to determine radionuclide release fractions, and the necessary equipment has been assembled.

In 1993 it is planned to complete development of the mathematical models, to carry out a further set of large-scale tests to support and validate the models, and to carry out active experiments on radionuclide release fractions under carefully chosen conditions. These last will be used, in conjunction with temperature and mass transfer data from the models and large-scale tests, to predict releases of radioactivity under fire accident conditions.

2. Progress and Results

2.1 Literature Review

The literature review has now been completed. The main results relevant to the release of radionuclides were noted in the 1991 Annual Summary Report. A new section has now been added on the behaviour of LLW under fire accident conditions. This considers information on the physico-chemical properties of components of LLW in relation to fire behaviour.

The products of decomposition of the organic materials present in LLW are very dependent on the temperatures achieved and on the availability of oxygen. Below 400°C, primary products are formed. Between 400 and 700°C, a wide range of products from secondary decomposition mechanisms appears; and above 700°C, formation of cyclic hydrocarbons, soot etc occurs.

Examples of reactions which may be relevant to the behaviour of LLW in fires include the following:

- The dehydrochlorination of PVC. This is rapid above 300°C and 75 organic decomposition products have also been detected.
- Polyisoprene (latex) decomposes to give a mixture of C_4 to C_{10} hydrocarbons, the composition depending on the temperature and the availability of oxygen.
- The pyrolysis of cellulose is a first order reaction giving a complex

range of products. Most available data relate to wood rather than to paper.

- Polyethylene decomposes by fragmentation of the chain. Under oxidative conditions, oxygenated and aromatic hydrocarbons are formed.

The information obtained will facilitate understanding of the mechanisms involved in the release of radioactivity from LLW.

2.2 Modelling Studies

Three aspects of fire behaviour need to be addressed in the current study: heat transfer in an array of supercompacted pucks contained in closed box; the pyrolysis of organic material in a puck exposed directly to fire and the associated heat and mass transfer; and the spread of fire from puck to puck.

In a box containing waste pucks which is exposed to a small external fire, heat transfer inside the box will take place by natural convection and by conduction through the box walls and the pucks. Only convection provides a sufficient rate of transfer to affect a substantial amount of waste. Numerical calculations for a 2D geometry have shown that, for representative conditions, temperature rises in the waste are small (less than 20C° in most of the volume). In these initial calculations, no direct thermal contact between the box floor and the base of the stacks of pucks was assumed. Preliminary indications are that greater rises in temperature (up to 200°C) are possible if limited contact (up to 25%) occurs. These calculations are being further refined.

The modelling of the pyrolysis of supercompacted waste containing mixed organic materials is complex. Decomposition will lead to the formation of volatile species which will migrate through the matrix. These may then ignite outside the pucks to provide an external flame enhancing heat transfer to the puck. The physical properties of the waste that affect heat and mass transfer (thermal conductivity, specific heat, permeability) will not only be temperature dependent but will also be extensively changed by the progress of pyrolysis reactions. The modelling of this situation is being approached in stages. First the HOTDOG code developed for the study of immobilised intermediate level waste will be used to calculate temperature distributions (with appropriate changes in property values and allowance for the heat of pyrolysis reactions). Then the production and permeation of pyrolysis gases will be included. The transport of gases can be modelled in the same way as that of water vapour in a cemented waste form.

This work requires the measurement of appropriate physical properties of waste forms in various stages of pyrolysis. These measurements are being conducted, and some results are available.

Preliminary consideration has been given to methods for modelling fire spread. It is intended to use the same basic approach as for the heat transfer calculations.

2.3 Large-Scale Tests

The first set of large-scale tests, to provide a basis for the modelling activity and to define suitable conditions for the active experiments, have been completed. Two types of test were conducted: high intensity heated panel tests, and pyrolysis experiments.

The preparation of specimens (supercompacted 200ℓ drums of simulated LLW) was described in the 1991 Annual Report on this project. Two types of waste composition were used: Waste 1 was high in cellulose content, and Waste 2 was high in rubber/plastic and contained more metal.

In the heated panel tests, the pucks were suspended in front of a radiant panel such that the heat flux through the base of puck (vertical) was 150kWm^{-2}. The tests generally confirmed that supercompacted waste is quite resistant to fire spread, and that no spring-back of the supercompacted structure occurred on heating. For the high-cellulose waste, there was some internal pressurisation, followed by failure of the drum and the ignition of volatiles in an external flame. Temperatures inside the waste fell initially, owing to endothermic pyrolysis, and then rose to just below 100°C. The high plastic/rubber waste behaved similarly, but there was no internal pressurisation. The total mass loss in a three hour test was in each case less that 10%.

Pyrolysis tests have been conducted for both waste compositions in an oven at 300° and 700°C. In all cases extensive pyrolysis of the organic components occurred, and volatile materials were condensed out in traps for subsequent analysis. Inspection of the puck contents showed that there had been extensive decomposition of the plastics and rubber present, and that there had been charring of the cellulose material. Full details of the temperature profiles within the waste were collected. Analysis of the results of these tests is still in progress.

2.4 Preparation for Active Tests

Active tests will be conducted to determine the release fractions of selected radionuclides as a function of temperature. Small scale samples (1.5ℓ) of supercompacted waste and waste components will be heated in an inert atmosphere and the released material trapped.

2.5 Future Work

It is too early to draw any general conclusions about the behaviour of LLW under fire accident conditions. Work in 1993 will concentrate on completing a second phase of large scale tests and using the results to develop and validate the mathematical models of waste behaviour. In addition, the active trials will be completed under carefully selected conditions, so that the results can be used in conjunction with the model output to predict releases of radioactivity under fire accident conditions.

Title: NON-NUCLEAR NON-DESTRUCTIVE TESTING METHODS TO DETERMINE FREE WATER, GAS PRESSURE AND MATRIX LEVEL IN WASTE DRUMS

Contractor: Battelle-Institut e.V., Frankfurt am Main,
Federal Republic of Germany

Contract No: FI2W/0018

Duration of contract: October 1991 to April 1994

Period covered: January to December 1992

Project leader: J. Eisenblätter

A. OBJECTIVES AND SCOPE

The objective of the project is the further development of various non-destructive testing (NDT) methods to check complete packages filled with radioactive waste for unwanted substances. In detail, the following properties are to be determined from outside:

- free water on the matrix surface,
- the matrix level, and
- the internal gas pressure.

The NDT methods to be applied were found to be suitable in a previous screening study (Contract No. FI1W/0227). These methods are /1/: acoustic impedance measurement, Lamb wave attenuation measurement, a pressure compensation method, and the analysis of cover resonances. These four NDT methods are to be integrated into one unit consisting of a mechanical device, which will execute the various handling operations stepwise, and a PC based measuring and control system. Main objects of investigation are full-size 200 litre drums of 1.5 mm wall thickness (rolling hoop and rolling channel drums) filled with concrete to different levels.

B. WORK PROGRAMME

Task 1: Acoustic impedance measurement (AIM) for detecting matrix and free water levels

Task 2: Measurement of Lamb wave attenuation to determine free water and matrix levels

Task 3: Measurement of internal gas pressure using the pressure compensation method

Task 4: Measurement of internal gas pressure by cover resonance frequency analysis

Task 5: General work: Integration of the NDT methods into a handling and measuring unit. Preparation of the test objects, information exchange, evaluation of the results, and reporting

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The work done so far includes sensor development or optimization, testing, and procurement (Tasks 1 to 4). The mechanical handling unit has been designed and constructed. The PC based measuring and control system has been designed; first steps of programming the unit were taken.

Progress and results

Task 1: Acoustic impedance measurement (AIM) for detecting matrix and free water levels

Various combinations of spring and hammer and their joints were tested in order to increase the mechanical stability of the probe head, in particular its fatigue strength. A laboratory scanning device was built which passes the probe head along a vertical line of the drum surface. For better discrimination between air and water additional vibration sensors were tested which receive the air-borne or structure-borne sound generated by the hammer. An airborne electrete microphone was found to be suited best for this aim. The discrimination between the filling materials air and water can be achieved by band-pass filtering a portion of the ring-down signal in the frequency range up to about 10 kHz. - A device has been built which uses an ink jet to mark the actual filling levels on the drum surface.

Task 2: Measurement of Lamb wave attenuation to determine free water and matrix levels

Commercially available ultrasonic probe heads for dry coupling were selected. Dry coupling is provided by rubber tyres which are oil filled. The transducers are placed in the oil bath; they are fixed to the axis. Because of the limited bandwidth of the three tested probe heads (Krautkrämer, PAC, Sonatest) an additional probe head has been designed and built which uses a broad-band transducer (Panametrics).

Task 3: Measurement of internal gas pressure using the pressure compensation method

Whereas in the previous screening study mentioned above the counterpressure was applied by a universal materials testing machine via a hydraulic cylinder, in the stand-alone unit to be built loading will be exerted pneumatically. The load frame was designed and constructed (see Task 5). All components were chosen and tested:

- displacement gauges for measuring the gap between pressure plate and cover,
- contact gauges for measuring the planeness of the cover,
- pneumatic bellows for loading the pressure plate.

Task 4: Measurement of internal gas pressure by cover resonance frequency analysis

An impact generator has been designed which uses a lever arm mechanism. A programme for identifying the resonance lines in the frequency spectra has been written.

Task 5: General work: Integration of the four NDT methods into a handling and measuring unit. Preparation of the test objects, information exchange, evaluation of the results, and reporting.

A mechanical device has been designed and built for executing all four non-destructive measuring methods. The drum will be handled automatically under visual control by the operator. The drum is put down by a crane onto a carrier with turntable. The main steps to be executed are:

- The weld seam is positioned by turning the drum to a fixed location

in order not to interfere with the scanning later on.

- The cover frequency measuring unit is positioned on top of the cover and the measurement is started by the impact generator.
- The drum is moved to a position under the load frame.
- The scanning unit is moved until contact is made with the drum wall.
- Scanning is started along a vertical line using AIM measurement. When it comes close to the rolling hoops or rolling channels, respectively, the probe head is lifted off.
- The scanning process is repeated with the ultrasonic transducers, measuring the attenuation of Lamb waves.
- The drum is turned by 90°, and the last two steps are repeated.
- The last step is repeated twice.
- The drum is inclined to measure the water on top of the matrix surface. Scanning is repeated along a vertical line, using AIM and ultrasonic measurements.
- The pressure plate will be lowered, until contact is made with the cover. The gap at the circumference of the plate is measured.
- The plate is loaded pneumatically. Compensation is achieved when the cover is plane. This is measured by contact gauges.
- The drum is unloaded and removed.

Valve terminals placed close to the mechanical handling unit contain the magnetic valves needed for activating the various pneumatic cylinders and the inputs and outputs of the sensors, which indicate the actual cylinder positions. These valve terminals are connected to the PC based measuring and control unit some 20 m away via a two-wire field bus system.

Information exchange took place at the Task 3 - Progress Meetings held in Cadarache and Jülich.

/1/ J. Eisenblätter, P. Schäfer, R. Weiß:
"Experimental study on the detection of free fluids and gases in waste packages by acoustic methods",
Report EUR 13868 EN (1992)

TESTS FOR PROCESS CONTROL DURING TREATMENT OF LOW AND MEDIUM R A D I O A C - TIVE WASTE IN PRACTISE

Contractor : N.V. KEMA, KFA Jülich, Laborelec
Contract No. : F12W/CT90/0019
Duration of contract: January 1, 1991 to December 31, 1994
Period covered : January 1992 - December 1992
Project leader : H.A.W. Cornelissen (KEMA N.V., coordinator), R. Odoj (KFA), Mr. Roofhooft (Laborelec)

A. OBJECTIVE AND SCOPE

Adequate management of radio-active waste that will be formed during operation of nuclear power stations, is an absolute necessity to warrant the protection of man and environment. Therefore the total waste treatment process from waste release up to interim/final storage has to be controlled. Continuous process control is preferable above verification just before storage because of its higher reliability, traceability and the possibility for corrections of the system.

This research project refers to the development of test methods witch are necessary to control the process of conditioning of radioactive waste. The emphasis lies upon measurement techniques and operations.

On the basis of the international exchange of information between the partners recommendations will be formulated which respect to standard testing methods and procedures where specific quality systems can be based on.

There is also a close co-operation witch CEA/CEN and Taylor Woodrow.

B. WORK PROGRAMME

B.1. Process descriptions of waste treatment
B.2. Chemical characterization
B.3. Radiological qualification test methods
B.4. Mechanical and physical qualification tests
B.5. Validation of test methods and evaluation.

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

Decisive elements of process control during waste management are tests in order to check if the criteria formulated by the authorities are met. Therefore it is necessary to determine which tests and procedures are appropriate.

In the project selections were made for chemical, radiological and mechanical/physical test methods and procedures, which will be further developed.

With the simulation programme DENSITY, activation inventory and homogeneity determination of 220 litre waste vessels could be optimized.

Promising test methods for cementated waste strength prediction turned out to be the maturity concept and sludge viscosity.

PROGRESS AND RESULTS

B.2. Chemical test methods

The research project is focused on test methods and procedures which can be applied during the operation of cementation. On-line test methods are preferable. However, if these are not available other test methods have to be introduced which may not disturb the continuation of the process [1].

For the chemical characterization it was recognized that it is important to determine the following properties and components.

Determination of acidity or alkalinity. Measurements of pH-value is necessary for the control and adjustment of alkalinity with respect to the removal of ammonia and to the reaction temperature. Measurements can be carried out by test papers or by using glass electrodes.

Inorganic constituents of the radwaste such as PO_4^{3-}, SO_4^{2-}, F^-, NO_3^-, BO_3^{3-}, NH_4^+, Ca^{2+}, Mg^{2+} and complexing agents can be determined by photometry and atomic absorption spectometry (AAS).

The above-mentioned species are known as cement poisons, which influence the cement hardening process. Some typical effects are given in table I. Depending on their concentrations, these cement poisons have to be determined more or less often. For this purpose photometry and AAS are well proven test methods.

Higher concentrations of organic carbon may cause problems during the conditioning process, especially in the presence of nitrates. Adequate determination methods are TOC (Total Organic Carbon determination) or thermogravimetry (MS).

TABLE I: Effect of Some Cement Poisons

species	effect on cementation
NH_4^+	bad influence on thermal characteristics of evaporator feed solution; retards cement setting
BO_3^{3-}	influences cement setting
PO_4^{3-}	influences cement setting
Mg^{2+}	influences cement setting
NO_3^-	negative influence on thermal behaviour of feed solution during evaporation process
C	higher concentrations of organic C retard cement setting
Cl^-	higher concentrations retard cement setting
SO_3^{2-}	influences mechanical stability of cement
$Ca^{2+}SO_4^{2-}$	influences mechanical stability of cement

In this project specific test methods were selected for further research. Therefore well defined mixtures are being examined qualitatively for cement poisons. The ions to be determined are: NH_4^+, Mg^{2+}, Ca^{2+}, BO_3^{3-}, PO_4^{3-}, SO_4^{2-} and NO_3^-. The test methods chosen are:
- ICP and IC by Laborelec
- photometry by KFA
- selective electrode and ICP by KEMA.

Special attention will be given to dissolution techniques.

B.3. Radiological test methods

With respect to radiological tests several measurements are important such as:
- dose measurements
- surface contamination
- total alpha, beta and gamma activity using proportional counters
- beta and alpha/beta determination by scintillation counting
- qualitatively alpha measuring in an alpha chamber, after extraction and electro deposition.

The methods to be used will depend on the nuclides to be determined. With an adequate measurement system, gamma radiation detection can be performed on-line during the cementation process. Alpha and beta measurements, however, require sampling from the waste and chemical separation.

In the project special attention is given to alpha, beta and gamma spectroscopy. The partners will exchange procedures on which bases alpha activity will be determined of a well defined sample. With respect to Sr-90 and T procedures will be exchanged for beta spectrometry. The gamma activity of a cementated waste sample will be determined by gamma spectroscopy.

Furthermore a computer simulation programme (DENSITY) developed by KEMA, will be applied for quick measurements of gamma radiation and homogeneity of the cementated waste. Findings of preliminary calculations are presented in figure 1. It can be seen that the best source detector geometry for nuclide inventory control can be done at the top or bottom centre to the vessel. The best place for homogeneity measurements is the side centre because of the maximum effect of the waste density [1].

B.4. Mechanical and physical test methods

In this research project the emphasis lies on non destructive on-line determination of strength development of cementated waste forms. Besides the importance of this property, strength is well correlated to other parameters like durability. Three methods for strength prediction were selected for further research being viscosity, maturity and pulse velocity. These methods are fundamentally different. Waste sludge viscosity is linked to its water content. Maturity is a measure of the degree of hydration of the cementated waste, while ultrasonic pulse velocity is a function of waste form density and Young's modulus.

In a preliminary experimental programme the feasibilities of these test methods was investigated. It could be concluded that especially viscosity and maturity are appropriate for strength prediction [2].

Maturity is a widely accepted test method in the concrete building industry. This concept basically involves integrating temperature development over time for the curing cement and correcting for factors such as type of çement used. By means of a correlation function, early strength gain can be derived from maturity. In Europe standard computerised equipment is available for these tests. The method is economically adaptable by simple thermocouple temperature measurements in the cementated waste. Some typical relations between maturity and seven days compressive strength are shown in figure 2. It can be seen that a measuring time of about six hours was needed to obtain acceptable sensitivity.

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[2] LEWIS R.J., CORNELISSEN H.A.W., "On-Line, Nondestructive Methods for Compressive Strength Prediction in Waste Cementation". KEMA Report 20251-CBP 92-812, 1992.

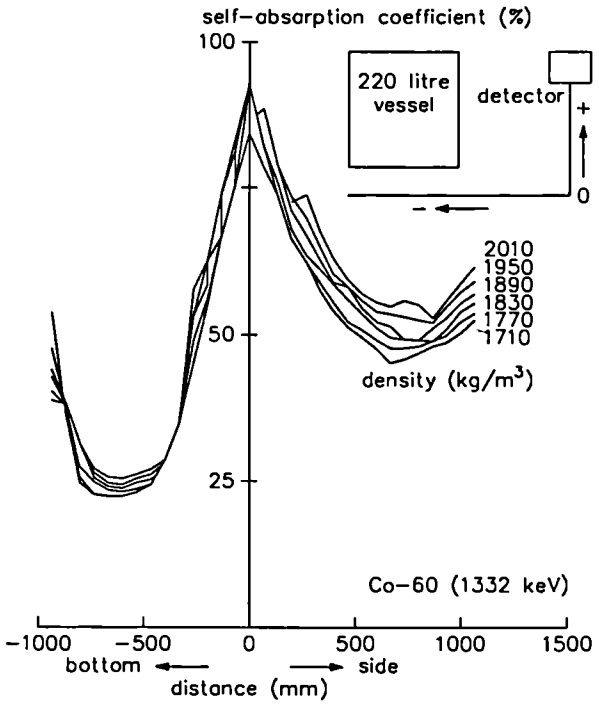


Figure 1: Computer Simulation of Effect of Density and Detector Position on the Efficiency of Measurements on 220 litre Vessels

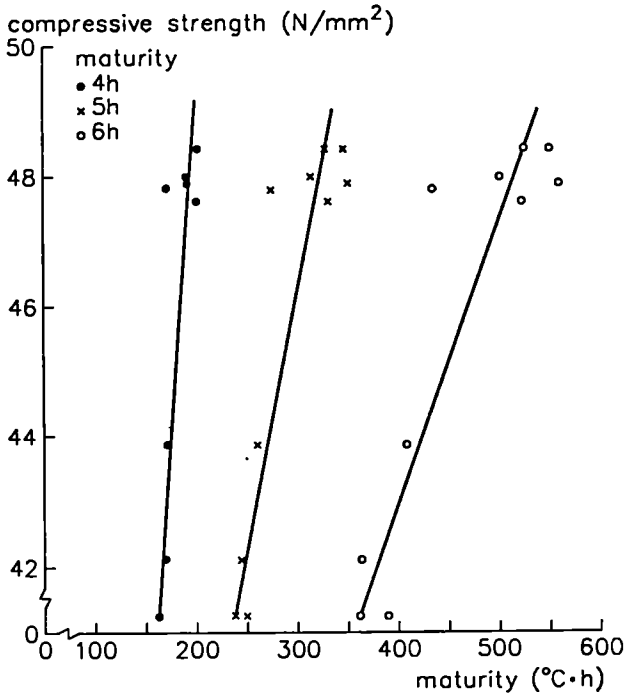


Figure 2: Maturity versus 7-days compressive strength of cementated waste (4% waste; Portland cement [2]).

Title : **Establishment of Non-Destructive or Partially Destructive Test Procedures for Determining the Characteristics of Waste Containers**

Contractor : CEA Cadarache
Contract No: FI2W/0021
Duration of contract : 1.10.91 to 30.9.95
Period covered : 1.1.92 to 31.12.92
Project leader : J. Misraki

A. OBJECTIVES AND SCOPE

In the frame of the low and medium wastes packages' characterization, this programme proposes to establish examination procedures relying on acquired experiences about real packages.
One of the main objectives is to limit to the minimum the destructive examinations; non destructive examinations having the advantage of not causing secondary wastes.

B. WORK PROGRAMME

After inquiries in various characterization laboratories in France, we propose to write assay procedures for the following :

B.1. - sampling methods for analysis (alpha, beta, gamma, ...),
B.2. - gamma scanning on packages,
B.3. - microorganism actions on embedded wastes (bitumen, cement),
B.4. - water content measurement in embedded wastes (Solo 40),
B.5. - radiolysis gas measurement,
B.6. - thermoluminescent dosimetry,
B.7. - tomography's applications on waste packages checking, (filling rate, homogeneity, bulk density, integrity of the package after aggressive assays, ...).

C. PROGRESS OF WORK AND OBTAINED RESULTS

C.1. Sampling methods for analysis

With the aim of establishing any standardization in the samples preparation, for analysis, in the low and medium activities wastes packages characterization, a first procedure heading :
General sampling methods for analysis (alpha, beta, gamma, ...) is presented.
It defines the preparation techniques useful in the manufacturing, applied to :

. physical, chemical and mechanical assays,
. scale 1 packages assays.

It applies to embedded wastes, in hydraulic binder, or polymer matrix. In every case, a solubilization procedure of the embedded wastes samples are proposed.

On the other hand, with regard to the size and the number of test tubes to make, propositions are made to resolve various restraints that are imposed on the characterization assays.
Indeed, when the assays must be carried out in series, (e.g. mechanical resistance after thermal cycles or x-ray expositions) it is necessary that tube test sizes are compatible among themselves. This makes it easier, in particular, for direct comparisons between obtained results, without using corrective factors. On the economic and exploitation levels, this standardization reduces the multiplicity of necessary equipments (mould, coring tools, ...).
Lastly, a method for expressing results, packages identification and sample follow up is proposed. The detailed procedure /1/ was presented to the members of Task 3 during the second progress meeting held in Cadarache (France) (March 31 - April 2, 1992).

C.2. Gamma-scanning

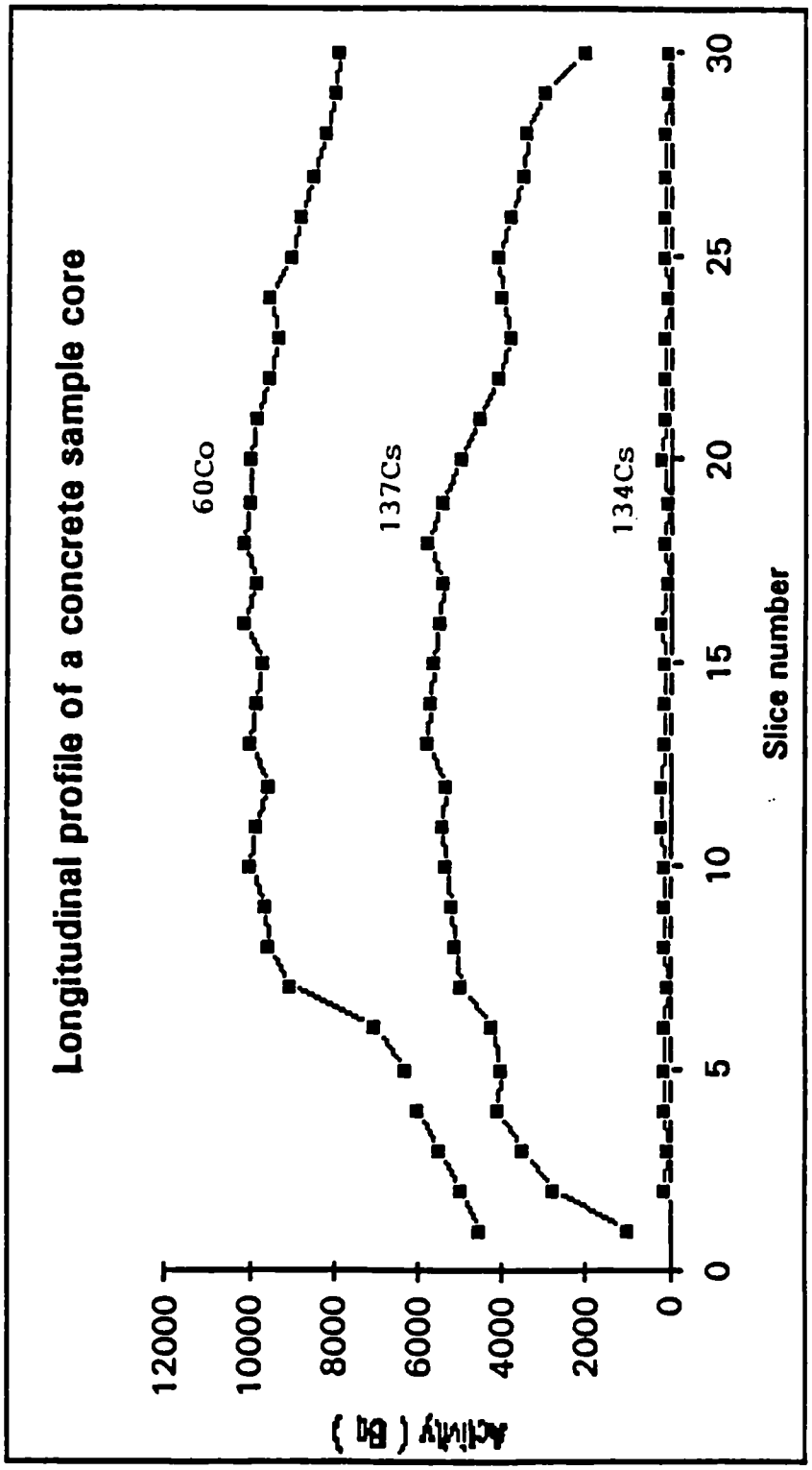
The fundamental safety rules and technical specifications of radwastes management organisms ask, in the frame of waste packages characterization, to measure mass activity and the distribution of this in the coated wastes. This is the radioactive homogeneity determination. A non destructive method is applied in a routine way to the packages. The report /2/ was presented to the members of Task 3 in the third progress meeting in Jülich (RFA) (October 10, 1992).
This progress report gives an account of a method for the non-destructive testing of radioactive packages and samples implemented for the purposes of characterization tests and checking evaluations.
It is specially applicable to managements for the evaluation of the uniformity of the distribution wastes and radionuclides within encapsulations.
The technique of gamma scanning spectrometry is described in order to characterise the packages containing the gamma-emitting radionuclides. A reminder is given on the principle characteristics and performances of three installations. This technique is then applied to two experimental cases : on sample cores taken from a package and on a drum of homogeneous wastes. This non-destructive test method offers the advantage of not generating additional waste and of satisfying the requirements of the technical specifications of the safety authorities with respect to radioactive waste management.
The three following figures show a longitudinal profile of a concrete sample core and the variation of ratio between section specific activity and package specific activity. All this information is obtained by the MARCO device.

References

/1/ DCC/DSD/SECI BE 92.037 - March 25, 1992
General Sampling Methods for Analysis (Alpha, beta, gamma, ...)

/2/ DCC/DSD/SECI BE 92.215 - September 30, 1992
Gamma scanning spectrometry

GAMMA SCANNING SPECTROMETRY



Output of MARCO results

Activité du colis

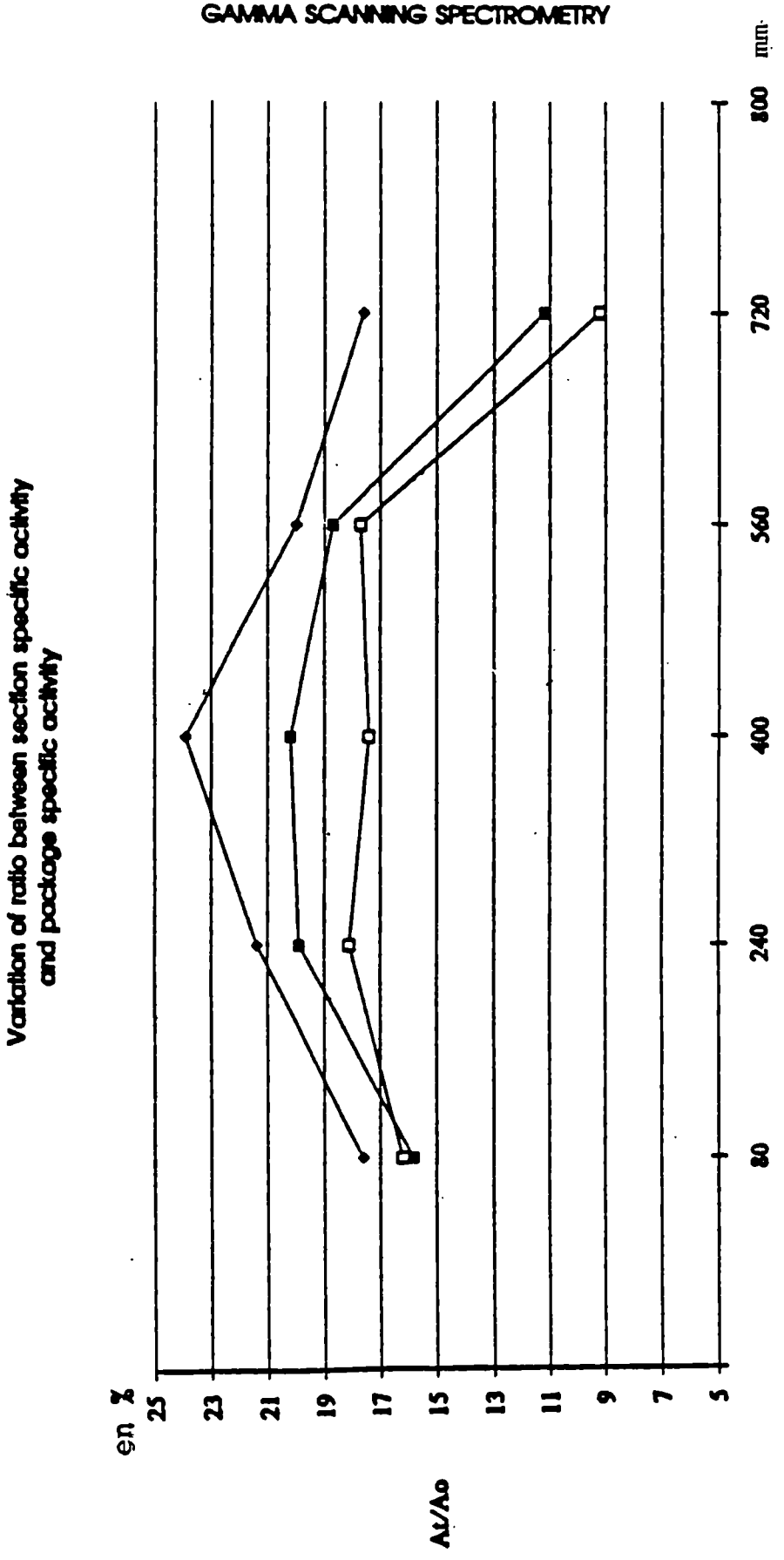
Radioéléments	Activité Ao kBq
Co-60	45642±84
Mn-54	3765,3±6,4
Cs-134	366,9±0,7

Contrôle de l'homogénéité radioactive du colis

	Repère tranches									
	T1		T2		T3		T4		T5	
Radioéléments	Activité (At)	At/Ao	Activité (At)	At/Ao	Activité (At)	At/Ao	Activité (At)	At/Ao	Activité (At)	At/Ao
	kBq	%	kBq	%	kBq	%	kBq	%	kBq	%
Co-60	7229,8±68,7	15,8±0,2	9089±76	19,9±0,4	9220±77	20,2±0,4	8568±72	18,7±0,4	5135,5±43,0	11,2±0,2
Mn-54	613±4	16,2±0,3	683,7±4,5	18,1±0,3	655,6±0,5	17,4±0,3	667±5	17,7±0,3	350±3	9,2±0,1
Cs-134	64,7±1,3	17,6±0,4	78,7±1,6	21,4±0,5	88±5	23,9±1,3	73,2±1,7	20,0±0,5	64,5 *	17,6

* valeur en limite de détection

GAMMA SCANNING SPECTROMETRY



Title:	Non-Destructive Examination of Nuclear Radioactive Waste Packages by Advanced Radiometric Methods
Contractors:	BAM Berlin, TU Munich, CEA CEN-Valrho
Contract N°:	FI2W-CT90-0023
Duration of contract:	from 1.9.1991 to 31.8.1995
Period covered:	from 1.1.1992 to 31.12.1992
Project Leader:	Dr. Peter Reimers

A. OBJECTIVES AND SCOPE

NONDESTRUCTIVE EXAMINATION OF NUCLEAR WASTE PACKAGES BY ADVANCED RADIOMETRIC METHODS

The radiometric methods to be applied to the nondestructive examination of nuclear waste packages are computerized tomography (CT), digital radiography (DR), and microtomography (MCT). CT with Co-60 and linac radiation is established at BAM since more than 5 years. A new scanner particularly designed for waste drums was installed at TU Munich during the first months of this year. It will be used for the work of this contract.
Computerized tomography (CT) offers the possibility to get information about the internal structure of waste containers. In many cases it is sufficient to make CT-measurements on selected parts of a package. Therefore a fast method to get a survey image of the total package is very useful. As shown in the work before (CEC Report 1985-1989), digital radiography is such a ndt-method. The disadvantage is that with a one detector system the measuring time is much higher than for a CT measurement. DR with a CT-multidetector system gives a distortion of the geometry of the object. Part of this contract is the development of a new data acquisition programme which fullfills the following conditions:
- Measuring time lower than 10 min for a 200 l drum
- Correct geometrical projection and intensity calibration, probably by software correction
- Wide energy range (400 kV X-ray, Co-60, LINAC-12 MeV)

For high energy computed tomography (HECT) a new detector will be designed with improved dynamic range and fast read out time. After design and construction of the complete detector array the performance test will deliver information about spatial resolution, density resolution and limits of data readout time.
Three methods will be developed to improve the information from DR measurements:
- difference image formation
- filtering processes
- interactive image processing.

The objective of the CEN-VALRHO work is the improved quality assurance of vitrified HLW packages. The purpose of this investigation is to develop a nondestructive tomographic examination method for vitrified waste packages.
The principal defects which occur during the fabrication of glass blocks are:
- cracks and cavities which increase the surface area exposed to leaching water
- molybdic inclusions which are water soluble.
The goal is to qualify and quantify those defects by a tomographic method.
The tomographic examination method will also be applied to estimate the water penetration into the glass block inside its canister, and the glass surface area actually in contact with the water. The consolidation effect of annealing the glass block to limit the degree of fracturation will be assessed using the same method.
The tomographic interpretations will be qualified by glass leach testing.

The objective of the work at TUM is to gain knowledge in taking representative samples within a quality control of low level waste containers using non-destructive and destructive testing procedures. This involves measurements by means of digital radiography (DR), computerized transmission tomography (TCT) and gamma scanning (GS) as well as adequate sampling techniques like core drilling followed by preparation procedures for subsequent chemical and radiochemical analysis.
All three non-destructive methods are considered to provide a basis for a reliable evaluation of the content in a given LLW container and for an optimization of a subsequent invasive sampling procedure.
DR and TCT are used to determine the density distribution and internal structures in the waste container whereas GS gives informations about present gamma rays emitting nuclides and their location.

As an interlaboratory comparison, the TCT measurements will be performed at TU Munich (^{60}Co source) and BAM in Berlin (LINAC).

B.WORK PROGRAMME

The work programme comprises 3 main tasks correlated to the 3 partners:
BAM - digital radiography (DR), computerized tomography (CT), and micro computerized tomography (MCT)
CEA - quality control of HLW-glass blocks
TUM - quality control of LLW-containers
The nondestructive investigation work of BAM focuses on three groups of waste subjects: drums, glass canisters, and waste samples.
The work programme comprises the following topics:
- CT investigation of real LLW and MLW packages
- Study of fissuration of HLW glass blocks
- Evaluation of crack length and geometry by image processing
- Study of representative sampling procedures
- Micro-computerized tomography of core samples

The work programme of CEN-VALRHO has the following topics:
- fabrication of non-radioactive glass blocks
- definition of the tomographic examination procedure and the detection limits
- definition of the image analysis procedure using a "Pericolor" system, measurement of the length of the cracks on the images and estimation of the total internal surface to calculate the fracturation ratio
- quantification of the molybdic phase percentage
- experimental validation of the tomographic interpretation using the leaching method developed in the CEC contract n° FI 1W 182.

The contribution of the Institut für Radiochemie, Technische Universität München (TUM), consists of the selection of four 200 l drums with different categories of low level radioactive waste as they are produced in nuclear power plants or nuclear research centres, the use of computerized transmission tomography (TCT) for providing reliable information about the internal structure and composition of these waste containers, the application of destructive sampling techniques to two selecteddrums followed by preparation procedures suitable for subsequent chemical and radiochemical analyses, and the derivation of rules for representative sampling on the basis of the collected tomographic informations. The time table for these tasks was updated and completed. The work at TUM was started at March 1st, 1992, and will be finished until August 31st, 1994. In addition to the tomographic measurements, the application of gamma-scanning techniques was included in the work programme to extend the non-destructive tools and to provide additional data for an adequate characterization of the radioactive waste.
According to problems in transporting radioactive waste drums from Munich to Berlin, the order of the tomographic investigations at BAM and TUM has been inverted: all drums will be examined non-destructively at TUM before they are transfered to BAM.

C.PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The state of advancement of the project is in due course of the contracted time schedule. The contract of the third partner TU Munich started on 1 April 1992.

Progress and results

1. At BAM the main progress was made in the following topics:

Evaluation of crack length
The evaluation of the crack length in HLW glass blocks from an analysis of computerized tomography measurements can be separated in two main steps:
- The generation of a binary image from the tomogram which is in general more or less noisy. Before an edge detection procedure can be applied a noise suppression is in general necessary.

- The determination of the crack lenght from the binary images can be performed by existing methods which must be only slightly modified.

In this working period a literature study was performed and as first approximation two existing image processing methods were tested. However, both methods give unsufficient results and therefore the methods reported in the literature must be eclected, tested and developed.

Exchange of measured data with the project partners

For data exchange the well known TIFF-format has been chosen to improve cooperation. TIFF-files can be processed on PC's as well as on Unix-workstations now. When converting data from the internal BAM created CT-format to TIFF, all measurement information will be included in TIFF and can be taken away later.

From TU Munich we have obtained a data set of fourty CT-measurements. Using a system for 3D-presentation named AVS, we have produced an image of the waste container as depicted in fig. 1. All data has been delivered from TU Munich in TIFF-format.

Coordinate transformation and geometric correction of grey-scale images

In some experiments planned in the scheme of this contract it is necessary to compare CT images before and after a physical or chemical treatment of the waste package under investigation.

Prior to any pixel-by-pixel comparison of two images acquired by computerized tomography, a geometric transformation of the image coordinates is required. In general, this requires translation, rotation, and scaling of one image to the particular coordinate system of the reference image, all of which can be represented by an *affine transformation.* With tomography, however, scaling is not necessary due to the identical viewpoint of both acquisitions.

The problem of fitting two images is in fact composed of two steps:

1) The transformation necessary to achieve congruency has to be determined. This means finding the translation in vertical and horizontal direction and the rotation angle.
2) The transformation has to be applied. This will in general require some kind of interpolation.

A literature research has been carried out on both problems.

2. CEN Valrho has produced three canisters with vitrified waste simulate in the PEV prototype vitrification unit at Marcoule which is representative for the facilities implemented in the R7 and T7 plants at La Hague.

Glass blocks A, C and D were sent to the BAM together with package E in September 1991. Their contents have been described in the previous report. Package E contains the control samples described below.

Block B, containing a significant molybdic phase, remains to be fabricated. However, it would be preferable to obtain the image analysis results for package E first, in order to determine whether the molybdic phase can be detected by tomography; if not, it would be useless to fabricate block B.

After examination, block C will be annealed with controlled cooling at Marcoule,

then returned to BAM. The X-ray opaque liquid could be injected in Berlin, thus making it unnecessary to send the container back and forth. When all the blocks have been submitted to tomographic examination, they will be returned to Marcoule for leach testing to determine the actual fracturation factor of each block.

Control Package E

In order to quantify the defects (cracks, cavities, molybdic phases) liable to be found in a vitrified waste package, phantoms containing carefully identified and calibrated defects must first be examined to determine the detection threshold for each type of defect. This is done using a control package containing four specimens, located in the cylindrical portion of a standard R7 canister (420 mm ID x 300 mm high).

The remaining volume was filled with ground glass to simulate X-raybeam attenuation by the glass matrix in a 400 kg block.

Image Analysis

The following scheme for the evaluation of the canister's content has been prepared by BAM and was accepted by CEA CEN Valrho during a meeting held at BAM on 12 Dec., 1992.

1. Determination of the degree of filling

The degree of filling is defined as the ratio of the percentages of air and glass respectively. It corresponds to the ratio of the number of pixels representing two different grey levels. One grey value is associated with glass - this one depends on the density normalization - the other one (usuallly zero) is associated with air.

2. Determination of the canister's content.

The canister's content can be determined based on a classification of every pixel of a given tomogram in one of the following categories.

- Cavities

Cavities are relatively large inclusions of air and can be clearly determined by grey level and geometry.

- Pores caused by air bubbles.

Air bubbles remain as small voids in the glass matrix and may cause problems because an area containing a lot of these small pores is represented by a medium grey-level.

- Metallic inclusions.

Metallic inclusions are detected by evaluation of grey-levels (density values).

- Molybdic phases.

Molybdic phases are detected by evaluation of grey-levels, too.

- Cracks.

The proceeding for the evaluation of cracks depends on the crack-types which have to be detected. Big cracks can be traced directly from the grey-level, small cracks can only be detected after the application of image processing methods.

- Glass matrix.

The rest which has not been classified until now belongs to the glass matrix or the steel container.
- Steel container.
Two proceedings are possible for the classification. A decision based on the grey-levels which refer to the density values or more precisely to the materials x-ray absorption coefficients seems to be obvious because these values are provided by computerized tomography. Problems will arise if objects with an extension of less than one pixel in one of the directions have to be detected. This concerns the detection of pores and cracks. To solve this problem, further geometry information can be used. For example we can make some assumptions for the detection of cracks. Their extension in length is always much higher than their extension in width and their radius of curvature is limited. A search algorithm might look for all objects that fullfill these prerequisites.

3. Evaluation of total crack surface
The parameter most relevant for the quality of a glass block is the number of cracks or the total inner surface, respectively. As an example the total inner crack surface of a HAW 35 canister has been calculated based on the statistic method reported in [1]. There is a relationship between the ratio of a surface and the volume in which it is comprised and the ratio of the length of a known number of test lines and their points of intersection with this surface. All prerequisites [1] have been assumed to be fullfilled. The calculation was based on 24 tomograms measured earlier at positions from 150 mm to 1040 mm above the canister's bottom. In all tomograms the number of points of intersection between 22 test lines and the cracks was determined. The minimum was found to be 44 and the maximum 124. The ratio of the average of these values and the length of the 22 test lines gives referring to [1] half the ratio of the crack area and the canister's volume. The obtained value has to be doubled again because each crack is confined by two surfaces.
The total inner surface of the canister in the range mentioned above was determined to 4.78 m^2. The area between the glass block and the steel container which has to be added was given as 1.17 m^2. Including the top and bottom surface this results in a total surface of 5.85 m^2 eventually exposed to leaching. Using the same method the surface of the main cavity in the middle of the canister was calculated as 0.12 m^2. The surface based on the average diameter of the main cavity which was measured using the tomograms like above is 0.118 m^2.

3. Progress of work at TUM in the period 1.3.92 - 31.12.92.

Setup of sampling equipment
For taking samples from 200 l or 400 l waste drums, a large glove box was designed and constructed under which the drums can be tightly placed by a hydraulic lift. It is equipped with a core drilling system allowing a sampling in vertical direction. The drilling tool is cooled by compressed air in order to avoid water or other liquids which could alter the physical and chemical properties of the sample.

Selection of radioactive waste drums

The original plan was to select four LLW containers which should represent the following waste categories

- mixed waste, cemented
- mixed waste, supercompacted
- ashes or evaporator bottoms, cemented
- scrap-metals, supercompacted.

However, it was not possible to receive drums with real supercompacted scrap-metals yet, since not too many nuclear power plants are willing to provide those objects for research purposes. The investigation programme therefore was slightly changed and includes now

- two drums, here named EG1 and EG2, with cemented evaporator bottoms from a nuclear power plant,
- one drum, here named EG3, with supercompacted mixed radioactive waste from nuclear industry,
- one drum, here named EG4, with mixed radioactive waste from a research institute.

All these containers were already transported to TUM and investigated by digital radiography and computerized transmission tomography.

Digital radiography (DR)

Digital radiography as a non-destructive survey method provides first informations about inhomogeneities and internal structures of a given object. At TUM a ^{60}Co source of an actual activity of ca. $7{,}7 \times 10^{12}$ Bq and an array of 30 plastic scintillator detectors are used to produce radiographs of waste containers of a height up to 2,0 m and a diameter of 1,4 m.

The positions for the later TCT measurements are marked in the radiographs and labeled with the corresponding heights.

In EG1, which is supposed to contain cemented evaporator bottoms, one can see a structure of increased absorbance in the centre of the drum (fig. TUM2). This structure is assumed to be a stirring tool, obviously used for mixing cement and concentrate and left in the drum after finishing the conditioning process.

Based on the DR results, the positions for the subsequent TCT measurements were defined and correspond with the marked lines in fig. TUM2.

Computerized transmission tomography (TCT)

The TCT measurements were carried out by use of all 30 detectors. The time required for one tomogram based on the data of 512 translations and 360 angles was ca. 15 minutes.

Fig. TUM6 shows 8 selected tomograms for the examined waste drum. In these figures, which do not show the real quality of the received tomograms due to the limited resolution of the printer, the colours approximately represent the density of a given area in the drum. However, this is not true for objects smaller than the lateral resolution of ca. 2 mm. Those objects appear to have a somewhat lower density than they really have (see for example the drum lining).

The TCT measurements completely corroborate the interpretations of the DR results:

Corresponding with the TCT given in Fig. TUM6, drum EG1 contains a complex shaped stirrer, which obviously was in use until the cement started to set. This fact can be derived from the typical tracks the stirrer left in the cement matrix at the end of its clockwise rotation (cf. tomograms in 500 mm and 600 mm height).
For complex structures many TCT measurements of a single object can be combined to construct a 3D image. Fig. TUM10 shows such a 3D representation of the stirrer in drum EG1, based on almost 100 tomograms. This 3D image was created at BAM in Berlin by means of an appropriate software package.

Gamma scanning (GS)
In addition to the original plan the application of gamma scanning techniques was included in the work programme to extend the non-destructive tools and to provide additional data for an adequate characterization of the LLW containers.

The scanning of the four selected drums, was started and is still in operation (cf. Fig. TUM1). It is carried out by means of a GERNOD scanner, which originally was developed by the KfA Jülich in cooperation with the german companies MEC (Eschborn) and EG&G Ortec (Munich).

Reference:

[1] Einführung in die Quantitative Gefügeanalyse.
H.E.Exner, H.P Hougardy.
Deutsche Gesellschaft für Metallkunde. Oberursel.

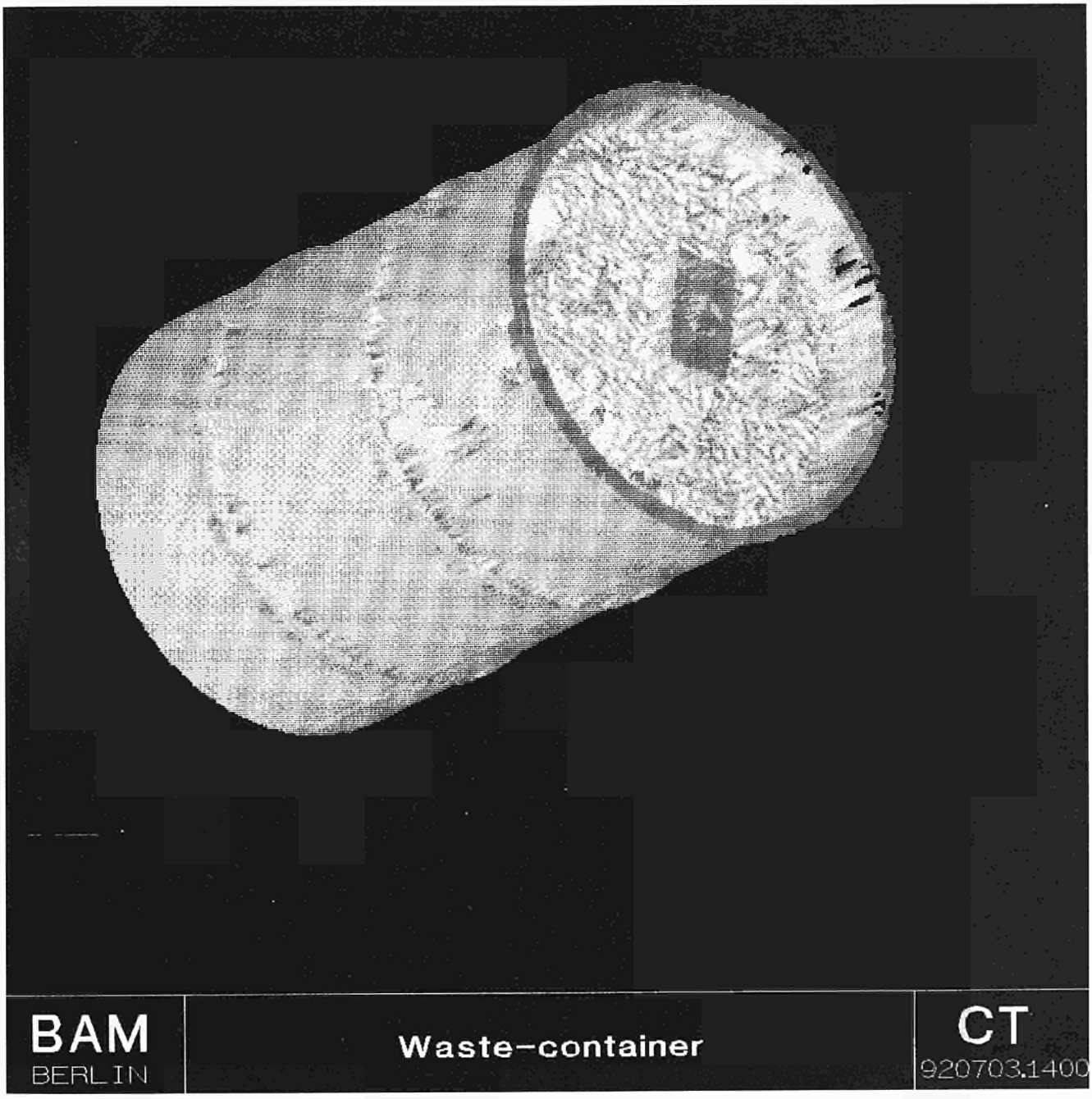


Fig. 1 **3-dimensional image of a LLW container.**

RCM	3D Image **Object:** 200 l waste drum with stirrer **Content:** Evaporator bottoms, cemented	TUM

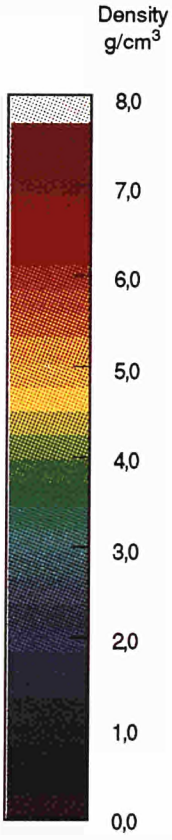
RCM

TCT

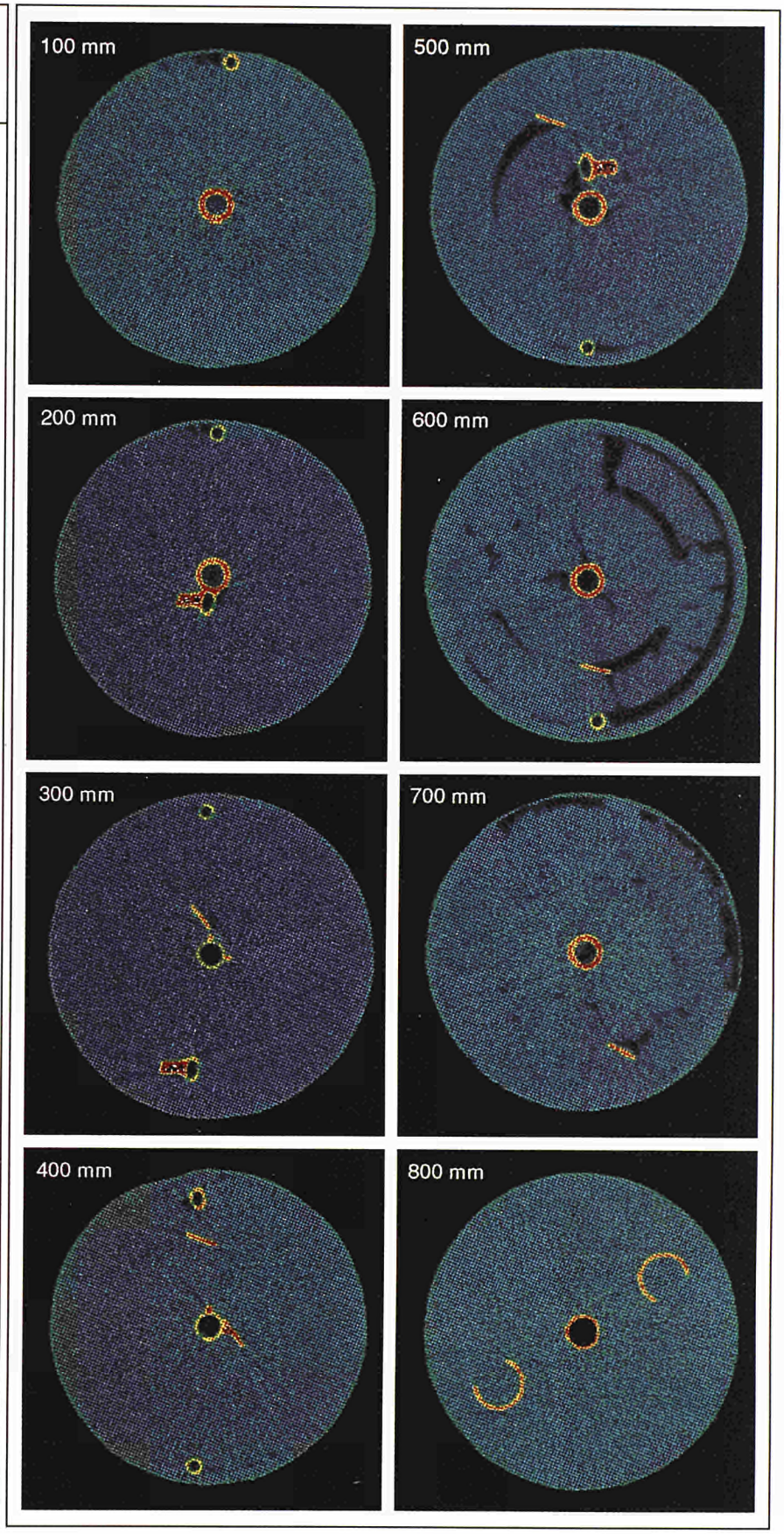
Transmission
Computed
Tomography

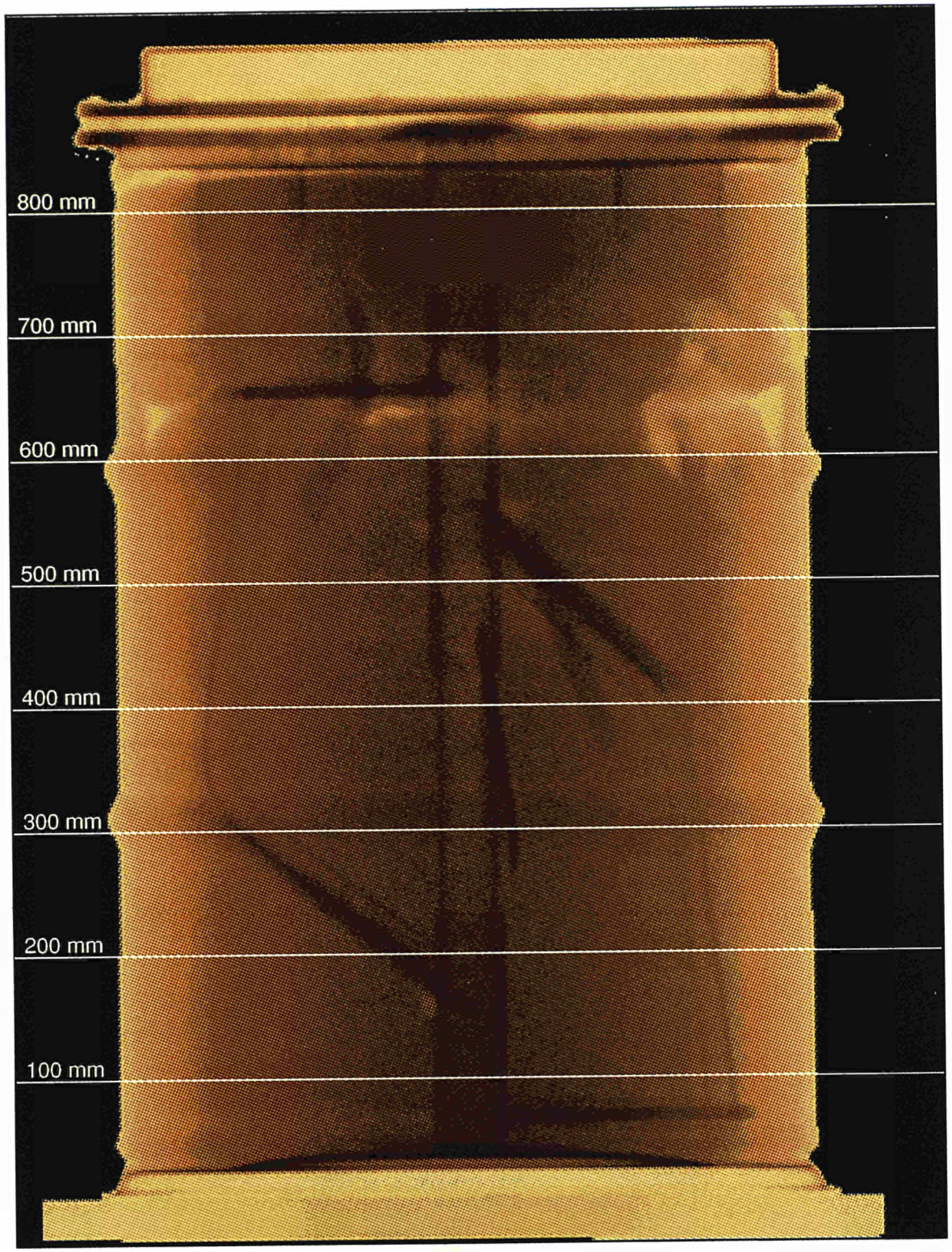
Object:
200 l waste drum
EG1

Content:
Evaporator bottoms, cemented



TUM





RCM	**Digital Radiograph** **Object:** 200 l waste drum **EG1** **Content:** Evaporator bottoms, cemented	TUM

Title: **HIGH ENERGY ACCELERATOR TOMOGRAPHY (HEAT)**

Contractors: AEA Technology, Harwell Laboratory UK.
BAM, Berlin, Germany.
Contract no.: FI2W/0107
Duration.: 1st January 1992 to 31st December 1994.
Working period: 1st January 1992 to 31st December 1992.
Project leaders: Dr. Martyn Sené (Harwell) & Dr. Bernhard Illerhaus (BAM).

A. OBJECTIVES AND SCOPE

The High Energy Accelerator Tomography (HEAT) project is a collaboration between AEA Technology, Harwell, UK and BAM, Berlin, Germany. The primary goal of the project is the development through design, testing and demonstration of a non-destructive technique for the generation of tomographic images of highly radioactive objects such as glass monoliths of high level radioactive waste. The technique is based on the measurement of gamma-ray transmissions with electron bremsstrahlung from an electron linear accelerator as the photon source. The novel aspect of the technique is the use of Cerenkov counters for the detection of the transmitted gamma-rays. Such detectors have a gamma-ray energy response that exhibits a low energy threshold and a non-linear response up to gamma-ray energies of several MeV. The use of detectors with such a response has three potential advantages in the context of computed tomography of highly radioactive objects. Firstly it should provide discrimination against the low-energy background from the objects significantly improving the signal to background ratio in measurements. Secondly, the discrimination against background should also relax the detector shielding requirements. Finally, the intrinsically low sensitivity of the detectors to the low energy portion of the bremsstrahlung spectrum should reduce the beam hardening effects which result from the rapid attenuation of this portion of the spectrum by waste packages.

The project builds on the tomography expertise developed over a number of years at BAM and the expertise in detector design and operation in AEA Technology.

B. WORK PROGRAMME

There are three main phases in the development of the HEAT technique, each corresponding to a period of 1 year:

1. The design construction and testing of Cerenkov counters, collimators and a bremsstrahlung converter.
2. The optimisation of counter performance for tomographic measurements.
3. The demonstration of HEAT on simulated waste.

These three phases are further subdivided into a total of 11 work packages:

WP1. Design of Cerenkov detectors.
WP2. Construction of Cerenkov detectors.
WP3. Testing of Cerenkov detectors.
WP4. Design and manufacture of collimators and bremsstrahlung converter.
WP5. Set up Harwell linac tomography tests.
WP6. Harwell linac tomography tests.
WP7. Assess implementation of HEAT at BAM.

WP8. Transport counters to BAM and set up.
WP9. Demonstration of HEAT at BAM with simulated waste.
WP10. Assessment of technique and final report.
WP11. Coordination of project.

C. PROGRESS OF WORK AND OBTAINED RESULTS

This report is concerned with work carried out during the first phase of the programme.

Careful modelling of the Cerenkov detector system, primarily using the Monte-Carlo electron/γ-ray transport code EGS4, enabled the choice of Cerenkov radiator material to be narrowed down to water or Silica Aerogel and suitable dimensions for the detectors to be determined. As a result of this work prototype detectors based on water and Silica Aerogel were constructed and tested in the laboratory with isotopic sources and with bremsstrahlung γ-rays using the Harwell electron linac. This completes Work Packages WP1 -WP3.

A suitable design of bremsstrahlung radiator has been agreed and the radiator, fabricated at BAM, has been delivered to Harwell.

A collimator system compatible with the geometry of the present BAM tomography scanner system has been designed to enable measurements in Phase 2 and Phase 3 of the project to be carried out. The main components, made of lead and the tungsten alloy Triamet® S18., have been fabricated and the system is at present awaiting delivery of the final components of its the computer control system. When these are delivered Work Package WP4 will have been completed. This will then complete all Work Packages scheduled for Phase 1.

The results of Phase 1 have indicated the necessity for some changes in Phase 2 of the programme, particularly a change in the location of the representative tomography tests for optimisation of the counter design from Harwell to BAM. Consequently WP7 (preparation for integration of the detectors into the BAM system), originally scheduled for late on in Phase 2 has been brought forward and work has already started.

C.1 Design of Cerenkov detectors

The first step in designing the detector system was careful modelling of the response of a Cerenkov detector to γ-rays in the energy range from 0 to ~10MeV. There are 4 processes that contribute to the Cerenkov detector response: i)the interaction of γ-rays in the Cerenkov medium, ii)Cerenkov light production by secondary electrons and positrons, iii)collection of the Cerenkov light by the photomultiplier and iv)Conversion of the Cerenkov light to photoelectrons at the photocathode of a photosensitive device.

The electron-photon Monte-Carlo code EGS4 [1] was adapted to model processes i and ii above. The use of the code was validated for Cerenkov detectors by calculating and measuring the response of a small block of SF5 glass to γ-rays from calibrated laboratory radioisotope sources. The satisfactory agreement between measurement and calculation gave confidence in the use of the EGS4 code.

Four materials were selected as candidates for Cerenkov media, with refractive indices spanning the range 1.06 - 1.70 (at ~400nm). This corresponds to a

detection threshold range for γ-rays of 1680 - 252 keV. The 4 materials were SF5 lead glass (refractive index, n = 1.70), Perspex (n=1.5), Water (n=1.33) and Silica Aerogel (n=1.06). Silica Aerogel is a transparent, mechanically fragile and highly porous solid consisting of colloidal particles of SiO_2 with sizes in the range 10-500nm [2].

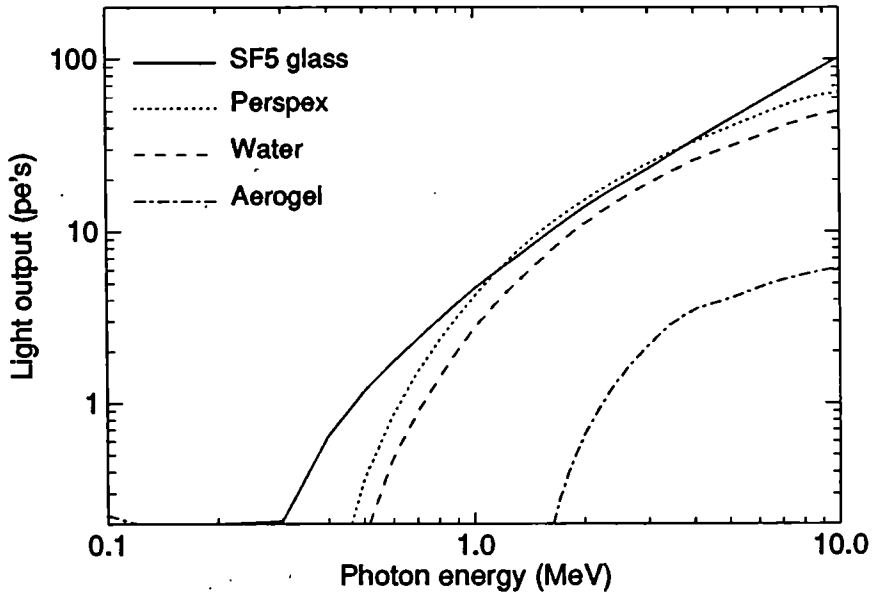


Figure 1: Light output for γ-rays incident on the front face of cuboid Cerenkov media as a function of γ-ray energy, in terms of the photoelectrons that would be liberated from a bialkali photocathode assuming 100% light collection.

The results of calculations using the EGS4 code assuming a bialkali photocathode but neglecting light collection, are illustrated in figure 1. This shows the predicted energy response of 20 x 20 x150 mm^3 detectors. From these calculations it was clear that of the four materials considered as Cerenkov media, water and Silica Aerogel would be expected to have the best performance. The former has greater light output, whilst the latter has a far superior discrimination against background radiation. SF5 glass and Perspex, whilst convenient materials to work with, would not have sufficient discrimination against background γ-rays and would have light outputs comparable with that of water. In comparing Silica Aerogel and water the higher γ-ray energy detection threshold of Silica Aerogel has other advantages as well as it superior discrimination against background. This is illustrated in figure 2 which shows the effective attenuation coefficient of a uniform block of vitrified waste as a function of its thickness for detection of transmitted 12MeV bremsstrahlung by a detector with a linear energy response (e.g. scintillation counter) and for water and Silica Aerogel Cerenkov detectors. The variation in effective attenuation coefficient arises from the rapid attenuation of the low-energy part of the bremsstrahlung spectrum and can cause artefacts in tomographic images. The insensitivity of the Cerenkov detectors, particularly the Aerogel detector, to low energy γ-rays significantly reduces the beam hardening effects.

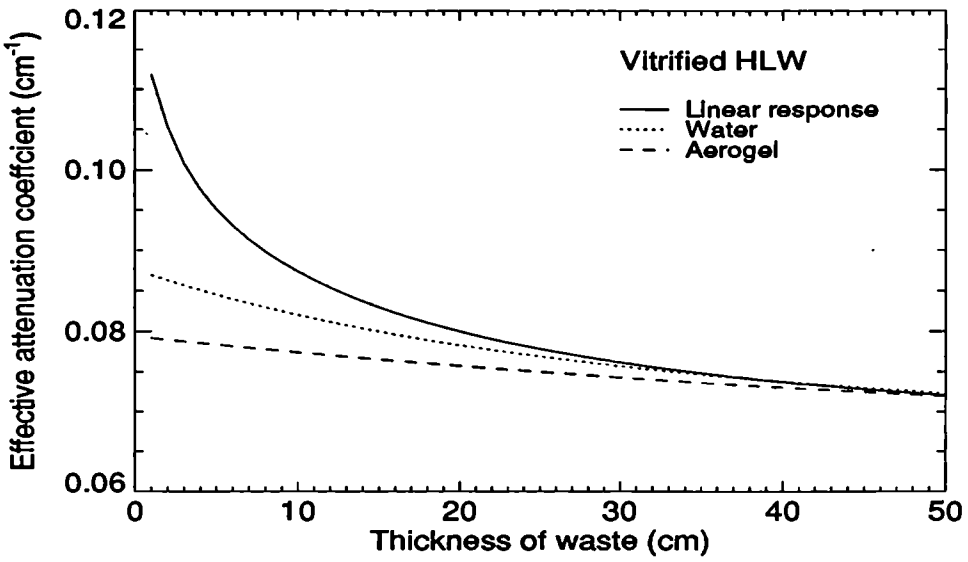


Figure 2: Calculated effective attenuation coefficient of a uniform block of vitrified waste as a function of its thickness, for detection of transmitted 12MeV bremsstrahlung by a detector with a linear energy response and by Cerenkov detectors based on water and Silica Aerogel.

In contrast to this, however, the significantly lower light output of Silica Aerogel, may be unacceptable in terms of limiting the dynamic range over which measurements can be made and/or increasing the measurement time required. It was therefore decided to construct prototype detectors based on both Silica Aerogel and water.
Before doing so, however, the efficiency of light collection in the detectors was considered. In the case of water, which has a low light scattering cross-section, specular reflection from the walls of the container is the most efficient means of light collection. In the case of Silica Aerogel, although the absorption length of the material for Cerenkov light is relatively long, the material has a high scattering cross-section. In this case, the most efficient light collection is obtained by surrounding the material with diffuse reflector with as high a coefficient of reflectivity as possible.

C.2 Detector construction

The calculations described in the previous section enabled the design and construction of prototype detectors to be carried out. The Silica Aerogel detector utilises a block of Silica Aerogel 30x30x150mm^3. The cross section of 30x30mm^2 is sufficient to capture a significant fraction of the electron/γ-ray cascade resulting from a γ-ray interaction in the detector and also allows space between detectors separated by 1° in the BAM geometry (see section C4 below) to have sufficient shielding between them to reduce crosstalk to a satisfactory level. The length of the detector is that for which calculations show that there will be maximum light collected from the material. This is a balance between the increasing light output and decreasing light collection efficiency with increasing length. Sheets of Silica Aerogel, purchased from Airglass AB of Sweden were cut to size using a carefully degreased bandsaw with fine teeth operating at high speed. The sensitivity of the

material to water and organic vapours means that the detector housing had to be sealed against ingress of water and other vapours. A suitable diffuse reflector for this detector was identified as a specialised membrane filter of mixed esters of cellulose manufactured by Millipore (Type MF). This has previously been found to have a coefficient of reflectivity of ~0.95 for Cerenkov light. [1]
The water-based Cerenkov detector consists of a cylinder of water with diameter 25mm. As in the case of the Silica Aerogel detector this diameter is sufficient to capture a significant fraction of the electron/γ-ray cascade resulting from a γ-ray interaction in the detector. The cylindrical shape enables better light collection for specular reflection into a circular photocathode than a square or rectangular cross-section. A suitable reflector for the detector is aluminised mylar. The detector housing, manufactured from stainless steel, is designed to allow the water to come into direct contact with the front face of the photomultiplier.
For both the water and Silica Aerogel detectors the light output is insufficient to allow the use of photodiodes for light collection and conversion. Consideration of the magnitude of the expected light output, the detector geometry the dynamic range and the linearity required enabled a suitable photomultiplier to be identified. This is a new 30mm diameter (25mm active photocathode diameter) EMI type 9125B [3]. The dynode chain of the photomultiplier operates at positive HT and is tapered to allow high anode currents and a wide dynamic range. The chain is mounted together with the photomultiplier in a housing that is well shielded against magnetic and RF interference.

C.3 Detector tests

The prototype detectors were tested in the laboratory with isotopic sources and with electron bremsstrahlung from the Harwell linac.
The laboratory tests were carried out to determine the low energy γ-ray response of the two prototype detectors. Initial tests were carried out with calibrated ^{60}Co and ^{137}Cs sources and ungated detectors. These two isotopes are major contributors to the background from much HLW. Examination of the charge spectra from the detectors with and without the source present clearly indicated that, although there were signals from both detectors due to γ-rays from the isotopic sources, they could not easily be separated from the detector dark noise. In order to obtain a more accurate estimate of the low energy detector response, at least for ^{60}Co, a measurement was made of the response of the detectors operating in coincidence with a fast plastic scintillation detector. In addition following indications of some intrinsic sensitivity of the photomultipliers to γ-rays, measurements were also made of the position sensitivity of the whole detector assembly utilising a well collimated ^{60}Co source.
The linac tests were carried out with bremsstrahlung γ-rays from a Ta bremsstrahlung radiator. The shielded and collimated detectors were placed approximately 1.4m from a bremsstrahlung radiator at the end of one branch of the electron beam-line in the Low Energy Cell of the Harwell linac. The bremsstrahlung beam was monitored by recording the signals from calibrated dose diodes placed between the radiator and the collimators in line with the collimator aperture at the same time as direct signals from the anode of the detector photomultipliers. Measurements were made at an electron beam energy of 10MeV for pulse widths in the range from 0.3–5μs.

The main results of the detector tests were:
1. Clear signals with the magnitude and energy dependence expected from calculation were observed from both water and Aerogel detectors. The magnitude of the signals from both detectors is sufficient for their use with a CT system such as that at BAM. Of the two detectors the Aerogel detector is favoured in terms of its higher γ-ray energy threshold, but, due to its lower Cerenkov light output, the contribution to the detector response from the intrinsic response of the photomultiplier is greater (see below).
2. Aside from the problems of the intrinsic sensitivity of the photocathode (see below), the operation of photomultipliers in the vicinity of an electron linac has was demonstrated. Operation at low HT and careful shielding enables their operation without saturation or significant electrical or magnetic interference.
3. A dynamic range of 300 above background noise was achieved without any special noise reduction techniques such as mounting signal processing electronics close to the detector. CT measurements of some HLW could be made with a dynamic range of 1000, which should be easily achievable. A target of a dynamic range of 10,000 does not seem too unreasonable.

The detector tests also indicated two outstanding technical problems which need to be addressed in Phase 2 of the programme.
i. The photomultipliers exhibited a significant intrinsic sensitivity to γ-rays, located almost exclusively at the photocathode. This will alter the overall response of the detectors (as opposed to the response of the Cerenkov medium) increasing their sensitivity to low energy γ-rays, particularly in the case of the Aerogel detector. If the effect of the intrinsic photomultiplier response is shown to be unacceptable in the representative CT measurements in Phase 2, then redesign of the counters in such a way that the photocathode is shielded from direct illumination by the incoming γ-rays. will need to be considered.
ii. The beam quality from the Harwell electron linac in the experimental area that would be used for the Phase 2 measurements is inadequate at present for the planned representative tomography tests. Examination of the possible techniques for improving the beam quality at this point suggests that suitable improvements would be difficult to achieve within the time and cost of the present programme. After some discussion it has therefore been decided that the Phase 2 measurements will be carried out at BAM and will be based on their present linac driven CT system. Apart from the change in location of the tests the only effect on the work programme for Phase 2 is the need to bring forward Work Package 7 in which consideration is given to the integration of the detectors into the BAM data acquisition system. This has already begun and is discussed in section C.6.

C.4 Collimator Design and Construction

Discussions between BAM and Harwell early on in the programme fixed the gross geometry of the tomography tests for both phases 2 and 3. The detector to collimator distance has been set at 2.7m. A total of 9 detectors will be used with an angular separation of 1°.
In designing a collimator system suitable for the chosen geometry three crucial factors must be addressed.

1. The thickness in the direction of γ-ray propagation must provide sufficient attenuation of the incident beam. Experience at BAM indicates that a factor of at least 10^5 is required.
2. The collimator aperture must be adjustable to allow for different spatial resolution and measurement times. In the present case the collimator opening is to be variable from ~1cm^2 (Phase 2 measurements) down to a few mm^2 (Phase 3 measurements)
3. Provision must be made for accurate alignment of the collimators with respect to the focus point of the LINAC.
The adopted design for the collimator assembly, mounted on an aluminium sheet, is shown in figure 3.

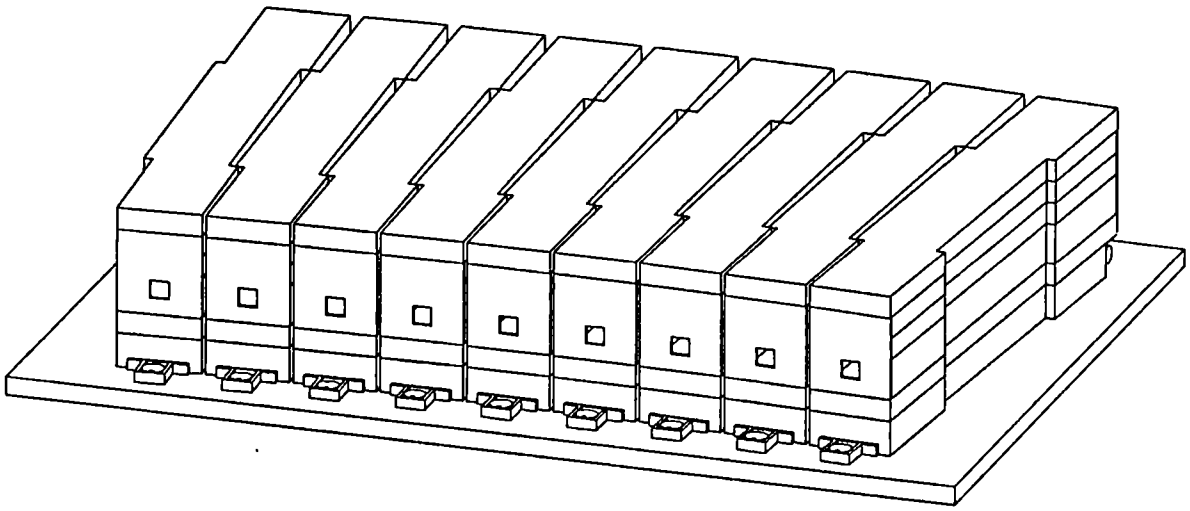


Figure 3: Perspective view of the front face of the nine fold collimator system, mounted on an aluminium baseplate.

Sufficient attenuation of the incoming γ-rays is ensured by the use of a new material Triamet® S18. This is a sintered alloy principally of tungsten and copper with a density and γ-ray mass attenuation coefficient similar to that of tungsten but with far superior machining properties. At a γ-ray energy of 4MeV (the energy at which the photon attenuation coefficient is at its minimum) a tungsten bar with an effective length of 150mm will provide the required attenuation of 10^5. Noting that the requirement for a variable collimator aperture restricts the effective length of the collimator to half the actual length of its housing, a collimator system with a housing 310mm long will provide sufficient attenuation.
The size of all 9 collimator apertures can be accurately set in the following way. At the heart of each element is a pair of carefully machined Triamet® S18 segments with highly polished flat inner surfaces that form the faces of a collimator slit of variable width. The outer surfaces of these segments interlock with their housings to ensure attenuation of all γ-rays that do not pass through the slit, irrespective of the slit width. The fine motion of these segments is achieved by a type of wedge-shaped gear reduction. Diagonal slots in high grade steel sheets are mounted on the top of the two segments to form a wedge. As the steel sheets are moved

forwards or backwards by means of a fine threaded screw, pins that are mounted on the two segments and protrude into the slots, are forced together or apart. The motion is centred accurately on the collimator axis. and is facilitated by ball bearings between the pins and the sides of the slots. Backlash in the mechanism is avoided by the use of two springs mounted between each segment and its housing to exert a slight pressure towards the closed state of the slit. This pressure ensures continued contact between the ball bearings and the sides of the slots in the steel plates on top of the segments. The threaded rods are driven by PC-driven stepper motors. One step of the motor corresponds to a rotation of 5° which translates to an accuracy in the position of the slits of better than 0.007 mm.
The collimator housings also have an interlocking shape to ensure attenuation of all γ-rays that do not pass through the collimator aperture. In addition the top and bottom of each housing is shielded with 20 mm and 12 mm of lead respectively.
Fine positioning of each element of the collimator assembly to ensure alignment with the focus point of the LINAC is achieved by means of screw adjustments at the front and back of the housing.
All of the parts of the collimator system have now been designed and drawn in detail using the AutoCad system. The pre-machined Triamet® components (16.4kg per collimator element) have been delivered to BAM. At present the fine machining is underway in the BAM workshop.
The computer controlled motor drive system has also been specified. This has been specially designed for this application in preference to a commercial CNC-system, which would have included a large overhead of features unnecessary for the present application. The system will allow all nine collimators to be simultaneously adjusted to the same aperture size. Other features included in the specification are zero-point adjustments and limit switches. The CNC-system will be controlled via a RS232 serial interface by a PC. The whole system, including the necessary software has been ordered and is scheduled for delivery in February 1993. This will complete Work Package 4.

C.5 Design and Construction of Bremsstrahlung radiator

In designing a Bremsstrahlung radiator the two primary considerations were the choice and thickness of the radiator material and the dissipation of up to 2kW of heat generated by stopping the electron beam in the assembly.
Two options for the choice and thickness of radiator material were considered. The first was a thin target of high-Z material (such as tungsten or tantalum) backed by a thicker target of low-Z material (such as aluminium). The second was a target of a high-Z material thick enough to completely stop the incoming electrons. Calculations, utilising expressions developed by Hansen and Fultz [4] (with corrections for transmission from Berger and Seltzer [5]) and by Findlay [6], indicated that the total output of the second type of radiator was greater for all γ-ray energies when integrated over γ-ray emission angles although the first type of target gave greater output at the most forward angles. The first type of target also had a higher ratio of high to low energy γ-rays in its spectrum. The second type of target was however much more compact.
Taking into account that the Cerenkov detector will discriminate against the low energy γ-rays the more compact target was chosen.

To overcome the problem of heat dissipation a radiator consisting of up to five separate tungsten plates cooled by pumped water is to be used. The target plates are held by three spacers in a water-tight housing consisting of a main cylindrical body with two face plates holding tungsten windows sealed with indium rings. This construction allows for easy change of target material and total thickness if required. British half inch BSP fittings are provided on the cooling water inlet and outlet to match with the cooling water supply.
The radiator assembly, fabricated in BAM, has been shipped to Harwell.

C.6 Interface with BAM data acquisition system

The detector array that is usually used with the BAM CT system consists of scintillator detectors equipped with photodiodes. As photomultipliers are required for the detection of the lower intensity Cerenkov light pulses, it is necessary to consider the development of a signal processing electronics which can accept inputs from both photomultipliers and photodiodes into the present data acquisition system. This approach is possible because both photodiodes and photomultipliers operate in current mode. A photomultiplier can, in principle, be linked directly into the system in place of the photodiode and its preamplifier, changing the capacitor in the integrating stage to match the higher current output of photomultipliers.
Apart from this the electronics for photodiode- and photomultiplier-based detectors will be identical. This is due to a change in the standard configuration of the linac signal processing electronics, which now utilises the fast switching IC (AFC2101, manufactured by Burr-Brown) shown in figure 4. In this circuit input H is only connected whilst gated by the linac pulse. After the linac pulse the output S and ground are connected to sample and hold circuitry for an appropriate time for digitisation. The integrating capacitor is also short-circuited by R until the start of the next linac pulse. This circuit design can accept any detectors operating in current mode.

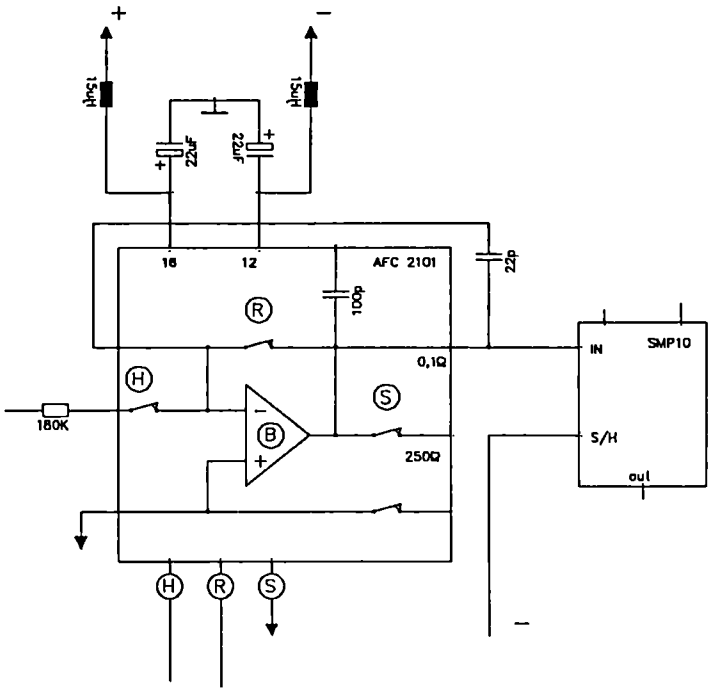


Figure 4: Functional diagram of AFC2101 fast-switching IC implemented at BAM.

In addition all the standard gating and synchronising pulses from the linac and the sample-movement CNC machine may be used as for CT measurements with other detector systems
At present the data acquisition system has been prepared as far as possible for measurements with the Cerenkov detectors. Fine tuning of the system will take place when the prototype detectors are transported to BAM early in 1993 for the first representative tomography tests.

C.7 Future Work

The next stage of the programme is the testing of the prototype detectors using the BAM CT system. In order to perform these tests two detectors of each type are required. A second of each prototype design is at present being constructed at Harwell. These will then be transported to BAM. After optimising the signal processing system for the Cerenkov detectors, tests of the linearity and noise (hence dynamic range) of the whole system will be carried out. The maximum dynamic range will be determined using wedge shaped samples of steel. Attenuation curves will be determined down to the noise level in the system.
These measurements will provide a direct indication of the performance of the detectors in CT. Improvements in the design of the detectors and the final choice between Aerogel and water can then be made, with further tests of improved designs, before a full set of the final design of detector elements are constructed and tested. In the final phase of the project the performance of these detectors will be compared with that of the standard detectors in CT of simulated HLW waste. In preparation for this BAM have already been supplied by CEA/CEN Valrho (in connection with CEC contract FI2W-023) with a glass test sample. This sample has the same outer dimensions as a commonly used high active waste cylinder and is filled with simulated waste glass. Included in the sample are several glass cylinders of different densities and a slit system for spatial resolution measurements. Isotopic sources will be used to simulate the low energy γ-ray background.

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PART A

Task 4

"Disposal of radioactive waste: research to back-up the development of underground repositories"

Topic 1: Research related to sites and their characterisation

Topic 2: Research on gas flow

Topic 3: Radionuclide migration in the geosphere

Topic 4: Modelling in the presence of uncertainty and management of data in non-homogeneous systems

TASK 4

Topic 1 **Research related to sites and their characterisation**

FI2W/0046 Simulation of the effect of long-term climatic change on groundwater flow and safety of geological disposal sites

FI2W/0049 Experiment of groundwater flow in a fracture for the validation of chemistry/hydromechanical transport coupled models for fractured media

FI2W/0050 Experiments in 600m borehole in the Asse II salt mine

FI2W/0051 Evaluation of a self-consistent approach to fractured crystalline rock characterisation

FI2W/0063 INTERCLAY II - A coordinated benchmark exercise on the rheology of clays

FI2W/0072 Methodology studies on sealing of boreholes

FI2W/0075 Paleoclimatological revision of climate evolution and environment in Western Mediterranean region

FI2W/0078 Water flow and solute convection through fractured rock

FI2W/0092 Geochemical validation of solute residence times: review and comparison for various geological environments

FI2W/0111 Decovalex Project: modelling of THM behaviour for fractured rocks

FI2W/0113 Decovalex Project: modelling of THM behaviour for fractured rocks

FI2W/0115 Underground laboratory at Tournemire: groundwater flow tests in clayish material

Topic 2 **Research on gas flow**

FI2W/0048 Development of HLW-borehole sealing

FI2W/0064 The refinement of soil gas analysis as a geological investigative technique

FI2W/0076 MEGAS: modelling and experiments on gas migration in repository host rock

FI2W/0093 Gas pressure build-up in radioactive waste disposal : hydraulic and mechanical effects

FI2W/0101 In-situ test on the permeability of salt for gas and brine

Topic 3 Radionuclide migration in the geosphere

FI2W/0039 Continuation of the migration experiments (lab. and in-situ)

FI2W/0065 CHEMVAL-2. A coordinated research initiative for evaluating and enhancing chemical models used in radiological risk assessment

FI2W/0071 OKLO-Natural analogue for transport processes in a geological repository

FI2W/0079 Development of a model for radionuclide transport by colloïds in the geosphere

FI2W/0080 Characterization and validation of natural radionuclide migration processes under real conditions on the fissured granitic environment (El Berrocal)

FI2W/0081 Fundamental studies on the interaction of humic materials

FI2W/0082 Rock matrix diffusion as a mechanism for radionuclide retardation: natural radioelement migration in relation to the microfractrography and petrophysics of fractured crystalline rock - Phase 1

FI2W/0083 Effects of humic substances on the migration of radionuclides: complexation of actinides with humic substances in natural aquatic systems

FI2W/0084 Colloid migration in groundwaters: geochemical interactions of radionuclides with natural colloids

FI2W/0085 The role of colloids in the migration of radioelements

FI2W/0097 The role of colloids in the transport of radionuclides in geological media

FI2W/0121 Analysis of the geo-environmental conditions as morphological evolution factors of the sand clay series of Tiber basin and the Dunarobba fossil forest

FI2W/0122 CHEMVAL 2: Thermodynamic database

Topic 4	**Modelling in the presence of uncertainty and management of data in non homogenous systems.**
FI2W/0086	Study of the coupling between "fractured medium" and "porous medium" flow models
FI2W/0087	Methods of handling non-homogeneities at different scales in radionuclide transport
FI2W/0088	The treatment of uncertainty in groundwater flow and solute transport modelling
FI2W/0089	Uncertainties in the modelling of migration
FI2W/0090	Unbiased guess, a concept to cope with fuzzy and random parameters
FI2W/0091	Review and development of methodologies for modelling with uncertainty and variability

TASK Nr. 4 - DISPOSAL OF RADIOACTIVE WASTE: RESEARCH TO BACK UP THE DEVELOPMENT OF UNDERGROUND REPOSITORIES

A. Objectives

The overall aim of this task is to provide a theoretical and experimental basis as well as data bases, concepts or models for understanding the long-term behaviour of potential host rocks as natural isolation barriers in order to support the safety assessment of radioactive waste repositories in deep geological structures.
The evaluation of the feasibility and safety of some design aspects of the construction and operation of underground repositories in different rock formations (clay, salt and granite) is also an objective of this work.

B. Research performed under the programme 1985-1989

The research areas covered were:

* development of measuring techniques for the detection and characterisation of fractures and faults in indurated clays;
* rock mechanics laboratory and in-situ tests in host rock media and benchmark of codes for salt (project COSA) and clay (project INTERCLAY pilot phase);
* assessment of mechanical performance of metal containers (project COMPAS);
* mock-up and in situ tests for emplacement and characterisation of candidate buffer and backfilling materials;
* radionuclide migration in the geosphere (project MIRAGE) including subprojects on the role of organic compounds, complexes and colloids (CoCo activities) on geochemical benchmark codes and development of thermodynamic database (CHEMVAL), and natural analogue studies (Natural Analogue Working Group, NAWG);
* study of the applicability of the fuzzy set theory for taking account of uncertainties in model parameters.

C. The present programme 1990-1994

The work to be carried out is subdivided into four topics:

Topic 1: Research related to sites and their characterisation

This topic mainly deals with the calibration and intercomparison of adequate techniques for assuring relevant properties of groundwater chemistry and groundwater flow in fractured rock on selected reference sites.
Studies are also carried on concerning:

* Rheology of clay, granite and salt, (i) to improve the understanding of large-scale rock mass behaviour through adequate laboratory or in-situ tests, (ii) to develop and test suitable calculation tools and (iii) to predict their material behaviour.

Benchmark exercises are undertaken within the project INTERCLAY (rheology of clay) and the project DECOVALEX (on the thermo-hydro-mechanical properties of fractured crystalline rock).

* Geoforecasting studies to predict future climate changes and simulation of their effects on groundwater flow in the Netherlands as well as paleo-climatological revision during the last 2 million years in the Western Mediterranean regions.

Topic 2: Research on gas flow

Various research efforts in the field of gas generation, gas release and migration through host rocks (in particular clay and salt) were grouped together in a coordinated project PEGASUS (Project on the Effects of Gas in Underground Storage facilities).

Topic 3: Radionuclide migration in the geosphere

Research under this topic concentrates on international projects and subprojects already started in the 3rd programme like:

* studies of the role of colloids, organic substances and complexes (CoCo activities)
* migration experiments in clay and fractured crystalline rocks
* natural analogues: study of migration processes for the understanding of long-term behaviour of geological isolation systems (Oklo study, El Berrocal study and Dunarobba study)
* geochemical modelling of radionuclide migration and extension of thermodynamic data base for use in transport models (CHEMVAL)

Topic 4: Modelling in the presence of uncertainties and management of data in non-homogeneous systems

The overall objective of this topic is to study alternative methodologies and concepts for the modelling and handling of data in the presence of uncertainty in radionuclide transport modelling, whereas advanced studies are focused on:

* investigation of methodologies of the treatment of uncertainty with reference to modelling studies (e.g. fuzzy sets, expert judgement, information theory, etc.)
* treatment of uncertainties in radionuclide transport modelling
* methods of handling non-homogeneities (e.g. dispersion) at different scales in transport models.

Simulation of the effects of long-term climatic change on groundwater flow and the safety of geological disposal sites.

Contractor: University of Edinburgh, U.K.; Rijks Geologische Dienst, and Rijksinstitut voor Volksgezondheid en Milieuhygiene, The Netherlands.

Contract No: F12W/0046

Duration of Contract: 42 months

Period Covered: 1st March 1992 - 29 February 1993

Project Leader: Professor G S Boulton, University of Edinburgh.

A: OBJECTIVES AND SCOPE

A1 Scope and background - Recent developments in glaciology, hydrogeology, geochemistry, geostatistics and mathematical modelling, together with enormously improved knowledge of subsurface geology in Europe and the resolution of palaeoenvironmental change, now make it possible to model, simulate and test complex environmental processes in the past and extrapolate them into the future. In making predictions about the future of radioactive waste repositories, models need to be stringently tested. Using them to simulate past events and testing them against geological evidence is a way, possibly the only way, of doing that.

A2 Aims of research and applications - To investigate the extent to which future environmental changes may affect groundwater flow in the vicinity of potential rock-salt radioactive waste repositories and the migration patterns of radionuclides after release into the geosphere.

A3 Degree of development of research. The programme involves the development of a coupled time-dependent, three dimensional, thermal/mechanical model of subglacial groundwater flow, and non-linear statistical approaches to modelling the future.

A4 Collaboration. There is a high degree of collaboration between the University of Edinburgh, the National Institute of Public Health and Environmental Protection (Netherlands), the Geological Survey of the Netherlands and the University of Paris-Sud.

B. WORK PROGRAMME

B1 Development of an ice sheet model to simulate Saalian glacial history in the Netherlands.

B2 Determination of the upper boundary conditions for groundwater flow and a consolidation/flow model.

B3 Simulation of the three-dimensional groundwater flow field within a supra-regional hydrogeological model extending from Scandinavia through Germany to the Netherlands.

B4 Acquisition of geological and hydrogeological data for the large-scale groundwater flow model.

B5 Applying and testing the subglacial groundwater flow model.

B6 Development of a site-specific model for the subrosion of salt.

B7 Testing the subrosion model at specific sites in the Netherlands.

B8 Simulation of future changes.

C: PROGRESS OF WORK AND RESULTS OBTAINED.

C1 State of Advancement

The programme is proceeding according to plan and the milestones set for the second year in the original proposal have all been achieved. The principal components of the programme in this second year have been as follows:

C1.1 Development of the ice sheet model (EDIN). The ice sheet model is now complete and is being routinely applied both to reconstructions of past glaciological conditions in Europe and to first attempts at prediction of future conditions.

C1.2 Groundwater flow model (RIVM and EDIN). Three groundwater flow models have now been developed. Two are in regular use and the development and the application of a third is now beginning. The standard METROPOL model has been applied to the whole standard transect from Scandinavia to Holland along which most of our modelling has concentrated. An amended METROPOL model has also been developed in which the groundwater head is not permitted to rise above the head given by the ice sheet surface. A third model is the vertically integrated model designed to investigate aerial patterns of flow in Northern Europe for periods of past and future climate change.

C1.3 The subrosion model (RIVM). A model of subrosion of salt has been developed in which the rate of subrosion is a function of effective pressure, the flux of groundwater past the salt surface and the geochemistry of groundwater. This model will be applied and tested over the next year.

C1.4 Geological boundary conditions (RGD). A full description of the hydrogeological geometry of the Mesozoic and Quaternary over the project area in northwest Europe has now been completed. In addition, a collation of hydrogeological data from the basement areas of Scandinavia has been completed in collaboration with workers from the University of Goteburg.

C1.5 Palaeoenvironmental boundary conditions (EDIN, RGD). A detailed reconstruction of the climatic and environmental sequence in northwest Europe from 200 Ka BP to the present has now been completed.

C1.6 GIS development (EDIN, RGD). Hydrogeological boundary conditions, palaeoclimatic data and model output are now being integrated within the framework of a geographical information system.

C1.7 Testing programme. (PARIS-SUD). During the new year a number of samples have been taken from stratigraphic sites in northwest Europe which may have been influenced by subglacial groundwater flow and subject to geochemical analyses in order to test the model predictions about past groundwater geochemistry. In addition, a borehole has been drilled, funded independently, but as an integral part of this project, in the area to the northeast of Hamburg where we believe a strong meltwater signal could be obtained. The borehole has been successfully completed and samples sent to Paris-Sud for geochemical analysis.

C2. Progress and results

C2.1 Boundary conditions derived from the ice sheet and climate model. The model has now produced a reconstruction of the following palaeoclimatic and palaeoenvironmental conditions in Europe during the last 200 Ka:

- Annual temperature variation in the Netherlands
- Mean annual temperature variation at a number of sites in northwestern Europe
- Palaeoprecipitation inferences for the Netherlands
- Perma-frost extent in northwestern Europe
- Ice sheet fluctuation in northwestern Europe
- Subglacial melting rate in time and space in northwestern Europe

C2.2 Models of groundwater flow. The palaeoclimatic and palaeoenvironmental boundary conditions listed above, together with the hydrogeological model which sets geometrical boundary conditions for flow have been used to infer the patterns of subglacial and sub-permafrost flow in the system of acquifers and acquitards overlying hydrological basement along the standard transect in northwest Europe (this basement is the Zechstein in Holland and part of north Germany, the Cretaceous in the Baltic region and Palaeozoic and Pre-Cambrian basement in Scandinavia). These models show that the hydraulic transmissibility of basement in the area north of the north German coast is so low that much meltwater would be forced to flow in tunnels. A prediction of the magnitude of tunnel flow has been made, which compares remarkably well with the pattern of esker distribution which would be expected from the inferred pattern of tunnel flow. Palaeoflow in the Mesozoic and Quaternary acquifers of north Germany and northern Holland, indicate a number of areas in which we would expect a strong geochemical signal to be retained. The borehole programme which has recently been completed is specifically designed to test these expectations.

The model has also been applied to understanding of the role of permafrost in the pro-glacial zone. An important new mechanism has been established, which relies on the buoyant forces which will be induced in the pro-glacial permafrost as a consequence of expulsion of water from beneath the ice sheet. These buoyant forces may generate large ground ice lenses at the base of the permafrost.

C2.3 Statistical extrapolation of past climate records is now relatively well developed and the first predictions of future climate have been used to drive the ice sheet and environmental model into the future. This predicts the maximum of the next glacial period in about 70 Ka from present. This maximum would extend to the northern coast of Germany. Work is now beginning on the inherent probability of predictive future changes.

C2.4 Publications. One paper has been published and one accepted for publication from this work. Three further papers are now in preparation, and it is anticipated that they will be submitted before the summer.

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Title : Experiment of groundwater flow in a fracture for the validation of chemistry/ hydromechanical transport of coupled models for fractured media.

Contractor : BRGM/4S/GEG

Contract n° : FI2W-CT90-0049 (DTEE)

Duration of contract : from 01/01/1991 to 12/31/1994

Period covered : from 01/01/1992 to 12/31/1992

Project Leader : S. Gentier

A - OBJECTIVES AND SCOPE

This project is a circumstantial study in laboratory concerning the relationship between the morphology, the flow and the chemical reactions water-rock. The objective is the achievement of an experiment designed for the validation of chemistry-hydromechanical transport of coupled models which integrate explicitly the morphology of the voids of the fracture and its variations.

The morphology of a natural fracture in a granite will be studied from profiles recorded on each side of the fracture and from the casting of the voids. The flow channels will be determined from the morphology of the voids and from radial flow experiments. The petrology of each side of the fracture will be studied. All these data will permit the choice of a few little fields on the sides of the fracture about which the micro-roughness will be analysed.

After this preliminary phase, radial flow tests will be performed on the fracture. The tests will be realized at various levels of normal stress and in temperature. During the tests, the chemistry of the water entering and exiting of the fracture will be determined. At the end of each experiment, the morphology of the fracture will be examined again.

B - WORK PROGRAMME

The scheduled successive phases for the achievement of the works are :

- design, fitting of the prototype of testing equipment and qualification tests,
- choice of the sample and initial characterization of the fracture,
- tests of percolation (3 or 4 tests according to the necessary duration for each percolation),
- presentation and interpretation of the results.

C - PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

At the end of this year, the state of advancement is the following :

- the prototype is assembled and the loading frame has been built,
- the wiring of most of the elements has been performed,
- the algorithms of the programs of data acquisition have been writen,
- profiles on each side of the fracture have been recorded,
- two technics to quantify the micro-roughness are being studied,
- the petrographic chart is being mapped,
- concrete repliquas and transparent resine repliquas have been realized,
- preliminary tests have been defined.

The main tasks have been the assembling, and the wiring of the prototype on the one hand, and the studying of micro-roughness technics on the other hand.

Progress and results

1. Fitting of the prototype and qualification tests (figure 1)

The prototype, all the connections of which have been performed, is constituted with :

* a loading frame, connected to a regulation system,
* a cell for the control of the temperature and of the Nitrogene pressure.

The cell is connected to :

- the control and distribution circuit for the pressurisation with Nitrogene,
- the injection circuit of the percolation fluid,
- the heating circuit of the fluid,
- the recuperation and weighting circuit of the fluid,
- the thermal gauges used to the measurement of the fluid temperature and to control of the heating system, and to the thermoelectric couples located around the sample,
- the four displacement gauges (LVDT) to measure the closure of the fracture during a percolation.

* a control and measurement pannel. This one contains all the electrical units we need :

- electronic conditionning of sensors (displacement, pressure, temperature, loading),
- thermoregulator of the temperature inside the cell,
- data acquisition and control unit (VXI system),
- microcomputer for real time control of the test.

All these units have been calibrated and put together in a bay. All the connections have been performed.

To perform the tests of qualification of the prototype, without taking any risk to damage the fracture to be tested later, concrete replicas of the fractured sample have been made.

The preliminary tests of the prototype have been defined and concern the hydraulical circuit, the injection system, the confining of the cell by Nitrogene, the heating device, the displacement gauges, different thermal gauges, the thermistors, the VXI data acquisition unit. They will constitute the next step of the fitting of the prototype.

The algorithm for the data acquisition is composed with two parts. A functionnal part to initiate the computer, control the wiring of the measurement channels and define the fifteen parameters of the test. A operationnal part to define the initial state, begin the measurements and the storage of the variables in files and modify the parameters as scanning rate, scales for restitution...

2. Initial characterization of the fracture

2.1. Acquisition of the profiles

On each side of the fracture, forty profiles have been recorded, distributed in four directions: two orthogonal directions and the two bisecting directions. From these profiles, after a statistical study, the topography of each side will be reconstructed by geostatistical methods.

2.2. Study of the micro-roughness

Two technics have been tested : the mechanical scanning microscopy and the confocal microscopy. The two technics are based on different principles and the studied fields are not the same : 5 x 5 mm for the mechanical scanning microscopy and 1 x 0.7 mm for the confocal microscopy. In the third direction the studied height is 0.696 mm for the first one and 0.512 mm for the second one. A example is presented figure 2. Oher technics have to be tested. Until now, it is still difficult to conclude on the technic to be chosen.

2.3. Petrographic chart

The petrographic chart is being mapped. This work is realized at the University of Bordeaux I (France). We use for this purpose a binocular lens, associated with a camera lucida. The magnification is x 10 x 16. The map is hand drawn.

The aim of this work is to know the spatial distribution of the monomineral but polycristalline sets constituing the surface of the fracture. This map has to be superimposed on the topographic map, to help to define the fields which will be chosen for the study of micro-roughness.

2.4. Other works

To complete the preparation of the first percolation, transparent resin replicas of the two sides of the fracture have been performed. An injection of dyed water will be realized to get a map of the flow and to better know the preferential ways of percolation.

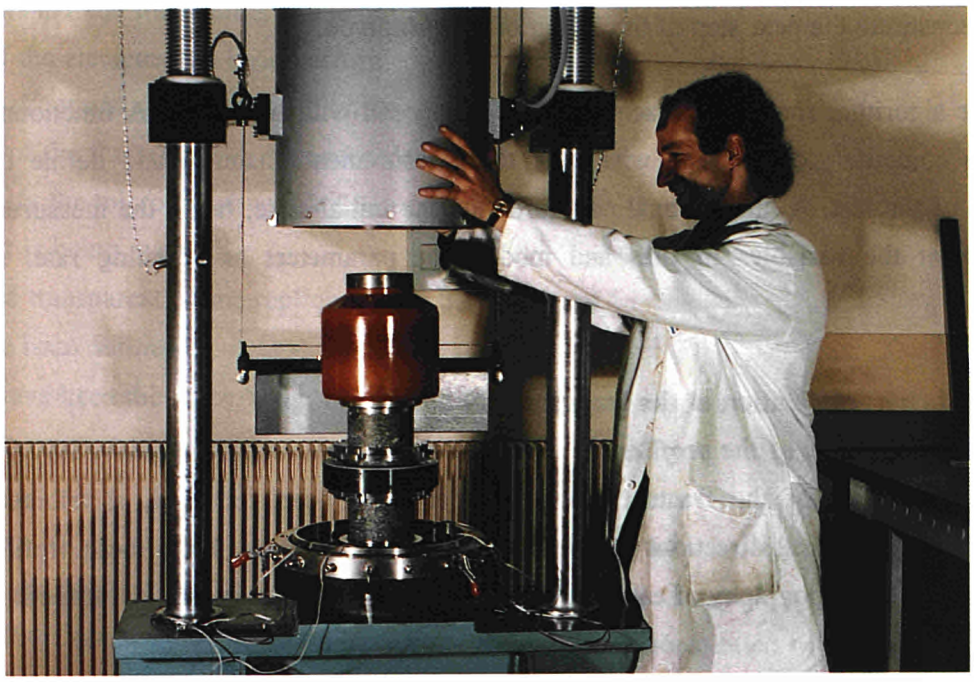


Figure 1 - View of the loading frame and of the cell

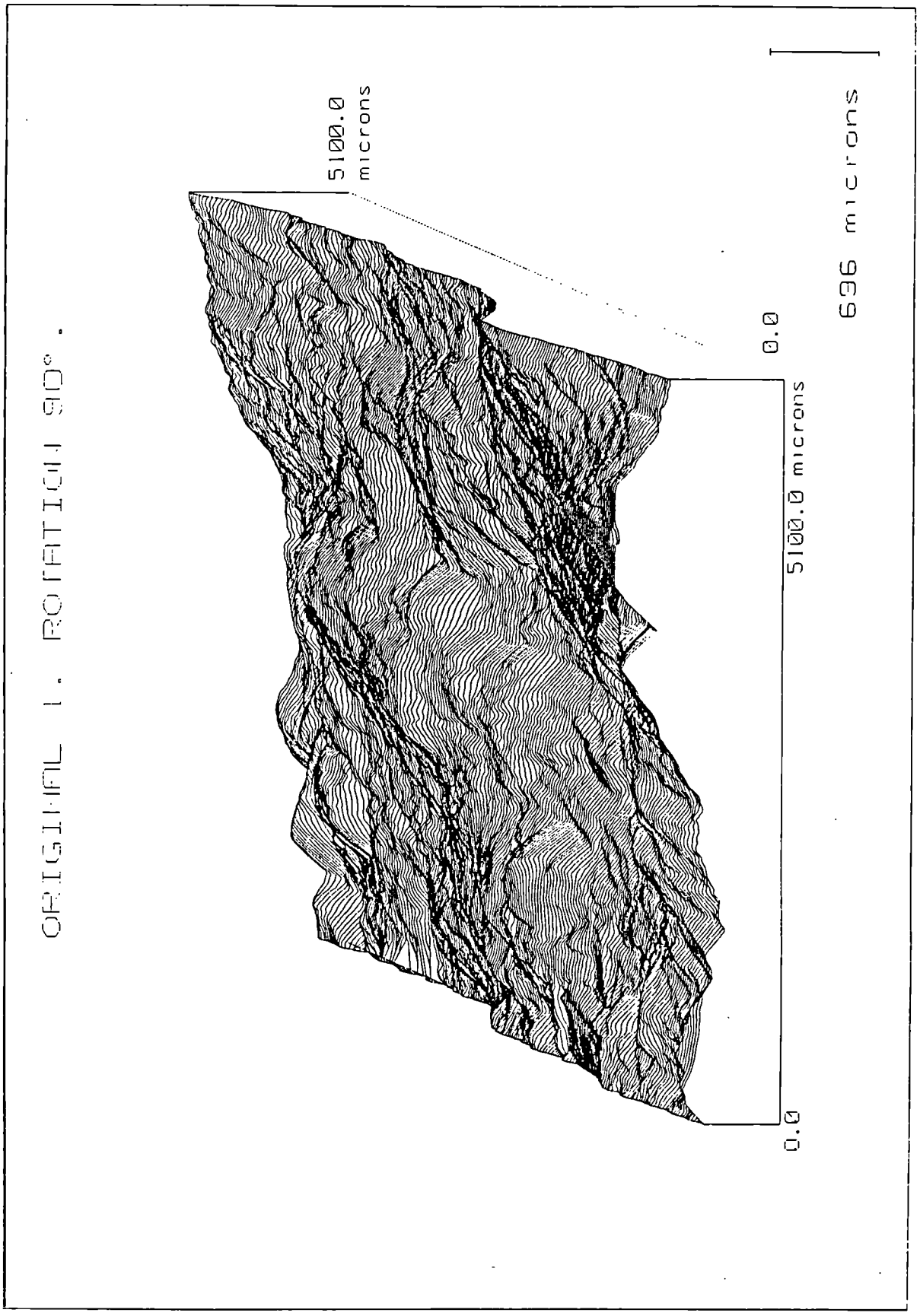


Figure 2 - Example of a micro-roughness study by mechanical scanning microscopy

Title:	Experiments in a 600 m borehole in the Asse II salt mine.
Contractor:	ECN
Contract no:	FI2W/0050
Duration of contract:	January 1991 to December 1992
Period covered:	January 1992 to December 1992
Project leader:	J. J. Heijdra

A. OBJECTIVES AND SCOPE

In order to assess the safety of disposal of radioactive waste in salt formations, models for the thermo-mechanical behaviour of rock salt that have been developed in previous programmes have to be verified by in-situ experiments. It has been proven by the COSA project that computations based on laboratory scale experiments do not accurately predict the in-situ measurements.

In this research programme the following in-situ measurements are carried out in the Asse II salt mine in Germany with measuring equipment developed in a previous programme under contract number FI1W/0084:

1. Determination of in-situ elastic behaviour of salt and convergence measurements at the bottom of the borehole with different pressures. The measurements will be carried out with the Variable Pressure Device (VPD) in the available 300 m hole.
2. Free convergence measurements of the salt wall at five depths in a borehole, i.e. at different salt pressures as soon as a 600 m deep borehole becomes available.

The experimental results obtained will be available to predict the behaviour of salt deposits and will give essential information to be used in safety assessment of disposal facilities for radioactive waste in rock salt, especially in the field of elastic behaviour and pressure dependency of creep.

B. WORK PROGRAMME

The tasks which need to be preformed during the contract period are:

1. Maintenance of installed equipment:
   Including the maintenance of the hardware and software required for remote instrument control and data transmission between the Asse salt mine and the ECN in Petten.
2. Execution of the experimental programme:
   The VPD measurements require that parameters (pressures) are changed and thus require local operation. The convergence measuring devices have to be installed in the borehole before measuring and removed afterwards.
3. Data collection and interpretation of the results:
   The automatically collected experimental data will be validated and interpreted.
4. Evaluation of experimental results:
   Consequences for the models used for the description of thermo-mechanical behaviour of rock salt resulting from the measurements will be evaluated taking into account the measurements performed in previous programmes.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The measurements with the VPD are considered as finished. Due to leakage, which occurred probably in the rubber bag due to the dehydration heat of the salt concrete, not all experiments planned could be executed. In view of the high costs and the results already obtained a rescue operation is not considered as feasible.
The free convergence measurements in the new to be drilled 600 m hole have not started up to now due to delay in the drilling of the hole.
As soon as a suitable hole is available the measurements can proceed. Extension of the contract will be requested.

Progress and results

1 Variable pressure measurements

The evaluation of he measurements with the VPD has been reported in [1].
It appears that the most probable value of the modulus of elasticity for the rock salt does not deviate much from the value found on laboratory scale samples which is about 25000 MPa. This in contrast to earlier assumptions in which the modulus of elasticity was reduced to account for primary creep and micro cracks. The values of the modulus of elasticity for different experiments together with a best fit average value is represented in Figure 1.

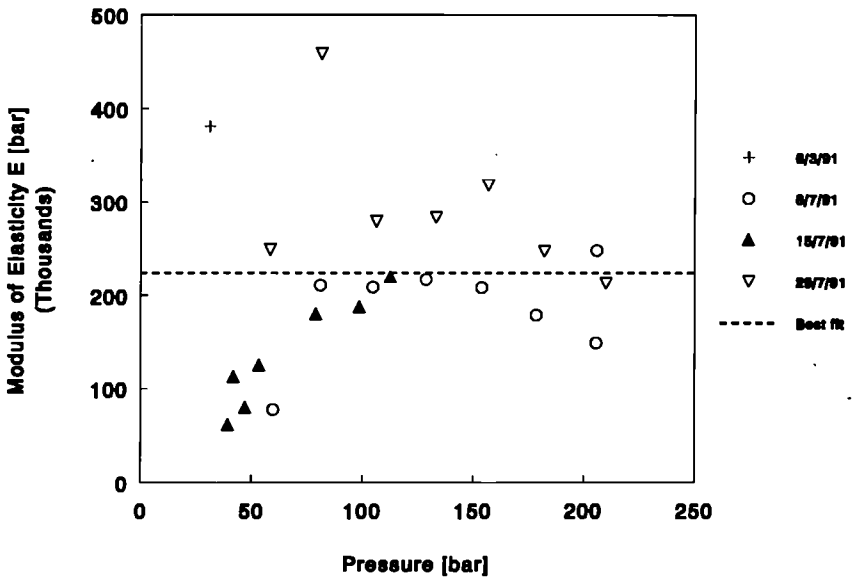


Figure 1 *Modulus of elasticity as a function of the pressure.*

2 Free convergence measurements

The evaluation of the convergence measurements in the 300 m hole has been reported in [4]. In this report it is shown that the measured convergence can be accurately predicted with the aid of a normalized convergence model based on analytical functions. The remaining unknown factor required to normalize the measured convergence is the rock pressure. This pressure has been estimated by means of a fitting algorithm, which fits the measured data to the normalised analytical solution. In this fitting procedure the rock pressure is used as a parameter to obtain the best fit. The result of this fitting procedure is given in Figure 2.

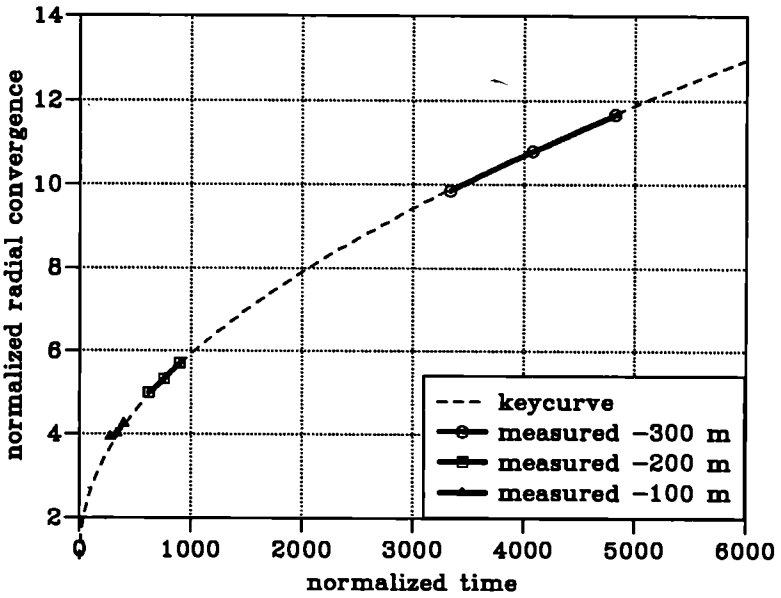


Figure 2 *Measured and theoretical convergence for the three locations in the 300 m borehole.*

The rock pressure derived by means of the above mentioned procedure for the three measuring locations is:

13.3 MPa at a depth of 850 m
15.4 MPa at a depth of 950 m
20.3 MPa at a depth of 1050 m

A parameter study into the influence of the constant A and the exponent n in the Norton creep law on the pressures showed that a 20 percent variation in A leads to a variation of only 5 percent in the pressure for both commonly used values of n (5.0 and 5.5).

List of publications

[1] Hamilton, L.F.M.; Prij, J.; Benneker, P.B.J.M.: Evaluation of the experiments with the variable pressure device. ECN-C--92-010, january 1992.

[2] Heijdra, J.J.; Prij, J.: Convergence measurements in a 300 m deep borehole in rock salt. ECN-C--92-016, may 1992.

Title: EVALUATION OF A SELF-CONSISTENT APPROACH TO FRACTURED CRYSTALLINE ROCK CHARACTERIZATION

Contractor: Golder Associates (UK) Ltd
Contract No: F12W/0051
Duration of Contract: From June 1991 to June 1994
Period Covered: January 1992 to December 1992
Project Leader: M. Brightman

A. OBJECTIVES AND SCOPE

The aims of the project are:

(i) to assess the errors in predictions of a nuclide migration in fractured crystalline rocks resulting from the application of inappropriate interpretation techniques;

(ii) to assess the impact of the "partial flow dimension" approach on the results derived from hydrogeological testing; and

(iii) to develop a methodology for constructing fracture network models to incorporate field flow dimensional information directly.

B. WORK PROGRAMME

The project has been subdivided into the following five tasks:

(1) to provide a literature review of the impact of the application of "partial flow dimension" interpretation on hydrogeological tests in fractured crystalline rocks;

(2) to evaluate, present and assess the impact of "dimensional" interpretation on some existing data sets;

(3) to simulate "dimensional" results within a fracture network model;

(4) to assess the available methods by which "dimensional" results would be incorporated explicitly into as fracture network model; and

(5) to demonstrate the impact of cylindrical flow versus variable dimension results on the output from a transport version of the fracture network model.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

The work in the year of 1992 has been concentrated on Tasks (3) and (4).

Task (3): the FracMan/MAFIC package developed by Golder Associates has been used to simulate packer tests in a fracture network, and dimensional behaviour has been observed;

Task (4): a methodology has been developed to incorporate flow dimensional information into discrete fracture network modelling;

In the mean time, progress has also been made on Task (5) to verify the feasibility and suitability of the established numerical tools in modelling particle transport in discrete fractures. In addition, Task (1) has been extended to cover field hydrogeological data available during the year of 1992 from projects in Sweden, Switzerland and Japan.

Progress and Results

C1. Tasks 1 and 2: Review and Data Analysis

Further data analysis and review of the application of the "partial flow dimension" approach in Stripa and Finnsjön Projects (of Sweden), Grimsel Test Site (of Switzerland) and Kamaishi project (of Japan) has lead to the following conclusions:

- flows of partial dimension commonly occur in fractured crystalline rocks; integer flow dimension (1D, 2D or 3D) is the exception, rather than the rule;
- improper interpretation by assuming an integer flow dimension for a well testing analysis may lead to errors of 2 to 3 orders of magnitude, and consequently lead to significant discrepancy in nuclide migration predictions; and
- an inferred flow dimension reflects the fracture geometry and connectivity in a fractured crystalline rock. An inferred low flow dimension from partial dimension analysis may indicate poor fracture connectivity, or flow restricted to well connected channel-like conduits. An inferred high flow dimension may indicate a better connected fracture system.

C2. Task 3: Fracture Network Simulations

A discrete fracture network was generated using the FracMan package, as shown in Figure 1(a). A borehole was placed at the centre of the network. Imposing boundary conditions on the exterior boundaries, synthetic packer tests results have been obtained by using the MAFIC package. Both constant-rate and constant-pressure tests have been simulated as transient flow condition in the fracture network. Figure 1(b) illustrates the drawdown and its semi-log derivative at radius of 1.725m and 2.16m versus testing time of a constant-rate test simulation. While Figure 1(c) shows the flow-rate at the borehole versus testing time of a constant-pressure test simulation. As can be seen, in both cases, the results are dominated by storage effects during the first hour (log(3600s) = 3.56); while after about 10 days (log(864000s) = 5.94), boundary effects start to dominate the results.

In order to interpret the synthetic tests results, as for field test data, "partial flow

dimension" type curves have been generated based on the generalized radial flow theory developed by Barker (*Water Resources Research*, 1988, p1796-1804). Partial dimensional type curves of constant-rate and constant-pressure tests are illustrated in Figure 2(a) and 2(b) respectively, flow dimension ranging from 1.0 to 3.0 with increment of 0.5. In our computerized type curve matching analysis, as shown in Figure 2(c), flow dimension in the type curves ranges from 0.5 to 3.0 with increment of 0.1 to achieve better resolution.

Type curve analysis of the synthetic data sets between 1 hour and 10 days in Figure 1(b) and 1(c) leads to flow dimension of 1.2 of the generated fracture network in the vicinity of the borehole in both cases, with excellent agreement as would be expected. Therefore, the integrated FracMan/MAFIC package, together with the computerized partial dimension type curve matching analysis, is capable of reproducing partial flow dimension of a packer test.

C3. Task 4: Incorporation of Dimensional Data in Fracture Network Modelling

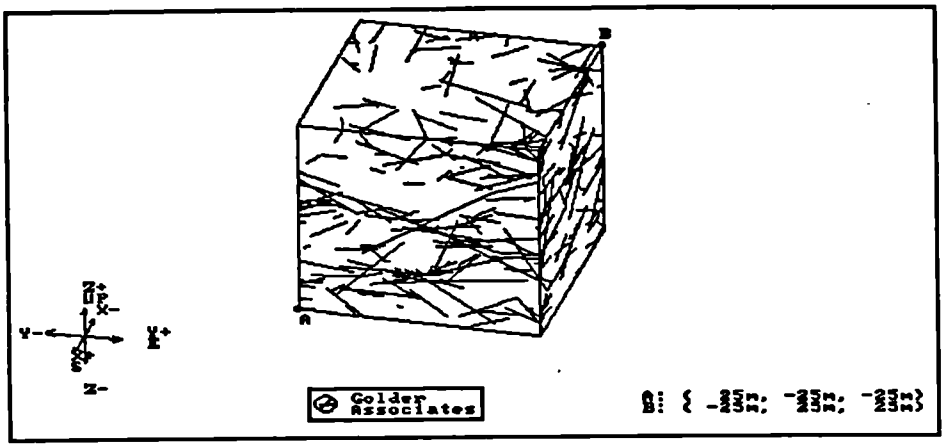
The proposed self-consistent approach is aimed at making flow and transport predictions in a fractured crystalline rock more consistent with field observations, by means of conditioning fracture network realisations to observed hydraulic test results and flow dimension as a prerequisite for predictions.

The methodology of this approach has been developed and outlined in Figure 3, together with the relation to the FracMan/MAFIC package components. Partial flow dimension behaviour largely results from heterogeneity in a fractured rock mass. There are two levels of heterogeneity: irregular fracture distribution in space and channelling within discrete fractures. The first level of heterogeneity of a fracture rock mass can be determined with satisfactory confidence, by means of conditioning fracture realizations to observed borehole logging and fracture trace mappings on exposed planes. Therefore, in the developed methodology, the partial flow dimension is directly used to condition/calibrate discrete fracture realisations to the second level of heterogeneity: the fracture roughness conceptual model and the related parameters.

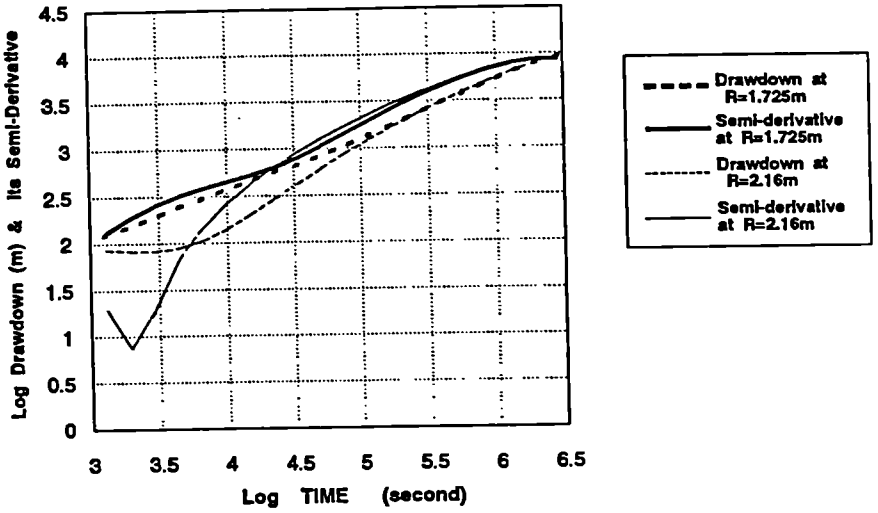
Simulations of different fracture roughness conceptual models are under way. There are four fracture roughness profiles available in the developed package: geostatistical, Fractal, empirical roughness and empirical non-stationary spatial process models. Numerical studies of these models are in progress.

C4. Task 5: Impact of the Dimensional Approach on Transport Simulations

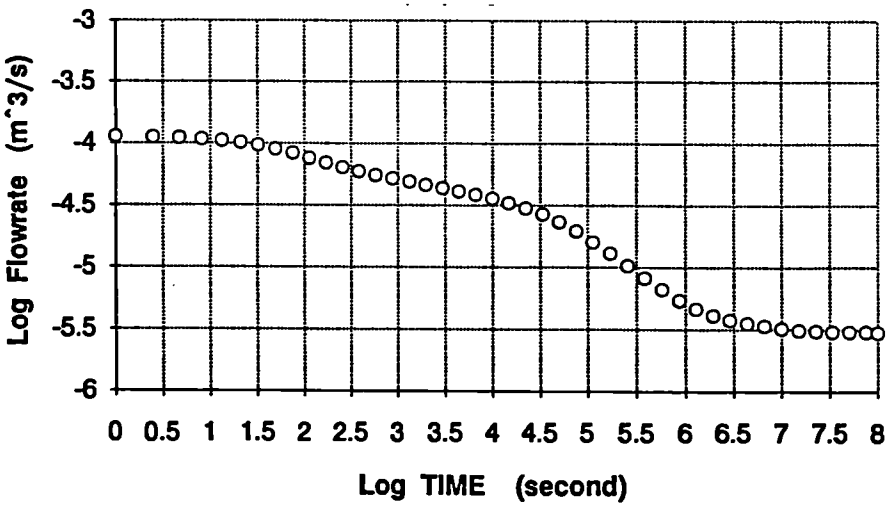
The MAFIC package is capable of modelling solute transport in discrete fracture networks by using a particle tracking approach (Hull *et al.*, *Water Resources Research*, 1987, p1505-1513). In order to verify the feasibility and suitability of the algorithm and keep problem simple, a large scale horizontal fracture was generated together with a borehole created at the centre of the fracture. Particles were released from the borehole. Particle distributions at various time steps have been simulated with different boundary conditions. The numerical solutions are in good agreement with comparable analytical and experimental results in the literature.



(a) FracMan generated fracture network

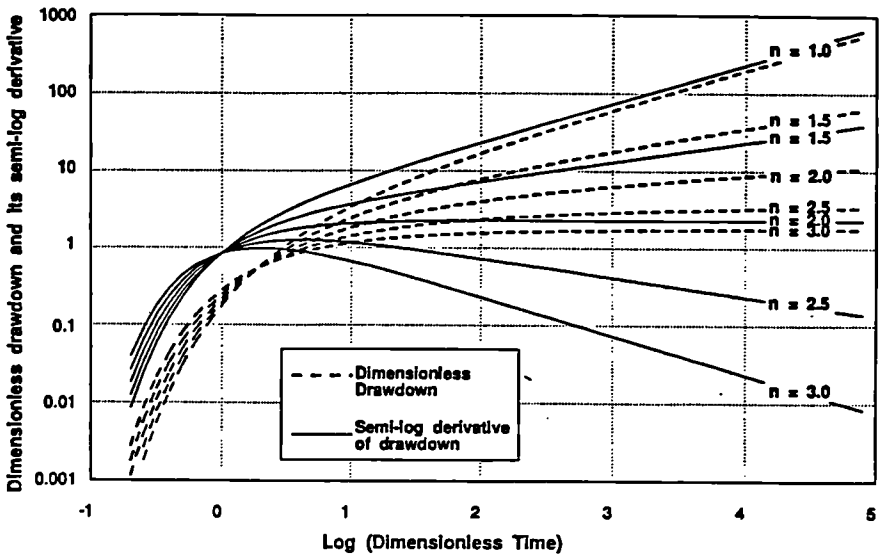


(b) Simulated drawdown and its semi-log derivative versus time of a constant-rate testing

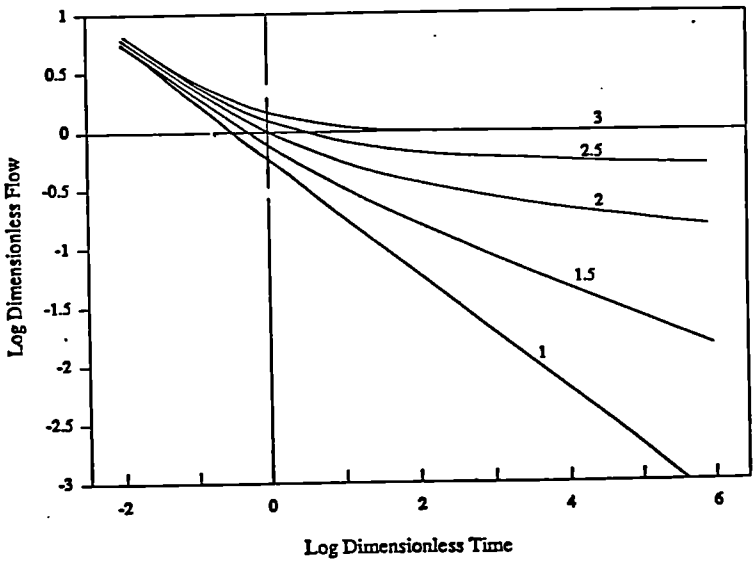


(c) Simulated flowrate versus time of a constant-pressure test

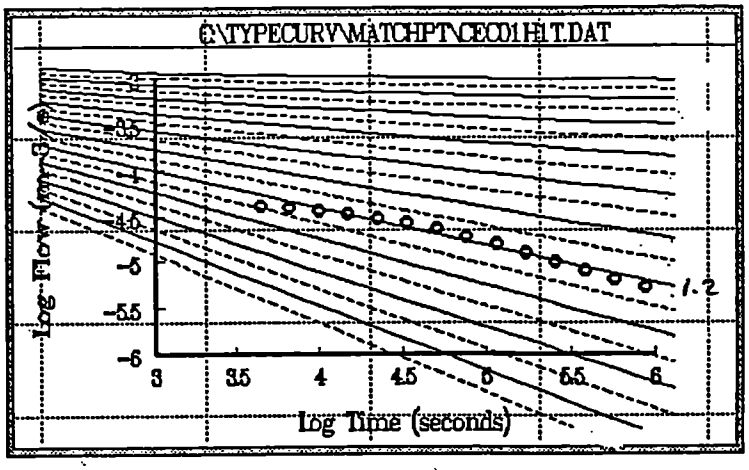
Figure 1 Simulated partial dimensional behaviour in a fracture network simulation



(a) Partial dimension type curves of constant-rate tests



(b) Partial dimension type curves of constant-pressure tests



(c) Computerized type curve matching of the constant-pressure simulation data

Figure 2 Partial dimension type curves and computerized type curve matching analysis

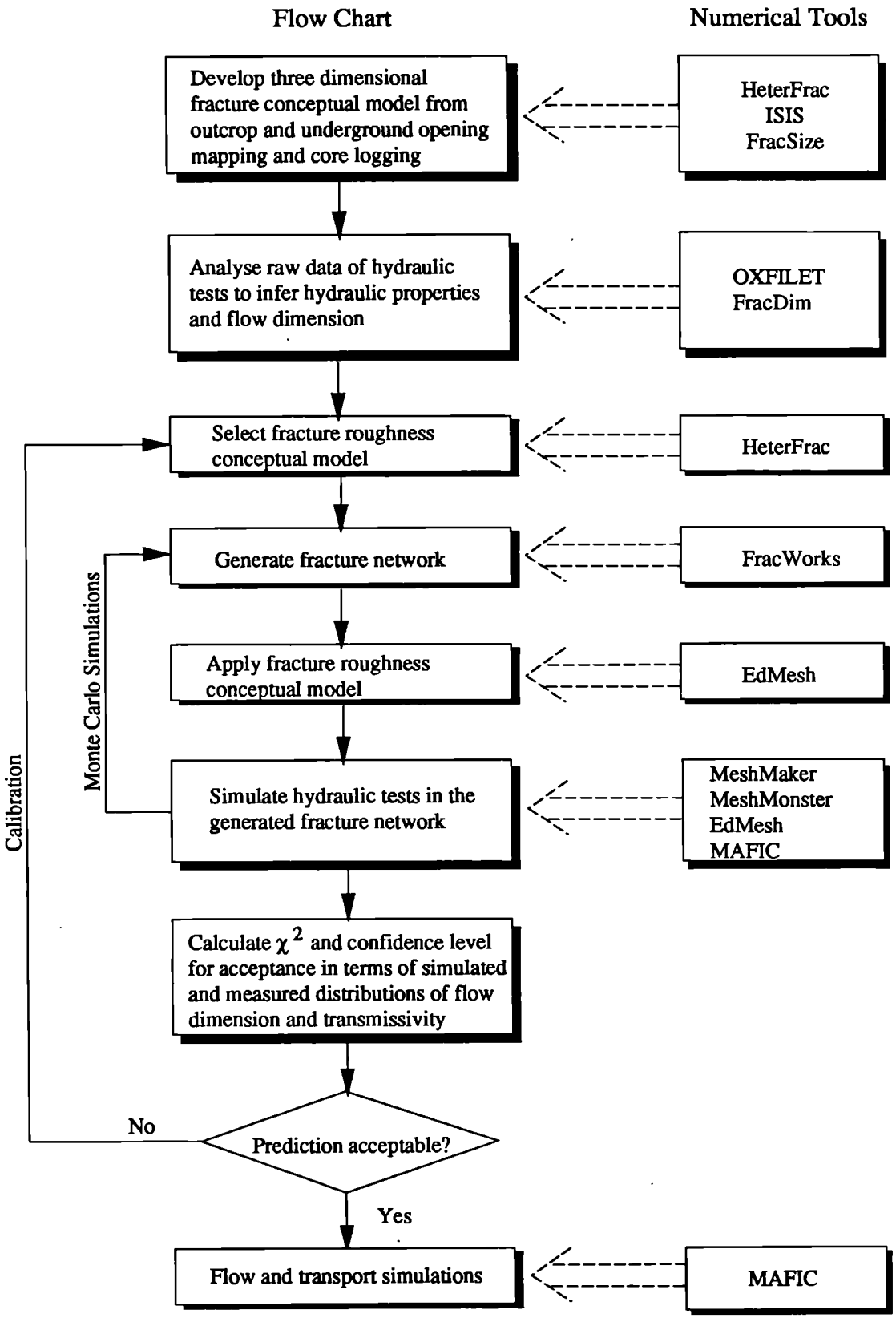


Figure 3: Outline of the modelling approach and the relation with FracMan/MAFIC package components

INTERCLAY II - A Coordinated Benchmark Exercise in the Rheology of Clays

Contractor:	WS Atkins Engineering Sciences
Contract No:	F12W-CT91-0063 (SSMA)
Contract Period:	June 1991 - May 1994 (36 months)
Project Leader:	N.C. Knowles

A. Objectives and Scope

INTERCLAY II is a coordinated benchmark exercise dealing with the numerical prediction of the rheology of clays. Its broad objectives are to improve confidence in long term predictions of geomechanical behaviour of clay in situations relevant to the underground disposal of radio-active waste. Eleven organisations are participating; in addition BNFL and ENRESA are providing sponsorship and have 'observer' status (Table I). A small Steering Committee comprising the coordinator, GCG and SCK provide the technical leadership.

B. Work Programme

There are to be 3 principal stages.

In Stage 1 the basic ability of popularly used models and the computer codes which contain them will be briefly reviewed. The review comprises a comparison of the theoretical capabilities of the codes and their performance on 4 simple, somewhat hypothetical problems.

In Stage 2 laboratory tests on reconstituted clays provide the basis for a computational benchmark problem. Participants are asked to replicate the measured laboratory behaviour as far as possible, in their calculations.

In Stage 3 "in-situ" behaviour will be modelled. Sources of well validated in-situ behaviour are relatively scarce and a specially designed heater test is currently in progress at SCK's Mol research facility. Various other "heater" tests at the Mol facility are stand-by candidates. If possible precise details of the actual in-situ behaviour will be withheld from participants so that their predictions are "blind".

C. Progress of Work

The chronological progress to date in terms of key events is set out in Table II and detailed in [1]. Two day plenary meetings of all participants were held in Epsom (4/5 July 1991) [2], Mol (20/21 January 1992) [3] and Fontainebleau (7/8 September) [4]. The Steering Committee has met periodically and in addition has maintained regular contact by telephone and fax, in order to progress necessary activities.

The achievements to date are best addressed stage by stage:
Stage 1 is now largely complete and four benchmark problems have been successfully addressed. All are hypothetical problems and serve as verification tests of the computer codes used ("verification" in this sense is defined as demonstrating that the mathematical formulation of the problem is correctly implemented and solved by the program. It says nothing about whether the mathematical formulation correctly replicates the real physical situation). The broad technical capabilities of the codes used by the various participants have also been reviewed in this stage and an attempt has been made to collate authoritative sources of data for Boom clay [7].

The four benchmarks are:
1.1 an axisymmetric 1-d approximation of a cylindrical (i.e. tunnel) excavation under isothermal and isotropic conditions [5].

1.2 a two-dimensional, axisymmetric approximation of the progressive excavation of a cylindrical tunnel in clay, again under isotropic and isothermal conditions [5]. (The approximations implied in 1.1 and 1.2 are relevant to deep repositories in clay - e.g. Mol).

1.3 a plane-strain representation of the somewhat idealised construction, operation and post-closure stages of a shallow 'lined trench' repository founded on clay [6]. (This was based on the Drigg LLW disposal facility operated by BNFL in the UK).

1.4 problem 1.1 extended to include a centrally located heat source [6].

In all cases interest centres on the ability of the various conceptual models (and the codes in which they are implemented) to predict steady state behaviour. To provide a proper basis on which to assess these verification problems the "physics" was fully defined - i.e. the loading, boundary conditions, material models and the numerical values of the parameters were all given. It was intended that the only variation between the participants' models would be code-specific (e.g. in the detail of the numerical discretisation or solution procedure used). Various popularly used constitutive models were defined in terms of both effective and total stress with data parameters selected to provide equivalent behaviour wherever possible. (The data relates to Boom clay for benchmark 1.1, 1.2 and 1.4 and to the Drigg site for 1.3, although in the latter case it was found that despite extensive geotechnical surveys the existing information was not in a form suitable for numerical models).

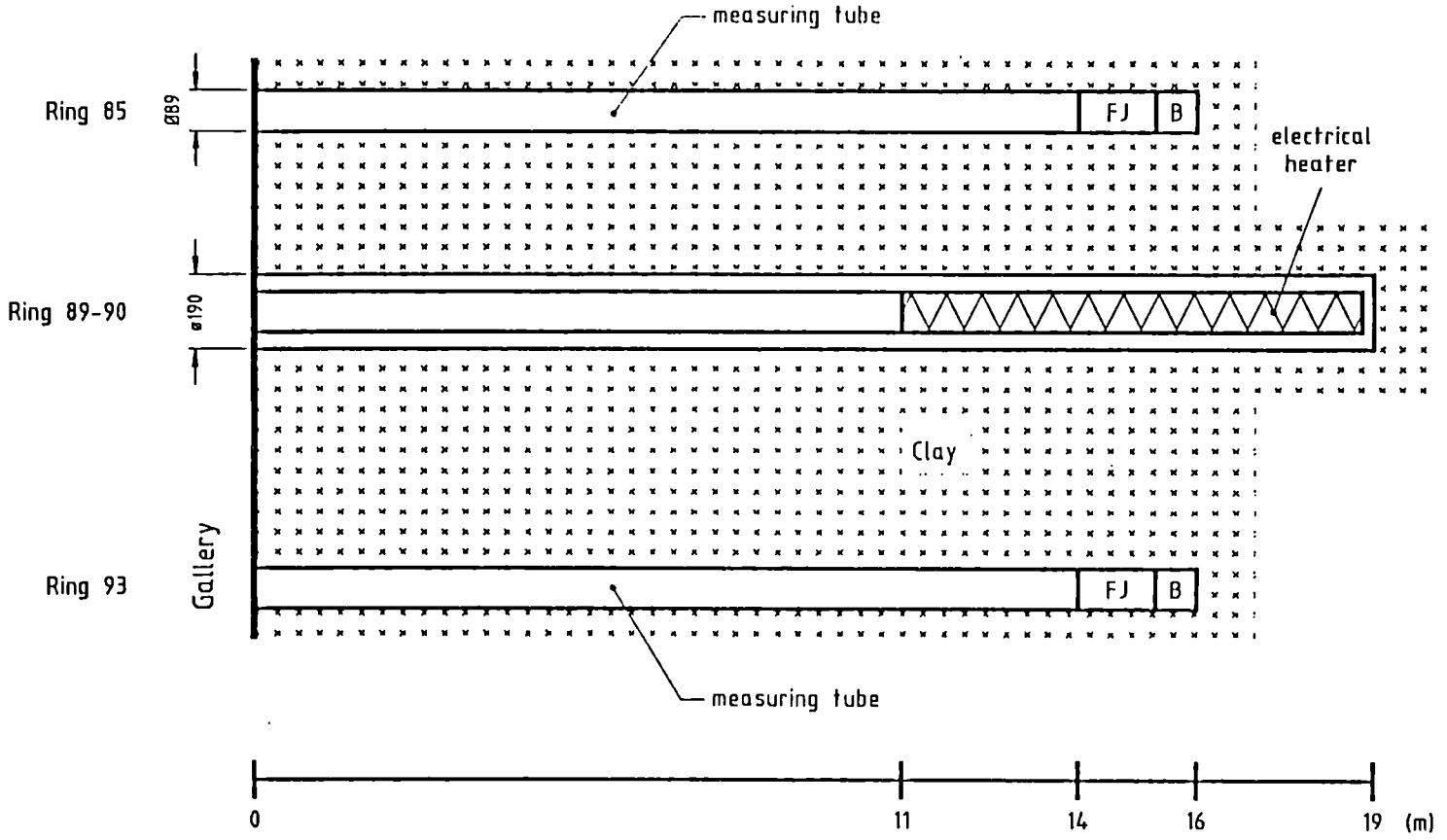
The results of stage 1 [11] broadly demonstrated that verification of computer codes is no longer a major issue (i.e. all codes were capable of predicting the same behaviour, given identical descriptions of the problem). Some differences were observed but these have been satisfactorily resolved following discussion and subsequent investigation. (In this respect two further smaller scale problems were posed to investigate aspects of problems 1.3 and 1.4).

In **Stage 2**, two benchmarks based on laboratory tests, have been agreed and the first is currently being tackled by participants. In both cases it has been necessary to compromise on the ideal of benchmarks based on existing laboratory tests in which the behaviour is fully quantified and self-consistent. A search, carried out concurrently with stage 1, highlighted the relative dearth of any authoritative data from suitable tests. Benchmark 2.1 is thus based around tests on kaolin carried out at Cambridge University some years ago [8]. For Benchmark 2.2 it has been decided to commission some new tests on Boom clay from the 240m level at Mol, which are currently in progress at ISMES Spa in Bergamo, Italy [10]. (These tests were not foreseen at the start of INTERLAY II and extend its scope, although the additional cost is being met from within the present budget allocation). In both benchmarks 2.1 and 2.2, the 'physics' is not fully prescribed, in that the material constitutive model is not defined. Participants will use their judgement and experience to match the "raw data" for the material to a suitable material model in their codes and are asked to then predict the behaviour measured in the laboratory. In the case of Benchmark 2.1, it is not yet clear whether the available raw data is sufficiently complete to be able to make predictions with confidence. For Benchmark 2.2, which involves Boom clay, there is a rather better understanding of the issues involved in material characterisation and the ISMES tests have been designed appropriately.

Stage 3 will be based on in-situ tests at Mol. One particular in-situ test ('ATLAS') has been designed and commissioned specifically for INTERCLAY [9]. It comprises a horizontal lined borehole some 19m long, 190mm external diameter, with an 8m long electrical heater located at the end of the borehold. It is equipped with sensors to monitor total and pore water pressures and temperatures in the horizontal and vertical plane. Two further smaller diameter parallel boreholes in the same horizontal plane are equipped with biaxial stress meters, flatjacks and a piezometer (Figure 1).

At the present time (December 1992), all 3 boreholes have been successfully drilled, the instrumentation installed and the data acquisition equipment commissioned. It is anticipated that the heating test will commence in early Spring 1993 in preparation for the calculation phase of Benchmark 3.1 commencing in September 1993.

In summary the INTERCLAY II project is largely on schedule and good progress is being made towards achieving its objective.



Legend : B : biaxial stressmeter

FJ : flat jacks + piezometers

Fig. 1 General arrangement of ATLAS tests at Mol (top view)

Table I - INTERCLAY II Participants

Coordinator:	WS Atkins	(UK))	
	GCG	(UK))	Steering Committee
	SCK/CEN	(B))	
	BRGM	(F)	
	CEA	(F)	
	EMP	(F)	
	ETSIM	(S)	
	G3S	(F)	
	GEODESIGN	(B)	
	ISMES	(I)	
	LGC	(B)	
	BNFL	(UK)	Observer
	ENRESA	(S)	Observer

References

1. INTERCLAY II "A Coordinated Benchmark Exercise on the Rheology of Clays", Progress Report for the period 1 June 1991 - 31 May 1992 - WS Atkins Science & Technology, July 1992.

2. INTERCLAY II Minutes of plenary meeting, Epsom, July 4/5 1991, WS Atkins Engineering Sciences.

3. INTERCLAY II Minutes of plenary meeting, Mol, January 20.21 1992, WS Atkins Engineering Sciences.

4. INTERCLAY II Minutes of plenary meeting, Fontainebleau, 7/8 September 1992, WS Atkins Science & Technology.

5. INTERCLAY II - Specification of Benchmarks 1 & 2, October 1991, WS Atkins Engineering Sciences.

6. INTERCLAY II - Specification of Benchmarks 3 & 4, February 1992, WS Atkins Engineering Sciences.

7. INTERCLAY II - Properties of Boom Clay - Bibliography GCG (London), August 1992.

8. INTERCLAY II - Specification of Benchmark 2.1, October 1992, WS Atkins Science & Technology.

9. CEC Benchmark INTERCLAY II - Installation Report of the ATLAS Equipment, November 1992, SCK/CEN.

10. INTERCLAY II Project - Benchmark Problem 2.2 - Thermomechanical Test on Boom Clay - ISMES Spa, 4.9.92.

11. CEC INTERCLAY II project - Report on Stage 1, WS Atkins Science & Technology, January 1993.

Date	Event	Purpose
June, 1991	Steering Committee Meeting, Braunschweig	Discussion of possibilities for benchmarks 1.1. to 1.4
July, 1991	Plenary Meeting, Epsom	Selection of Benchmarks
August 1991	Benchmarks 1.1 and 1.2 - Specification issued in draft form	
September, 1991	Benchmarks 1.1 and 1.2 - Specification frozen	
December 31 1991	Results required for Benchmarks 1.1 & 1.2	
January, 1992	Plenary Meeting, Mol	Discussion of Benchmarks 1.1 and 1.2 results. Specification of Benchmarks 1.3 and 1.4
February, 1992	Benchmarks 1.3 and 1.4 - Specification issued in draft form	
March, 1992	Benchmarks 1.3 and 1.4 - Specification frozen	
July 31 1992	Results required for Benchmarks 1.3 & 1.4	
September, 1992	Plenary Meeting, Fontainebleau	Discussion of benchmarks 1.3 and 1.4 results and further results for 1.1 and 1.2
October, 1992	Specification of further studies on 1.3 and 1.4 issued. Specification for Benchmark 2.1 issued	

Table 2 Summary of INTERCLAY II Key Events

Title: SEALING OF BOREHOLES IN CRYSTALLINE ROCKS
Contractor: BRGM, SIF BACHY, MOTT MACDONALD
Contract N°: FI2W - CT 910072
Duration of contract: from 1/10/1991 to 30/09/1995
Period covered: 1992
Project Leader: BRGM (J.-F. OUVRY)

A - *OBJECTIVES OF THE PROJECT*

The objective of the study is the theoretical design of an in-situ borehole-sealing technique that is applicable to fractured crystalline rock, as well as its subsequent implementation. The sealing or backfilling of boreholes in, or around, sites for the disposal of radioactive waste, usually is done with compacted bentonite, or a bentonite or cement slurry. It is proposed to design a special product that combines a bitumen emulsion with clay and other substances. A fracture identified in crystalline rock will be selected for injection testing. The fracture space, measured in drill cores, will be studied in the laboratory and the data will be processed statistically. Tests with water will enable the study of the hydraulic behaviour of the fracture, before and after slurry injection, to define the efficiency of the method.

The contract combines the competence of several partners, including BRGM (F), the SIF BACHY company (F), and MOTT MACDONALD Civil Company (UK).

B - WORK PROGRAMM

- Bibliographical compilation and synthesis of earlier works.
- Laboratory tests for optimization of the the slurry composition.
- In-situ tests of the fracture (geophysics, water injection) and laboratory work (definition of the fracture space on core samples)
- Slurry injection into the fracture, geophysical estimation of its penetrability, and quality control of the injection by means of sample studies and water tests.

C - PROGRESS OF WORK AND OBTAINED RESULTS

State of progress

During the preceding phase of the work, a bibliographical study was made of work on the resealing of boreholes during radioactive-waste disposal. Furthermore, a suitable test site in fractured crystalline rock was sought and a selection was made of several potential components of an injection slurry.

During 1992, the work continued in three directions:

1 Four experimental drill holes were sunk and the natural fractures in their cores were very carefully investigated.

2 Several of the fractures intersected by drilling, were subjected to water tests for defining the hydraulic behaviour of the test area.

3 Several slurries of different compositions were tested for their hydraulical and mechanical properties.

Progress and results

Boreholes

The four boreholes drilled were cored. The fractures in the cores were carefully mapped and compared with the available data on regional fracture patterns. This showed a good correlation between the two data sets.

Hydraulic behaviour of the fractures (Fig. 1)

The main objective of these tests was the definition and characterization of all fractures, which form a connection between the borehole that should be sealed and the surrounding boreholes. The selected fracture(s) will later be injected with the selected slurry. A second campaign of hydraulic tests, after this injection, will make it possible to define the quality of the sealing product through comparison of the results.

In this respect, three parameters seem to be essential:

- The selected fracture should let pass a certain volume of injected water, which should be sufficiently large and variable with the pressure applied.

- Communication between the injection hole and the observation wells should be sufficient for the latter to record either the water inflow related to injection, or pressure variations.

- Water-flow rates recorded in the observation wells should be sufficiently large to enable the appreciation of the efficiency of the injected slurry.

The test principle rests on the measuring, for a fixed injection pressure, of the injected water volume, and of the pressures (and/or flow rates) measured in neighbouring observation wells. The tests, carried out with various increasing pressures, enable the calculation of a unit absorption rate of the fracture, which characterizes its hydraulic behaviour.

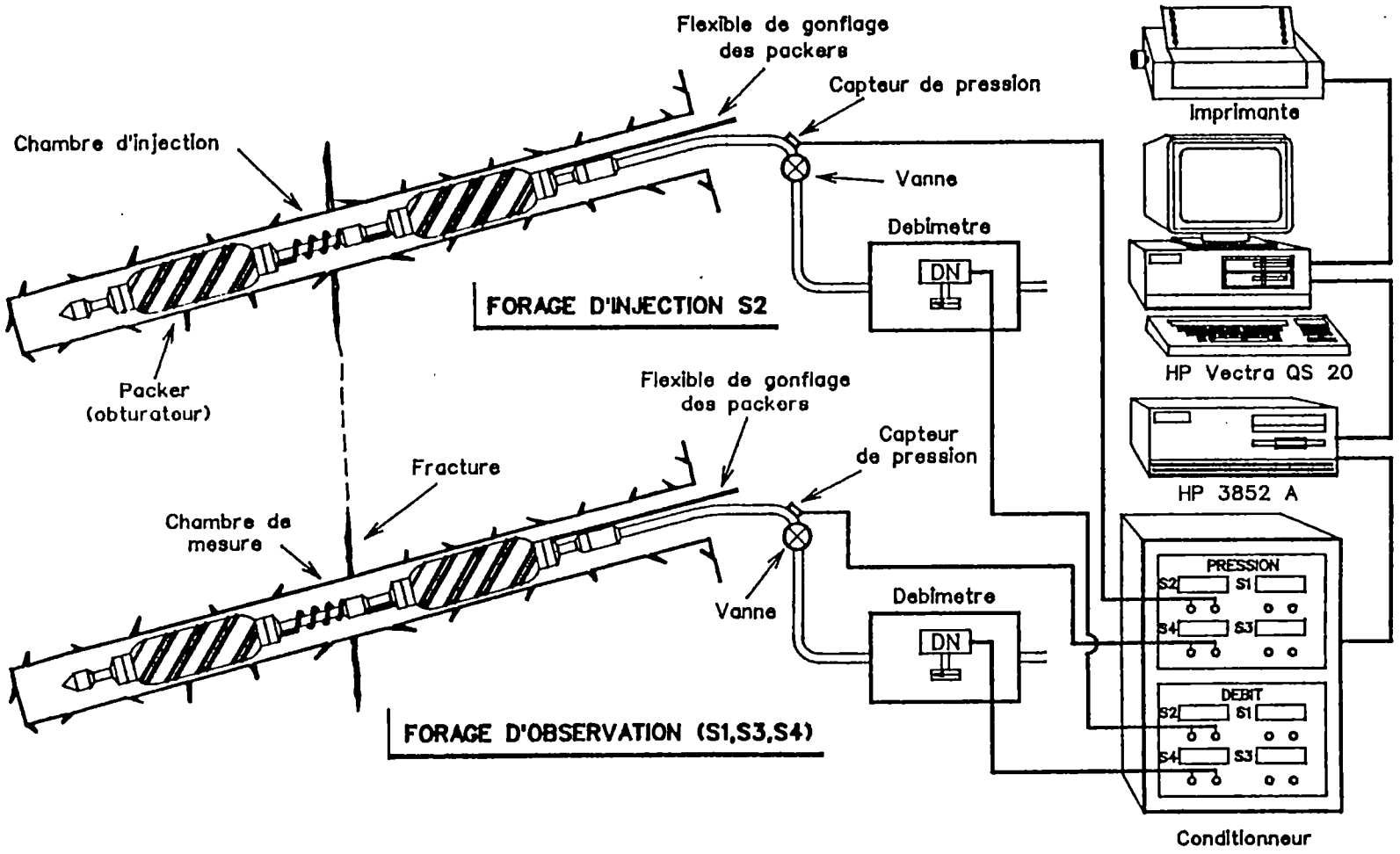


Figure 1 - Layout of the experimental rig for water tests

The tests use a system of four double packers (one for each hole), which makes it possible to isolate in each hole one or more well defined fractures, and to test several combinations of fractures by means of simply shifting the packers in the holes (Fig. 1).

Interpretation of the results led to the selection of several fractures, from which the final injection discontinuity will be selected. Other studies, presently being carried out and investigating the fracture morphology and its three-dimensional representation, should lead to further refinement of the choice.

Injection slurries

Selection of the basic components of the injection slurries is done by comparing several parameters, which are mainly related to particle dimensions, their ability to penetrate tiny fractures, and the stability of their properties. A large number of laboratory studies (stability, filtration, viscosity and rheology) was carried out to define the mineral and hydrocarbon phases used. Several slurry formulas were retained for further and more thorough study of their mechanical properties (Table 1):

- Two slurries with a moderate stiffness (M12 and M13), based on silica smoke and calcium hydroxide, were selected for their filtration and viscosity properties.

- Two very stiff slurries(83 and 101) were selected that contain the same amount of calcic bentonite and a variable quantity of ultra-fine cement (Spinor A).

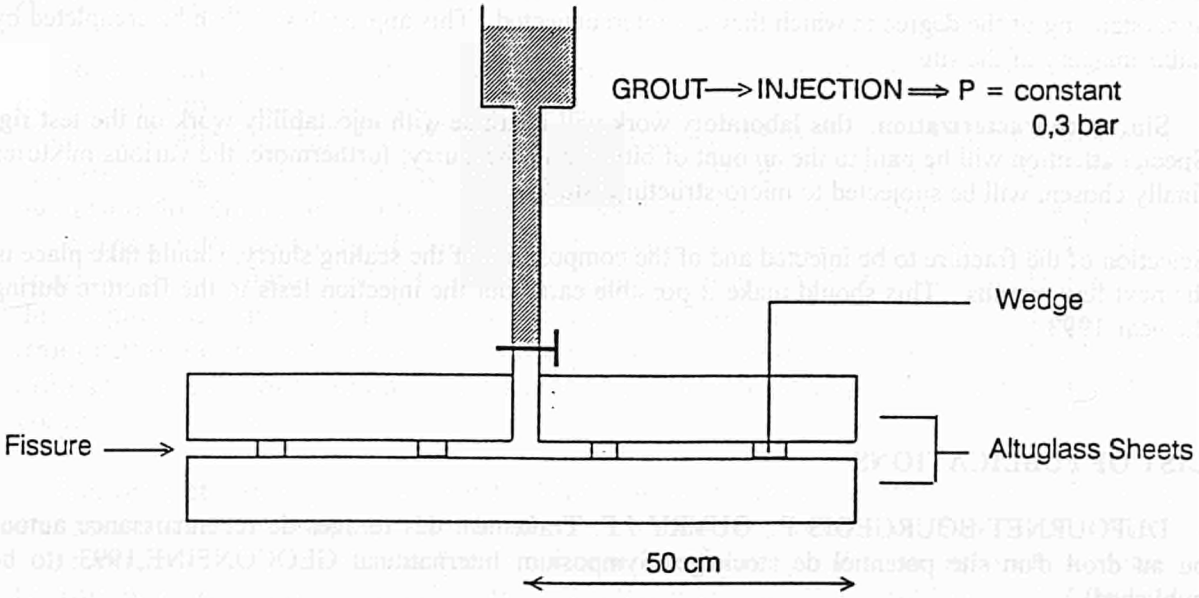
- A bituminous slurry, more stable and viscous, was selected for its rheological properties and its filtration capacity (122b).

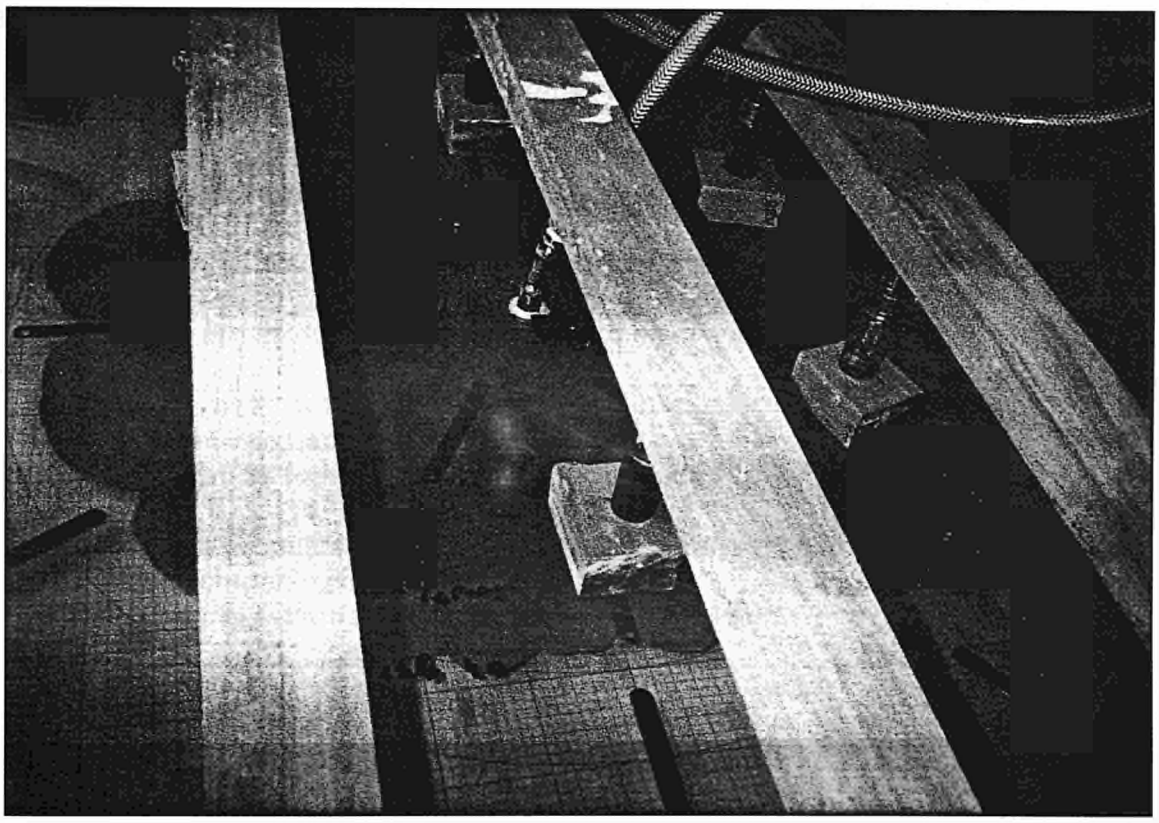
SAMPLE	M12	M13	83	101	122b
Lime	85.7	64			
Silica	114.3	86			
Additives (% dry extracted)	1.5	2			
Argisil GT (calcic bentonite)		30		200	
Spinor (cement)			200	150	150
Foca (calcic bentonite)			200		
RF			3	3	12
Kaolinite					50
Bitumen					150

Table 1 - Composition of the five slurries retained for further study of their mechanical properties

A device was developed for defining the penetrability of the slurry (Fig. 2). The fractures that were modelled between two plexiglass sheets had a width that was les than 0.40 mm. A fixed volume of slurry was injected in the centre of one of the sheets, and its sub-circular lateral extension was then studied.

Figure 2 - Layout of the experimental rig for characterization of slurry penetrability





Perspectives

During the year 1993, the work will mainly cover the further understanding of the points mentioned above.

- **Fracture characterization**: casts taken of cores will be used for studying the surface condition of fracture walls, as well as their degree of opening. This will lead to better definition of the fractures that can be injected; as well as to better definition of the injection-slurry composition. Graphic three-dimensional representation of the fracture networks intersected by the boreholes, will lead to better understanding of the degree in which they are interconnected. This approach will then be completed by radar imagery of the site.

- **Slurry characterization**: this laboratory work will continue with injectability work on the test rig. Special attention will be paid to the amount of bitumen in the slurry; furthermore, the various mixtures finally chosen, will be subjected to micro-structural studies.

Selection of the fracture to be injected and of the composition of the sealing slurry, should take place in the next few months. This should make it possible carry out the injection tests in the fracture during the year 1993.

LIST OF PUBLICATIONS

- DUFOURNET-BOURGEOIS F., OUVRY J.F. Traitement des forages de reconnaissance autour ou au droit d'un site potentiel de stockage. Symposium International GEOCONFINE,1993 (to be published)

Title:	Paleoclimatological Revision of Climate Evolution and Environment in Western Mediterranean Regions.
Contractor:	ENRESA
Contract nº:	FI2W-0075
Duration Contact:	48 months
Period covered:	From January to December, 1992
Project leader:	C. Bajos

A. OBJECTIVES AND SCOPE

To evaluate the security of a high level waste repository it is necessary to determine how future climate changes will affect the safety of the repository. The magnitude and likelihood of these changes can be inferred from the study of past climate changes. However, up to date, scarce data is available about past climate evolution in Spain and other Western Mediterranean countries. This project is concerned with the study of climatological changes occurred during the last 2 million years in the Western Mediterranean regions, which will be of importance for developing scenarios for the safety analysis of a high level repository in Spain. Even though the techniques to be used in the study will provide information with different time scales, special emphasis will be placed on climate changes during the last 1000 years.

The project is being carried out by ENRESA as the main contractor and BRGM as an associated contractor. Work about climate evolution in Spain has been subcontracted to the Instituto Tecnológico y Minero de España. BRGM is responsible for the review of past climate data from Southern France, Italy and North of Morocco and for the development of scenarios.

B. WORK PROGRAMME

The project has been subdivided into the following tasks:

1) Synthesis of the environment in Spain over the last two million years.
   Period of performance: June 1991 to April 1993.

2) Paleoclimatic and environmental study of Quaternary deposits in the Tajo Valley.
   Period of performance: June 1991 to April 1994.

3) Study and dating of travertines in Spain as a paleoclimatic and paleoenvironmental index.
   Period of performance: June 1991 to April 1994.

4) Climatic reconstruction of the last thousand years in Spain on the basis of dendrochronological series.
   Period of performance: June 1994 to April 1995.

5) Paleoenvironmental reconstruction and construction of future evolution scenarios.
   Period of performance: June 1991 to April 1995.

C. PROGRESS OF WORK

State of advancement.

During this period the teams of research workers have been definitively set up for each of the different sub-projects and are now working at full pace, such that the delays in the initial working schedule have been compensated almost entirely. There may be only a slight delay of about 3 months in task 1, which will not affect the time schedule of the remaining tasks within the project.

Progress and results.

Task 1: Synthesis of the environment in Spain over the last two million years.

Up to date, 80% of the chapters have been received although some of them in draft form. It is expected that all chapters will be received before the end of the year. This delay in the delivery of the originals by the different authors implies that this task will have a delay of about 3 months in relation with the original program.

Task 2: Paleoclimatic and environmental study of Quaternary deposits in the Tajo Valley.

To date, two areas with terraces have been selected in the Tajo River to carry out field work (Figure 1). One of then is located on the stretch between Talavera de la Reina and Malpica and the other is immediately upstream and downstream of the city of Toledo. A third area is still to be defined.

Field work began last summer in Talavera de la Reina. A total of 14 terraces have been identified in the area studied, between the lowest, at +2-3 metres, on the lower alluvial plain and the terrace located at +195 metres, which is embedded in the bedrock of the Raña (Plioquaternary deposits). Soil samples have been collected from these areas and analyzed at the Soils laboratory of the Centre for Environmental Sciences.

The initial results obtained from the study of the soils developed on the alluvial plain, and lower and intermediate terraces indicate that they were formed under a semiarid mediterranean climate. On the contrary, the soil samples collected from the upper terraces and Raña indicate a more humid mediterranean climate.

In conclusion it may be stated that in the Talavera de la Reina - Malpica sector, paleoedaphic criteria may be used to identify soils formed under conditions of greater relative humidity during the lower Pleistocene-upper Pliocene, as opposed to soil formed during the middle and upper Pleistocene and Holocene periods under semi-arid conditions similar to those currently existing.

These provisional results may be confirmed in the near future, once the study of other sequences of the Tajo Valley have been completed.

Task 3: Study and dating of travertines in Spain as a paleoclimatic and paleoenvironmental index.

Field work in Central Spain, Mediterranean Coastal Area and Iberian Chain zone (Figure 1) has progresses as planned.

Field work in the Reguerillo Cave and adjacent Karstic areas, in Central Spain, has been completed. The interpretation of a paleomagnetic anomaly in the stratigraphic series of the Reguerillo Cave, has made it possible to date the succession of events occurring in the zone in the Pliocene-Lower Pleistocene, among them a large flood which will have to be interpreted within a wider framework.

Work has been initiated in the Mediterranean Coastal Area. The dating and palynological determination from the boreholes covering the entire lower terrace (Würn) of the Banyoles Lake are now available. Eighty samples have been taken for oxygen isotopy. Future work will include sampling in the intermediate and upper terraces.

The studies in the Iberian Chain zone will concentrate fundamentally in the travertine terraces of the River Guadiela and adjacent basins, where the geomorphological cartography has already been completed. In addition, seven detailed sedimentological columns have been studied and fossil fauna samples taken.

Other areas for future research will be: The tufa at the Lagunas de Ruidera, in the Southern Plateau and several karstic caves in the Cantabrian Coastal Area.

Task 4: Climatic reconstruction of the last thousand years on the basis of dendrochronological series.

To date, tree sampling has been initiated in Galicia (Ancares and Invernadeiro Mountains), Guadarrama (Los Molinos) and Urbión (El Muchachón y Castillo de Vinuesa), (Figure 2) and new visits will be made to these areas next Spring.

Sierra de Ancares.

Five trees were chosen in the upper reaches of the River Ortigal and eight in the area of Cabanabona. A total of 22 samples have been extracted in 13 trees of the species *Quercus pyrenaica*, located between 1.200 and 1.300 metres above sea level and with diameters ranging from 90 to 144 cm. Their age may be between 320 and 340 years old.

Sierra de Invernadeiro.

Ten trees (*Quercus pyrenaica*) were selected at an altitude between 1.100 and 1.200 metres which, given their diameters -between 91 and 124 cms.- appeared initially to be long-lived specimens. The number of rings detected in the 20 samples obtained provide information on the last 400 years.

Los Molinos.

Although certain chronologies were already available for this area, its central geographical location, where widely varying climatic environments meet, made it advisable to gather as much information as possible. For this reason, new samples were taken from the area known as Los Molinos, at an altitude of between 1.100 and 1.200 metres. Twelve trees of *Pinus sylvestris* providing 23 samples were taken. A first approximation suggests an age of less than 250 years old.

El Muchachón.

This area is located at a height of between 1.600 and 1.700 metres, where excellent specimens of *Pinus sylvestris* measuring up to 179 cms. in diameter are to be found. Thirteen trees were selected, from which 25 samples or cores were extracted. It may be estimated that the information provided will cover the last 400 years.

Castillo de Vinuesa.

The species *Pinus uncinata* was sampled on the sides of this mountain, above 1.800 metres. Nine trees were selected with diameters of between 70 and 91 cms. The chronology which it will be possible to construct on the basis of the 17 cores extracted will very probably cover between 420 and 450 years.

Task 5: Paleoenvironmental reconstruction and construction of future evolution scenarios.

Work has progressed according to schedule in the preparation of a synthesis about the situation of Spain during the Quaternary in relation to the environment in other Western Mediterranean Countries.

Regarding the simulation work, a meeting was held in Madrid among all participants in the project to discuss the location of the site to be modelled (paleosite). A preliminary library research indicates that several areas within the Tajo basin could be adequate. Further research will take place to decide the location of the site by November 93.

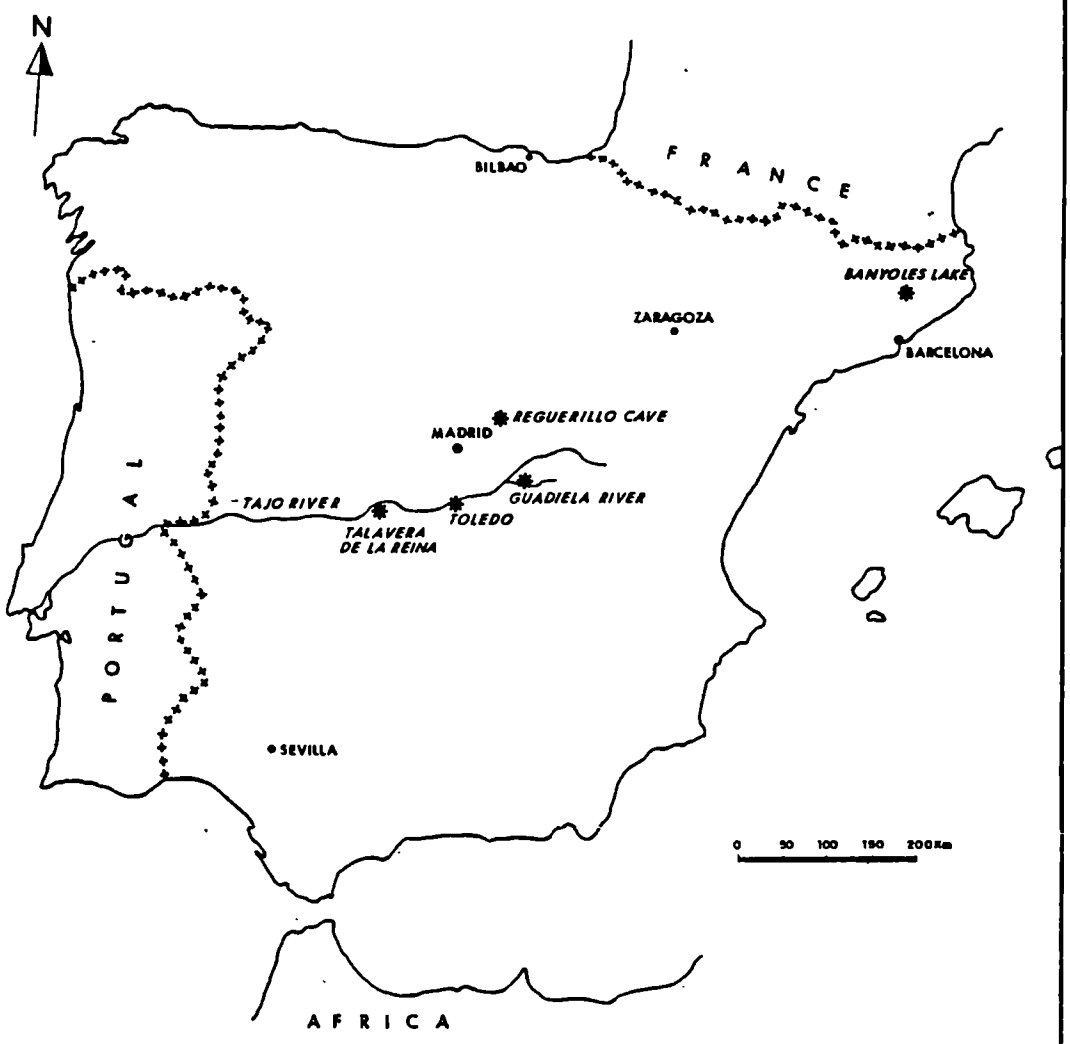


FIGURE 1 – FIELD WORK SITES FOR TASKS 2 AND 3

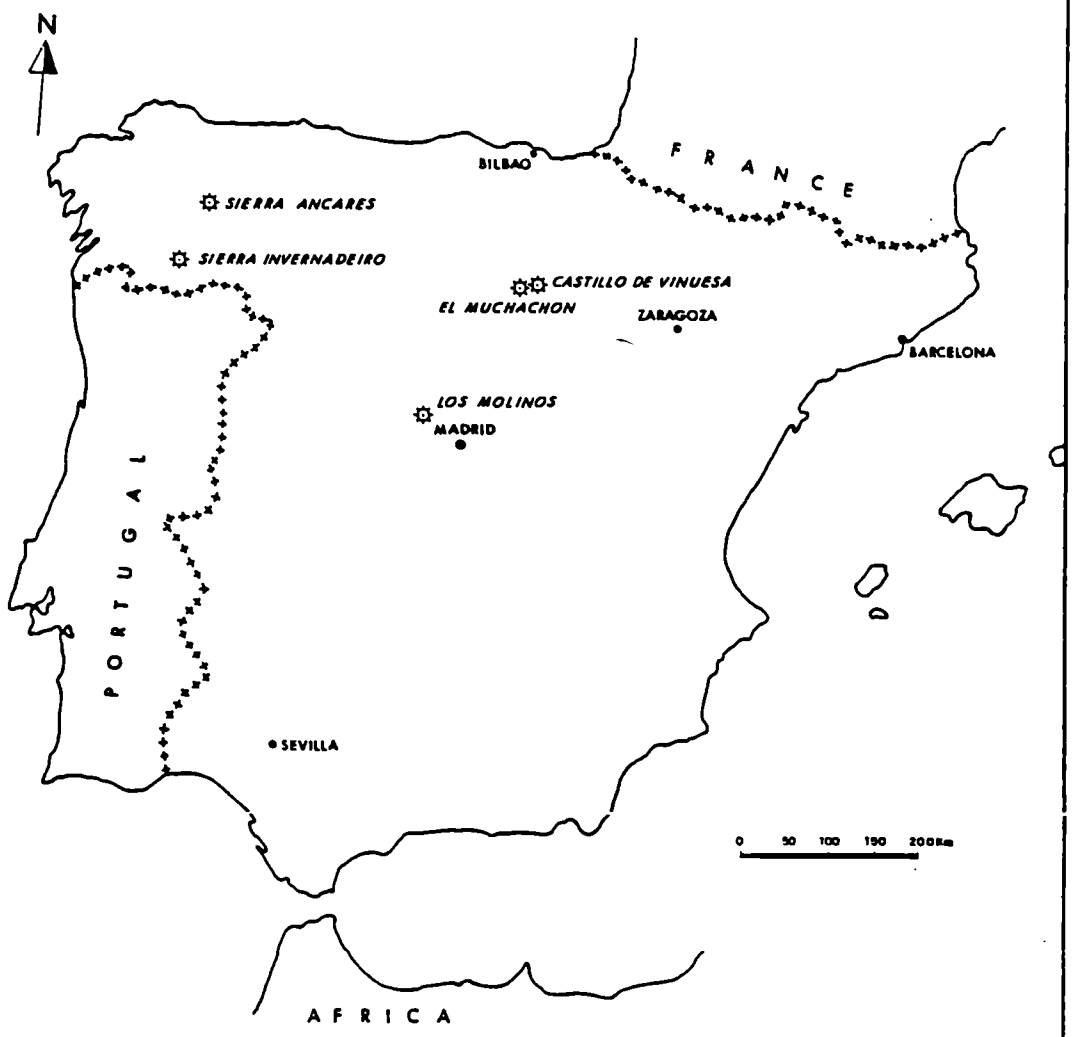


FIGURE 2 – SAMPLING SITES FOR TREE RING STUDIES (TASK 4)

Title: WATER FLOW AND SOLUTE CONVECTION THROUGH FRACTURED ROCK

Contractor:	**UK Nirex Ltd**
Contract No:	**F12W/0078**
Duration of Contract:	**1 February 1992 to 31 January 1993 (extension required)**
Period Covered:	**1st April 1992 to 31st January 1993**
Project Leader:	**Dr A J Hooper**

A. OBJECTIVE AND SCOPE

The objectives of the work are to quantify the extent to which bulk water movement through a layered volcanic sequence at Sellafield (the Borrowdale Volcanic Group) occurs through small fractures amenable to a statistical description. In addition, the work will assess the feasibility of obtaining individual fracture flow data by the techniques developed by Nirex at its research site (Reskajeage Quarry, Cornwall, SW England). An assessment will be made of the use and application of the techniques within the site investigation programme at Sellafield.

The work is being coordinated by UK Nirex Ltd, in conjunction with AEA Technology. Field work at the Sellafield Site will be supervised by Nirex's Geological Consultant, Sir Alexander Gibb and Partners.

B WORK PROGRAMME

1. Examination of geophysical and core logs to determine depths, orientations and average spacing of anticipated flowing fractures.
2. Initial double packer testing of borehole with a packer spacing less than average flowing fracture spacing.
3. Optimisation of packer spacing and test boundary conditions, based on initial observations.
4. Determination of distribution of fracture conductivities.
5. Input to stochastic discrete fracture network code and consequent predictions of flow over long lengths of borehole.
6. Comparison with measurements of flow over long lengths of the borehole.

C PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

A preliminary interpretation of fracture geometry has been produced, using wireline geophysical data and core logs obtained from boreholes 2,4 and 5 at Sellafield. This represents completion of Programme Item 1. A review of equipment to perform the field work identified under items 2,3 and 4 has been completed and the necessary equipment is being procured. In order to fit into the overall Nirex programme, an extension in time has been requested, to enable field work to be performed in mid 1993. The main problems in performing these tests is the specified resolution of transmissivity of 10^{-12} m^2s.

Progress and Results

1. Fracture Network Geometry

The positions and orientations of fractures in the BVG, sampled from Sellafield boreholes 2,4 and 5 have been classified by the British Geological Survey by cross matching planar features interpreted from the FMS/BHTV log with fractures located during core inspection. From this dataset, which currently provides data relative to the borehole, a number of potentially water conducting fractures have been identified and their orientations determined. As the BGS core inspection is performed on a partial dataset, there are errors inherent in this number of potentially water conducting fractures. The feasibility and significance of reducing these errors by correlation with a complete on-site discontinuity log is currently under discussion.

Four preferred fracture orientations relative to the borehole are identified: Set "a" dips moderately steeply to the NE. A less pronounced set "b" dips moderately to the south east. Two additional sets are also evident and are variably developed in the different boreholes. Set "c" dips moderately steeply to the north north west and set "d", steeply to west south west.

Boreholes 2,4 and 5 are effectively vertical. Any deviation occurs at a high angle and consequently high angle fractures are less likely to be intersected. Therefore, stereographic projections of uncorrected borehole data are biased. Figure 1a indicates weighted stereonets of the data, where a correction factor has been applied to reduce the bias of the uncorrected stereonets.

The frequency of anticipated potential flowing fractures, derived from the BGS core inspection, and subject to the above assumptions is given in Figure 2.

Additionally, preferred orientations of fractures from a small dataset of outcrop observations are plotted in Figure 1b. Consideration of Figures 1a and 1b indicates similarities between borehole and outcrop derived orientations.

2. Fracture Transmissivity Measurements

This incorporates consideration of programme items 2,3 and 4. A review of approaches which could be used to obtain fracture transmissivity data has been completed. The principal conclusions of this review are as follows, and are currently being incorporated into a field specification for the work:

2.1 Number of tests

- A large number of tests will be required (of order 100 tests) to provide input data for the fracture network model. Clearly, it will be an advantage to have a relatively standard and simple approach to analyze the data, so that data analysis does not become excessively time consuming. For this reason, a test that produces data which may be treated by simple models will be advantageous.

2.2 Test Type

- A simple pulse test analysis assumes that the pulse duration is short compared to the period over which recovery occurs. A programme to predict the pressure decay in the zone following a finite duration pulse has been written for Nirex. This has not yet been extended to calculate the transmissivity of the formation. A simple code could be written to analyze such finite duration pulse tests (where pulse duration is more than 10% of the recovery period), but it is probably better to attempt to apply pulses of effectively "infinitely short" duration. Since it requires approximately 20 seconds for the Schlumberger MDT tool to inject the fluid into the test zone, zones with transmissivities below $10^{-9}m^2s^{-1}$ should be analyzable with the instantaneous pulse assumption. The errors incurred in analysing higher transmissivity zones with the "instantaneous pulse" assumption are currently being assessed.

- The MDT tool can be used in a constant flowrate mode (either injection or abstraction) to determine transmissivities greater than 10^{-9} m^2s^{-1}. In principle, zones having transmissivities intermediate between those that may be determined using either the simple pulse test analysis or a constant rate injection (or withdrawal) test, could

be analyzed using a superposition approach. However, such an approach requires the well bore storage to be determined, so that leakage to the formation during application of the pulse can be determined. It will be necessary to test whether the well bore storage properties measured from the casing test will be the same as the properties measured in-situ, where the packer is inflated in a borehole of variable diameter and wall smoothness. Well bore storage data from the Reskajeage tool string is currently being assessed to determine the extent to which the well bore storage varies between tests, and how the in-situ values compare with those measured in casing tests.

2.3 Operational Limitations

- In order to derive the transmissivity of the formation from the decay of the pressure pulse, it is necessary to know the well-bore storage properties. The storage can be calculated at the beginning of each test, if it is assumed that leakage into the formation is negligible during the pulse "application" (this is the modified slug test, described by Neuzil, currently being used at Reskajeage). It is estimated that this assumption would be valid for transmissivities less than $10^{-9}m^2s^{-1}$.

- In order to derive a relatively complete distribution of fracture transmissivities, measurements down to $10^{-12}m^2s^{-1}$ will be required. This will require sensitive instrumentation and test design. Transmissivities as low as $10^{-11}m^2s^{-1}$ are currently measured at the Cornish Research site. The Schlumberger MDT tool has a lower inherent equipment error and consequently a lower detection limit. However, a reconfiguration of the Cornish site wireline packer system, to incorporate down-hole shut in valves should improve the detection limit of the Cornish system. It should be stressed that any of the systems reviewed will be operating near detection limits to achieve the lower end of the fracture transmissivity distributions. This will increase the uncertainties in the derived data and the use to which it can be put.

3. Stochastic Fracture Network Model.

A geometric model of the site has been developed using the NAPSAC Stochastic fracture network code. This model is subject to inherent uncertainties due to simplifications, assumptions and sparsity of data on which it is based. It will be revised on the basis of more rigorous fracture analyses.

No small scale fracture transmissivity data have been input to this model, as programme items 2,3 and 4 are not complete.

4. Predictions/Measurement Comparison

A series of 50m straddle length measurements of transmissivity have already been made in boreholes 2,4 and 5 at Sellafield. These will be used to compare with predictions from the final NAPSAC model to be generated from programme item 5 (see section 3 above)

List of Publications

None of the work under this contract has been published during the reporting period.

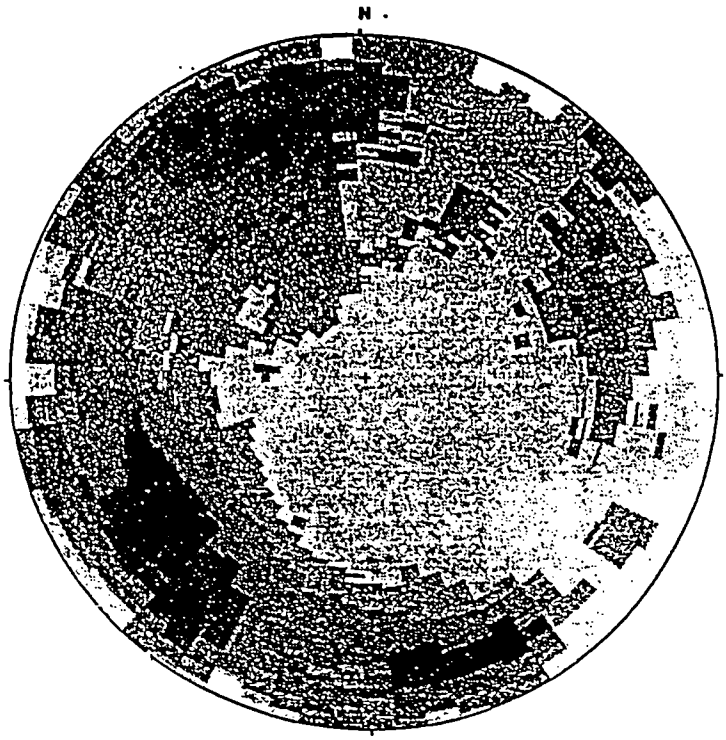


FIGURE 1a.
Orientation from borehole data, corrected for vertical bias.

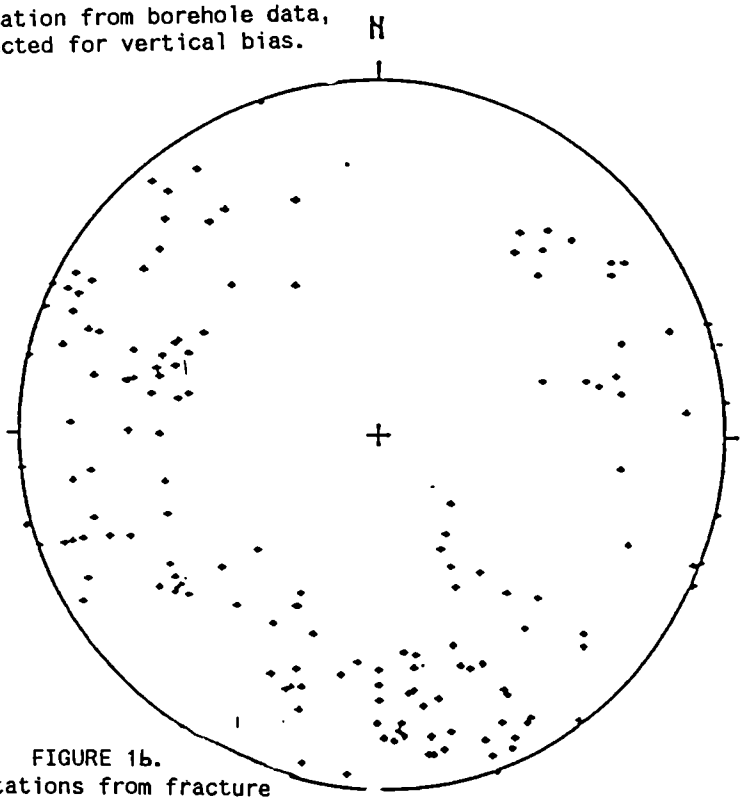


FIGURE 1b.
Orientations from fracture traces at surface

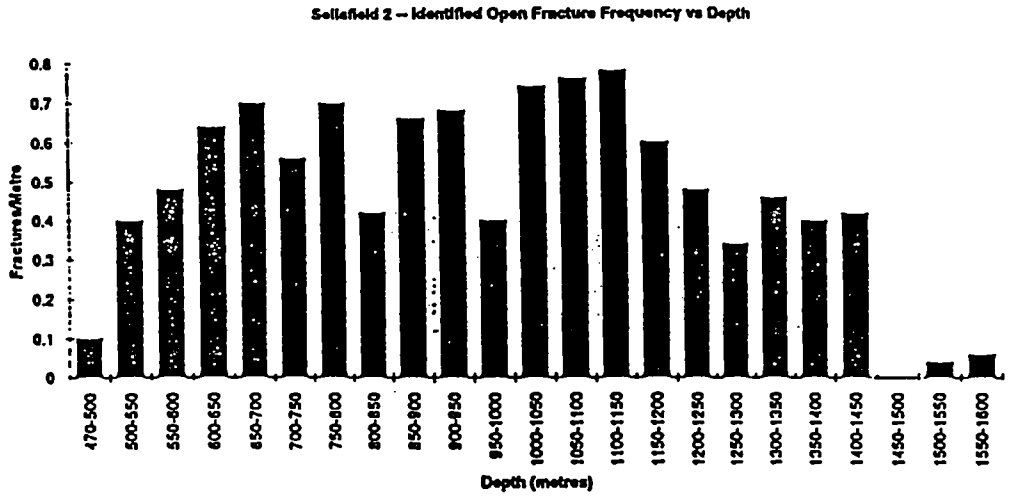


FIGURE 2. Frequency of potentially open fractures derived from BGS core inspection - Borehole 2.

Title:	Geochemical validation of solute residence times: review and comparison for various geological environments
Contractor:	BGS (NERC)
Contract No:	FI2W-CT91-0092
Duration of contract:	from 1 April 1992 to 31 March 1995
Period covered:	1 April 1992 - 31 December 1992
Project Leader:	Dr PJ Hooker

A. *OBJECTIVES AND SCOPE*

The scope of the project is to assess the uses of geochemical and isotopic techniques in the estimation of groundwater movements over the long time-scales appropriate to the disposal of radioactive waste in various and 'reference' hydrogeological environments. The objectives are:

- To compile relevant geochemical data for various European hydrogeological environments from different sources.
- To review the validity of these data under the various hydrogeological and geochemical conditions and their consistency with hydrodynamic information. The review will highlight the contrasts between the geological and hydrological histories of the various European locations (e.g. structure, tectonics, permeabilities, climate etc.).
- To assess the concept of 'reference' hydrogeological environments to illustrate principles, features and limitations of groundwater residence time estimations.
- To identify specific data needs, 'gaps' and uncertainties.

B. *WORK PROGRAMME*

1. Review of the literature for methods and data for estimating solute and groundwater residence times in various hydrogeological environments.
2. Discussions and collaboration with appropriate European research groups concerned with radioactive waste repository investigations and groundwater tracer techniques.
3. Gaining new data from measurements in european laboratories on samples from (a) investigations being carried out by UK Nirex Ltd., if available, and (b) other appropriate groundwater systems.
4. Reporting on the different stages of work as they are completed. The expected reports comprise two review reports, a progress report on new data and a final report.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

In 1992, the work programme has mainly been focussed on initiating and carrying out the reviews of the state-of-the-art. The first review task has concerned the scientific basis of each geochemical and isotope method applicable to estimating groundwater residence times. This first review report on methodologies is in draft form. It outlines for each method the systematics and assumptions, the sampling techniques and precautions, the analytical procedures, the applications and interpretation and limitations. A library search for relevant papers in the literature produced 342 references which have been entered into a database in Endnote™, with the authors' names, titles and keywords which include the locations of the various studies. A printout of Endnote™ forms the Appendix of the first review report. In 1993 a second review report will be produced which will describe data from a selected number of hydrogeological case studies involving different rock types.

Progress and results

1. Review of the literature for methods and data.
It is logical that the first task should be concerned with a review of the different geochemical methods and isotope techniques applicable to solute and by inference groundwater residence times. Clearly, the ideal tracers for estimating groundwater residence times are not only wholly conservative, tracking the groundwater flows in a faithful manner, but also have an associated property of time e.g. radioactive decay. The geochemical and isotope sytems reviewed are:

Tritium; C-14; Cl-36; I-129; noble gases (He etc.); Sr-87; U-series (with Rn); stable O/H isotopes; B isotopes; C-12 and C-13; others e.g. common Ca/Na/Cl.

For each method the systematics and assumptions, the sampling techniques and precautions, the analytical procedures, the applications and interpretation and limitations have been described.

A library search for the relevant papers in the literature was followed by a sift of the listing to identify the useful references. Copies of the identified papers were made and placed in an ordered archive. A database of the literature containing over 340 references has been entered into Endnote™ with the authors' names, titles and keywords. Among

the keywords are the location and rock types involved in the studies. These copies of relevant papers and the Endnote™ bibliography form the foundation of the review tasks under item 1.

In 1993, a second review task dealing with data from a selected number of various hydrogeological case studies involving different rock types will lead to a second report.

2. Collaboration with appropriate European groups.
This item is in an early phase of advancement.

3. Gaining new data.
It is hoped that appropriate groundwater samples from the Sellafield area in Cumbria, England, can be obtained for new measurements that may throw light on the nature of the groundwaters that affect the proposed deep repository. Of especial interest is the possible application of boron isotope measurements to constrain the origins of salinity. Other areas for new measurements e.g. the Paris Basin, are also being considered.

4. Reporting.
The first review report on the different methodologies applicable to estimating groundwater residence times is in draft form.

List of publications

None has been produced in the reporting period.

Title : DECOVALEX project: modelling of THM behaviour for granitic rocks.
Contractor : CEA/IPSN
Contract n° : FI.2W/0111
Duration of contract : 3 years, (from january 1st, 1992 to december 31st, 1994.
Period covered : 1992 (1st year of contract)
Project Leader : J.Cl. GROS, CEA/IPSN.

A. OBJECTIVES AND SCOPE

The work presented in this report is part (1st phase) of the international DECOVALEX project (international co-operative project for the DEvelopment of COupled models and their VAlidation against EXperiments in nuclear waste isolation).
The objective of this project is to study the importance of THM (thermo-hydro-mechanical) processes in the transport of radionuclides from the repository up to the biosphere.
Several teams work on the same simple exercises of modelling underground disposals in elastic fractured rocks. The DECOVALEX project also aims to improve and to compare the different calculations codes, and to compare and compile experimental results.

The DECOVALEX project is composed in its first phase (october, 1991 to september, 1992) of two bench-mark tests and one test case. The first bench-mark test is a far-field study of a very fractured rock mass, the second one is a near-field study of a reduced number of fractures, and the test-case study the real behaviour of a single fracture.
Results presented in this report concern the first bench-mark test (far-field model).

B. WORK PROGRAMME

Bench-Mark Test n°1 is proposed by M.DURIN (CEA/DMT, France) and H.BAROUDI (INERIS, France). It is a 2-D modelling of the reactions, by THM processes, of a rock mass, (3000mx1000m) to a radioactive wastes disposal about 500m deep. The rock mass is made of an elastic rock cut into numerous blocks by two sets of orthogonal fractures. A non-uniform hydraulic gradient is imposed at the top of the rock mass, and a zero water flux at the bottom and on the two sides. The temperature at the top is imposed, there is a zero heat flux on the two sides and, at the bottom, a heat flux such that the vertical gradient of temperatures equals the geothermal gradient.

The work programme is as follows:

- Selection of a discrete approach to model the rock mass.
- Selection of three 2-D codes based on the finite elements method : one for the mechanical calculation (VIPLEF), one for the thermal calculation (CHEF), and one for hydraulic (HYDREF). These codes were developed by the Ecole Nationale Supérieure des Mines de Paris.
- Addition to the HYDREF code of a joint-element taking into account both a thermo-hydraulic approach by a quadratic estimation of the density, the viscosity and the temperature of the fluid, and a hydro-mechanical approach by a quadratic estimation of the joint aperture.
- Coupling THM with CHEF, VIPLEF and HYDREF.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

We chose to model the rock mass by a discrete approach, i.e by representing all the blocks and discontinuities. Our aim is to compare results obtained by a study with an equivalent continuous medium to those obtained with a discrete medium. It should also be possible to determine , by varying the density of fractures, a threshold below which it is not justified to choose an equivalent continuous medium.

We have adapted the informatical tools of the Ecole Nationale Supérieure des Mines de Paris to the specific needs of a water circulation in a set of fractures.
We take into account a variation of the temperature and of the geometry of the joints for the calculation of the hydraulic parameters.

In this study, we have made two basic assumptions :

. all the water flows take place only in the fractures. We neglect the flows in the porosity of the blocks.

. all the heat flows take place only in the blocks. We neglect heat transfers through the water flows.

Most of the time used for this study was dedicated to the creation and improvements of the informatical tools.
Concerning the mechanical approach, we had done a calculation without temperatures, in order to validate the behaviour of joints in the case of a big mesh. We deduced two things from this test :

. following a bad interpretation of data, we had a big hole for the cavity, and we saw our mistake at the workshop in Stockholm, May 18-20, 1992. This "cavity" gave us a lot of problems, concerning the mesh around the hole as far as the use of such a simple joint model. A lot of supplementary tests were necessary.

. the very important displacements around this big "cavity" proved both the good running of the code (in particular joint-elements) and the limits of the joint model used.

Progress and results

Results were obtained on the good meshes. We present them in the order of calculation: thermal approach, thermo-mechanical coupling and thermo-hydro-mechanical coupling. They concern the first fracture spacing, d = 100m.

1 - Thermal results

The thermal loading is the most important factor to be taken into account in all the studies on wastes disposal because of its influence on mechanical and hydraulic behaviours.
We computed the temperatures and the thermal fluxes at twelve dates, from t = 0, to t = 5000 years for temperatures, from t = 0 to t = 500 years for heat fluxes.
The maximum temperature increase is almost of 25 % and the residual increase after 5000 years is 1.60 %. After 5000 years, the maximum temperature is still higher than the natural maximum one of the rock mass, (5°K at 500m deep).

2 - Thermo-mechanical coupling

The influence of the temperature is quite well known, mostly for equivalent continuous models. On the contrary, the influence of water when temperature is not constant is not well known, in particular when water flows are limited to the joints.
The maximum displacement is reached at t = 150 years, whereas the maximum of temperature takes place earlier (t = 50 years).

The free surface of the rock mass is risen of about 10 cm by the tilt blocks, and we can expect great perturbations of the water flows in this zone. After 5000 years, the blocks of the cavity are back to their initial size and their residual displacement is not very important. On the contrary, tilt blocks do not come back to their initial place.

3 - Thermo-hydro-mechanical coupling

All the displacements are computed considering the initial state as a zero displacement state. We have important numerical problems at time t = 150 and t = 200 years: thermo-hydro-mechanical computations give results in very good accordance with thermo-mechanical ones, but hydraulic results are absurd, (hydraulic heads greater than 125 m or negative, negative pressures...). The displacement amplitude is bigger, but the behaviour stays, the same with, in particular, a dilated zone (cavity) and a tilt blocks zone (straight above the cavity). The maximum displacement is reached after 150 years and is almost 25 mm bigger than for the thermo-mechanical computations.

Consequently, the results at the other dates are to be taken with some reservations, in particular concerning the hydraulic flux.

The maximum stress is reached after 50 years and is 1.50 MPa smaller than the thermo-mechanical maximum. The influence of water circulation in the joints is then a reduction of the stresses and an increase of the displacements.

This exercise rises several problems:

. it would have been better to choose a more precise mechanical behaviour of the joints, preventing the blocks from interpenetrating, which would avoid all the problems in hydraulic computations,

. it seems curious to impose an important hydraulic head at the top of the model and to consider it as a free surface in mechanical computations; that is why we have imposed a pressure varying in the same proportions as the hydraulic head,

. the importance of this hydraulic head can also explain the excessively high values of fluid flux in joints that we computed from time t = 0 to t = 150 years.

List of publications

DECOVALEX
Memorandum - 1st Meeting of the Steering Committee, Paris, France, October 28, 1991.

DECOVALEX
Memorandum - 2nd Meeting of the Steering Committee, Stockholm, Suède, May 20, 1992.

DECOVALEX
Memorandum - First Workshop, Stockholm, Suède, May 18-20, 1992.

A.BOUGNOUX & G.VOUILLE (ENSMP/CGES)
Presentation of Bench-Mark-Test n°1, First Workshop, Stockholm, Suède, May 18-20, 1992.

A.BOUGNOUX & G.VOUILLE (ENSMP/CGES)
DECOVALEX - BMT1 - "Far Field Model", Progress report, June, 1992. Rapport SERGD 92/38.

A.BOUGNOUX & G.VOUILLE (ENSMP/CGES)
DECOVALEX - BMT1 - "Far Field Model", Final report, December, 1992.

Title: Participation to the International cooperative project for the DEvelopment of COupled models and their VALidation against EXperiments in nuclear waste isolation - "**DECOVALEX**"

Contractors : (1) Agence Nationale pour le gestion des Déchets RAdioactifs (**ANDRA**)
- France -
(2) Commissariat à l'Energie Atomique (**CEA**)
Direction des réacteurs Nucléaires - Département de Mécanique et Technologie
- Service d'Etudes Mécaniques et Thermiques -
- France -
(3) **INERIS**
Groupe Géotechnique et Atmosphère Industrielle - Laboratoire de Mécanique des Terrains - Ecole des Mines de Nancy
- France -
(4) United Kingdom Atomic Energy Authority (**AEA**)
Theorical Studies Department - AEA Decommissioning and Radwaste
Harwell Laboratories
- United Kingdom -

Contract n°: FI2W-CT-91-113

Duration of contract: November 1991 to October 1994

Project leaders: L. DEWIERE / F. PLAS (ANDRA: Coordinator), M. DURIN (CEA), H. BAROUDI (INERIS), A.H. HERBERT (AEA D&R)

A/OBJECTIVES AND SCOPE

Hydro-thermo-mechanical processes in jointed rock is very difficult task to treat but may be of importance in nuclear waste performance assessment. This called for an international cooperation in peer review for code developers, to develop a data base and to provide bench-mark tests and test cases of HTM processes. So DECOVALEX is an international coordinated project for three years dealing with the study of coupled hydro-thermo-mechanical modelling processes in fracturated rock and associated computer codes [1][2].

The aim of the CCE contract is the participation of the European research teams to the international DECOVALEX project. The research programme is coordinated by ANDRA. Three laboratories are collaborating for this contract:

* CEA/DMT using the equivalent porous media modelling concept with CASTEM/TRIO codes,
* INERIS whith develope the discrete block network modelling approach with UDEC code,
* AEA D&R using the discrete fracture network modelling approach with NAPSAC code.

B/WORK PROGRAM

The DECOVALEX programme is developed according to the following main phases:

Phase 1 (October 1991 - # march 1993) : Three exercices were defined:

(1) Bench-mark Test 1, called "Far field model" (CEA/DMT, INERIS, France)

This BMT is designed to simulate the processes in a large rock mass with a repository located at depth of about 500 meters. The model is two-dimensional, measures 3000 m × 1000 m and contains two sets of intersecting fractures (figure 1). Three fracture spacings are defined 25 m, 50 m, 100 m. A non-uniform hydraulic head acts at the ground surface and zero flux is imposed on the bottom and lateral boundaries. The heat flux from the repository is assumed to decay exponentially with time.

(2) Bench-mark Test 2, called "Multiple fracture model" (AECL, Canada)

This BMT consist of an assemblage of nine blocks, separated by two sets of discontinuities (planar fractures). This model measures 0.75 m × 0.50 m and is confined along all boundaries (figure 2). The rock mass is subjected to in-situ stress and thermal loading as well as hydraulic gradient. No-flow and aduiabatic conditions are imposed at top and bottom of the model. The heat flux acting along a section of one of the lateral boundaries will include expansion of the ock mass and cause shearing in the model.

(3) Test Case 1, called "Coupled Stress-Flow model" (NGI, Norway)

To obtain the experimental data needed to quantify the effects of joint deformation and joint conductivity, a testing facility has been designed and built by the Norvegian Geotechnical Insitute. With this apparatus, joints can be closed and sheared under controlled conditions while fluids can be flushed through the joint. Deformations, flow rates and stresses are recorded simultaneously. The boundary stresses applied by flat jacks result in pure normal stress when the same pressure is applied in the flat jack. An increasing shear stress occurs when differential pressure is applied. The proposed coupled stress-flow model have input data derived from Stripa studies. The options of linear and non-linear joint deformability are given and different loading conditions are specified.

Phase 2 (# march 1993 - October 1994) :

Test cases and Bench-mark tests of the phase 2 will be defined at the end of the phase 1.

C/ PROGRESS OF THE WORK AND OBTAINED RESULTS

State of advancement

DECOVALEX phase 1 is now almost closed. The CEA/DMT only treated the BMT1, the INERIS the BMT1 and the BMT2. Preliminary results were presented at the first DECOVALEX workshop on may 1992 at Royal Insitute of Technology, Stockholm, Sweden [3].

New Bench-mark Tests and Test cases for the phase 2 were proposed and discussed during the first work-shop. The principle of a Test Case 2 that is a revision of the test Case 1, and a Bench-mark 3 proposed by ANDRA and its associated research teams were accepted by the steering commitee [2].

Progress and Results

Phase 1

a) BMT2

INERIS didn't meet important problems for the modelisation. The principal difficulty was to chose the best mesh and timestep. However for the smallest mesh value (2 cm), the time of calculation was about 20 hours. During the first work-shop, comparison with others research team results didn't show significant differences [4][5].

b) BMT1

CEA/DMT treated the BMT1 for the three fracture spacings. Obviously the hydraulical results are differents but the directions of the changes are the same. The mechanical results are not significantly different [6][5].

INERIS treated the thermo-mechanical problem for the three fracture spacing. Due to the large number of discontinuities, it was only be able to solve the hydro-thermo-mechanical processes for the fracture spacing of 50 meters [5].

The comparison between the CEA/DMT results and the INERIS results gives similar values.

Phase 2

ANDRA, CEA/DMT, INERIS and AEA D&R defined a new Bench-mark Test (BMT3) with the collaboration of NGI. It is to simulate the processes in a fractured rock mass and improve the modelling approach to be applied to a tunnel above a heater in a repository. Three sequences will be distinguished : Sequence 1 : Initial hydromechanical equilibrium, Sequence 2 : Excavation of a tunnel. back to a new hydromechanical equilibrium, Sequence 3 : Thermal loading while the tunnel is opened.

The tunnel is located at 500 meters depth. The model measures 50 m × 50 m around the tunnel (figure 3). The initial fracture network comes from Stripa data and contains more than six thousand discontinuities.

Each research team involved may use any approach (continuum, discontinuum, other...) and make any simplification needed to solve the problem. The modelling process must be clearly defined.

References

[1] DECOVALEX
Memorandum - 1st meeting of Steering Committee at Hotel Mercure, Paris, France.
October 28th, 1991.

[2] DECOVALEX
Memorandum - 2nd meeting of Steering Committee at Royal Institute of Technology, Stockholm, Sweden
May 20, 1992

[3] DECOVALEX
Memorandum - 1st workshop at Royal Insitute of Technology, Stockholm, Sweden
May 18-20, 1992

[3] Rapport CEA/DMT/92.161
"Projet DECOVALEX - Cas test champ lointain - Etude thermique "

[4] Rapport 694 RP CER 92.003
" DECOVALEX - Etude du cas AECL (BMT3) - Premiers calculs H -T -M "
INERIS

[5] DECOVALEX - 1st Progress Report - CCE Contract n° FI2W-CT91-113
Rapport ANDRA 694 RP AND 92.001

[6] DECOVALEX - 2nd Progress Report - CCE Contract n°FI2W-CT91-113
Rapport ANDRA 694 RP AND 92.003

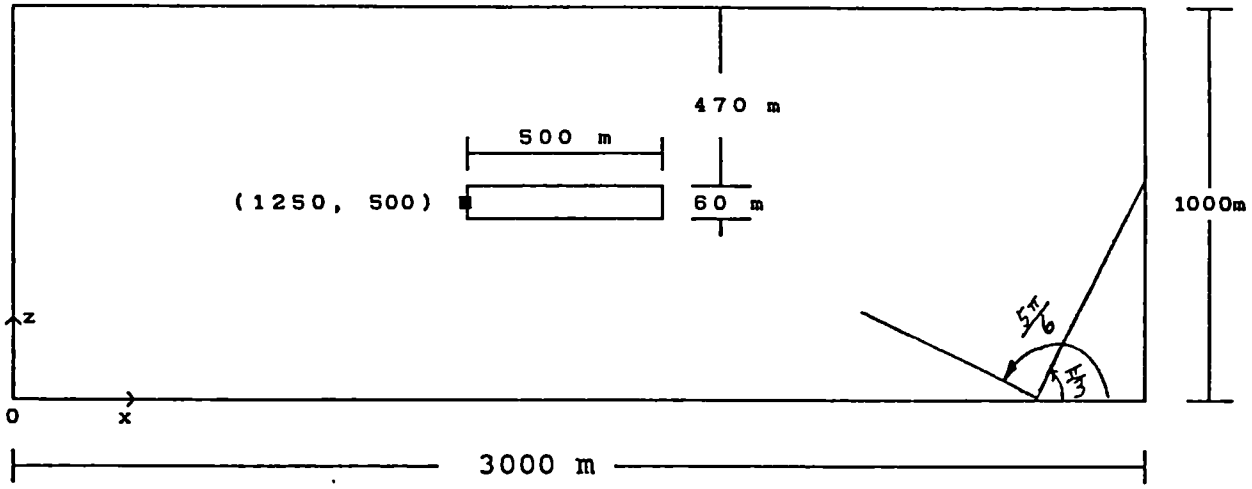


Figure 1 - Model geometry and fracture sets of the far field model

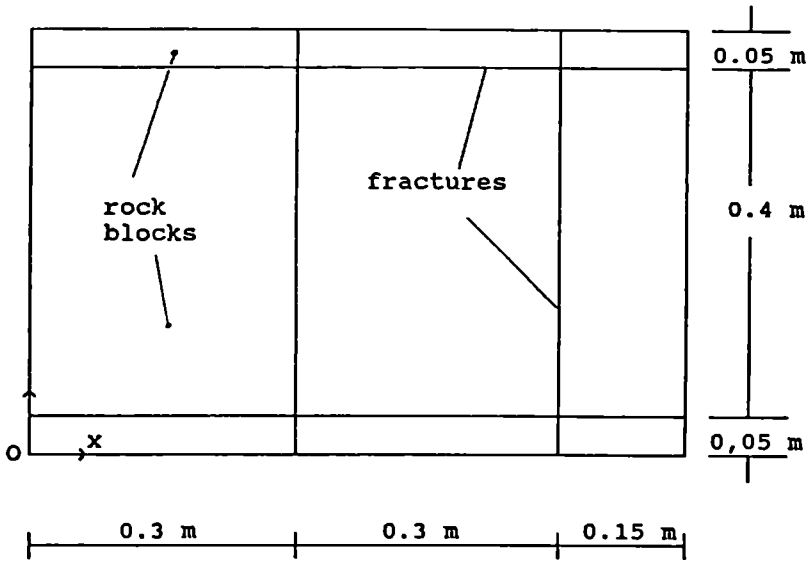
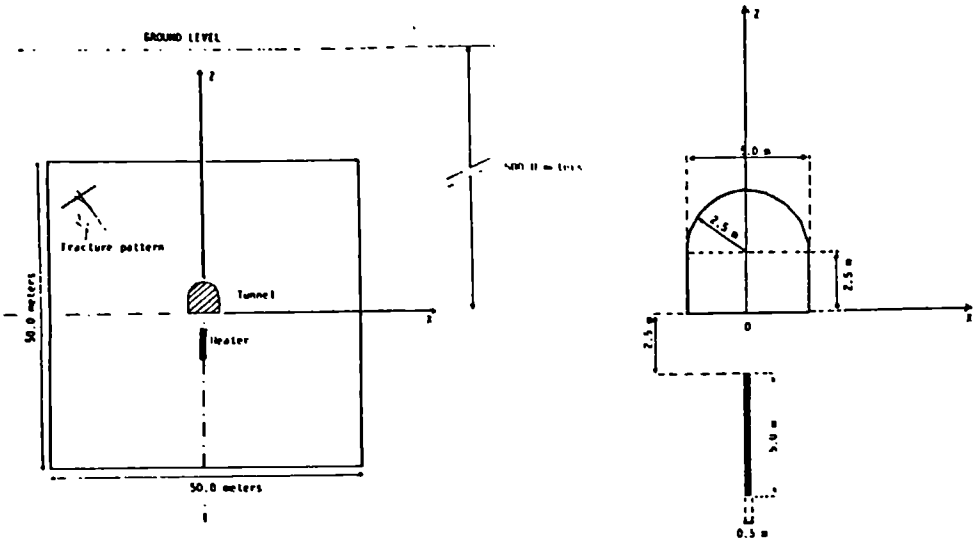


Figure 2 - Geometry of the multiple fracture model



a) Whole model

b) Tunnel

Figure 3 - Geometry of the BMT3

RESEARCH PROGRAM PERFORMED IN THE CLAY UNDERGROUND LABORATORY OF TOURNEMIRE

ANNUAL PROGRESS REPORT 1992

A. F. BARBREAU

Title: Etude des écoulements dans un massif argileux - Laboratoire souterrain de Tournemire
Contractor: Commissariat à l'Energie Atomique, Institut de Protection et de Sûreté Nucléaire, Département de Protection de l'Environnement et des Installations
Contract n°: F12W/0115
Duration of contract: From 01/01/1992 to 31/12/1994
Period covered: 36 months
Project leader: A. F. Barbreau

A. OBJECTIVES AND SCOPE

The Institut de Protection et de Sûreté Nucléaire (Département de Protection de l'Environnement et des Installations) of the Commissariat à l'Energie Atomique is developing, in the framework of its R and D safety programs, in situ research concerning the confining properties of geological formations. Two sites have been selected, one in clay and the other one in shales. These kinds of underground laboratories are called "LEMI": Laboratoires d'Etudes Méthodologiques et Instrumentales.

The objectives of the LEMI are to provide the opportunity to carry out in situ experiments and to get samples in natural deep conditions, in order to be able to determine the properties of geological medium and to set a transfer model. The LEMI of Tournemire is devoted to the study of clay.

Any industrial or nuclear purposes are excluded in this kind of underground laboratory.

B. WORK PROGRAM

The general IPSN research program at Tournemire concerns geotechnical, hydrogeological and later on, thermal properties of Toarcian clay. To meet these objectives geologic and hydrogeologic survey, rock sampling for laboratory analyses, hydraulic test in boreholes, isotopes study, scale effect experiments and modelling are contemplated. For supporting this research regarding a very low permeability medium, it is intended to develop new methods, apparatuses and devices, if it is necessary.

In situ research work concerning argillaceous formations has been started at the end of 1990. The selected site is a hundred years old given up railway tunnel, 1885 meters long, in the close vicinity of the village of TOURNEMIRE, in the South of France. This tunnel, crosses a 200 m thick toarcian clay formation; the overlying limestone layers are 270 meters thick, so the geotechnical and hydrogeological conditions can be considered as representative of those of a deep repository.

This site is unfit for any radioactive waste disposal operation, but very interesting for basic studies on clay. Considering the large possibilities of scientific investigations presented by this site, ELF, a French oil company, is associated with the CEA/IPSN in the use of the tunnel, outside of the CEC contract.

The present report gives a summary of the state of development of the program at the end of 1992.

C. PROGRESS OF WORK AND OBTAINED RESULTS

1. General geological and hydrogeological investigations

A general geological survey of the area has been carried out to precise the geological environment around the tunnel: It has mainly included a detailed geological and structural mapping and the determination of the main hydrological et hydrogeological features of the area.

The geological formations near the site are constituted by sub-tabular sedimentary layers of the lower and middle Jurassic Period. The stratigraphic formations involved in the Tournemire environment are the following:

Hettangian: limestones and dolomites (200 m)
Carixian: limestones with interbedded marls (45 m)
Domerian: marls and clay (argilites) (40 m)
Toarcian: marls and clay (argilites) (200 m)
Aalenian: limestones (with interbedded clay) (60 m)
Bajocian and Bathonian: massive limestones and, in upper Bathonian, dolomites (430 m). Above the tunnel, this series is about 200 m thick. This formation constitutes the "Causses" table. The springs and draining lines connected with the different aquifers, in the region, have been investigated to precise the main hydrogeological features.

The prevailing lower limestone formations of Hettangian and Carixian contain the general lower regional aquifer below the domerian and toarcian argilites of very low permeability. At the place of the tunnel, the aquifer of these limestones is in charge below the domerian and toarcian clay and its head is roughly located at mid-height inside the Toarcian formation.

The limestone layers from Aalenian up to upper Bathonian are the reservoir for the upper regional aquifer. At Tournemire, this aquifer lies in the lower part of the Aalenian and should feed the toarcian clay just below.

The water flow through the toarcian argilites, which could behave hydraulically as a semi-permeable medium, is supposed to be vertical downwards.

The tunnel, in the longest part, is inside the Toarcian formation of which the dip is weak (5°).At 1700 m from the south entrance, the tunnel crosses a big fault which brings into contact Toarcian argilites and Hettangian limestones, producing a spring in the tunnel at this place.

2. The 1990-1991 drilling operations

After the first geological and hydrological survey, it has been decided to carry out boreholes to get additional and more precise information on the depth, lithology, statigraphy and hydrology of the geological layers around the LEMI.

Six boreholes (5 vertical downwards and 1 vertical upwards) have been drilled, respectively 231 m (DC) 169 m (CD), 144 m (DI), 118 m (DM), 30 m (DS), and 65m (CA) long, with demineralized water to allow isotopic analysis. The most part of these boreholes has been cored.

Four boreholes have been equipped with the ground water monitoring system, the BAT filter tip, which is designed to allow pressure measurement and water sampling in low permeability rocks. One of the BAT filter tips has been set at the top of the domerian formation (CD), constituted also of clay, which is just below the toarcian clay, and three other BAT filter

tips have been located at different levels of the toarcian clay (DI, DM, DS), to get information on the hydraulic gradient.

The downwards 230 m long borehole (DC) had the aim to investigate the hydrology of the carixian limestones, underlying the domerian clay and the upwards 65 m long borehole (CA) had the aim to investigate the aquifer of the lower aalenian formation overlying the toarcian clay. These 2 boreholes are equipped with a pressure gauge respectively set in carixian and aalenian limestone.

Data provided by these different pressure measurement probes are permanently recorded and sent to IPSN by a computer teletransmission system. So, the aquifer head at different levels and its evolution in time can be continuously monitored.

Many permeability tests at different levels have been performed (mainly pulse tests) as well as geophysical loggings: natural gamma, gamma gamma, acoustic log, and neutron log. The results of the permeability tests show that the permeability of the two toarcian and domerian clay formations is very low, between 10^{-11} and 10^{-13} m/s. The permeability of the calcareous carixian and aalenian formations is substantially higher: The Carixian has permeability of about 10^{-8} m/s and the Aalenian of about 10^{-6} m/s.

The aquifer heads, in the carixian and in the aalenian limestones have been found in accordance with the values which could be deduced from the hydrogeological regional and local system data (springs, draining lines, etc.) It has not been possible up to now to determine the actual head in the argilite formation, because of the very long period to reach the steady state after the perturbation induced by the drilling operation resulting from the very low permeability of this kind of rock. Some of the values look in discrepancy with the values which could be deduced from the flow model set up to give a first approach of the groundwater circulation in the Toarcian.

Dilatometer tests have also been carried out in the Toarcian. The argilites look very stiff.

3.*Detailed structural study*

A detailed structural study has been performed, based on observation in quarries and on core samples. Three states of stress have been identified: a N-S Pyrenean compression (Eocene), an E-W extension (Oligocene), and an Alpine compression. Limestone formations are extensively fractured; in toarcian clay, some faults have been observed but they are filled in by calcite.

4. *Preliminary modelling*

On the basis of the first available data, a first flow model into the clay has been performed at the beginning of 1992, to be used for the conception of the following programs and in particular to precise the characteristics of the new drift contemplated for carrying out the scale effect experiment. Its objectives were:

- to get an opinion on the duration of the transient state after the excavation of the drift
- to evaluate the possible rate of discharge of water into the drift itself
- to get an order of magnitude of the transfer time in the geological formations to constitute a framework for the interpretation of the geochemical and isotopic studies.

The two main results are:

- the transient period to reach the steady state after a significant perturbation is very long (several years), This means that the different tests which will be performed in the argilites should be interpreted in transient state
- the value of the ground water head at different levels in the Toarcian is close to the value of the topographic level at this point. Combined with the very low permeability of the rock, it means that the flow discharge rate by drainage which can be anticipated, even in a drift 100 m long, will be very low (below 10 cm^3/h).

5. Isotopic study

It is possible to get information on the age of the ground water by using natural radio-isotopes such as ^{14}C, ^{36}Cl, ^{129}I, and the ratio U/Th. In other respects, stable isotopes ^{13}C, ^{18}O and ^{2}H can provide information on the origin of water: for example the presence of meteoric or connate water.

Unfortunately, in the case of Tournemire argilites, the difficulty for extracting water from the argilites has jeopardised up to now the possibility for performing an exhaustive research program regarding the natural isotopes. By the time being, it has been only possible to extract pore water by distillation, which has limited the investigations to ^{18}O and ^{2}H for the liquid phase and ^{13}C, 14C and ^{18}O for the solid phase (fracture minerals). So, a valuable dating of pore water has not been possible nowadays.

In these conditions, it is difficult to get a good representation of the groundwater transfer in the argilites. However, the first investigations on the liquid phase extracted by distillation from cores of CD and CA boreholes give information:

- a peak in the concentration in ^{18}O (solid phase) and ^{2}H (distillation) has been observed nearby the tunnel, produced probably by the influence of the tunnel on the water content of the rock.
- an other peak has been observed in the first analyses at -60 m; more recent analyses raise some controversy on this result: the peak at -60 m may be interpreted either as a mixing in meteoric and connate water resulting probably of diffusion phenomena or as an artefact.
- as far as the solid phase is concerned, the content of ^{13}C and ^{18}O in the fracture minerals shows that the "mixing" hypothesis is possible; the measurement of ^{14}C content in fracture carbonate minerals indicates that no ground water significant circulation has occurred in the toarcian argilites since at least about 20,000 years.

These preliminary results have, of course, to be precised and confirmed by other studies.

6. Laboratory study of core samples

Laboratory study has been performed on sixteen argilite samples coming from the CD borehole. Mineralogical and petrographical investigation by X diffractometry has provided the mineralogical composition of the clay, which is mainly composed of quartz, calcite, kaolinite and mica; it contains also about 10% of illite-montmorillonite and, in some samples, a few amount of chloride, pyrite, dolomite and siderite.

The water content, very low, is between 1% and 3%. The main porosity is referred to a radius of access to pores equal or lower than 0.02 μm. Permeability is between 10^{-13} m/s and 10^{-14} m/s, to be compared with values measured in boreholes.

Geomechanical testing shows that the seismic wave velocity in toarcian clay, measured in laboratory, is high (approximately from 3000 m/s to 4000 m/s for P waves and 1500 to 2200 m/s for S waves. The Young's modulus (E) is between 10,000 and 15,000 MPa and the Poisson's ratio is between 0.15 and 0.20.

7. Conclusion at the present stage of the program

The geological and hydrogeological conditions of the environment of the LEMI of Tournemire are well known,, by the time being, but the properties of the argilites as mentioned above, are such that the determination of fluid pressure and fluid transfer through this type of rock, by in situ experiments, is very difficult. This means that it is now untimely to carry out a scale effect experiment by ventilation test in a drift as it was initially forecast for the second phase of the program. Additional laboratory studies and new in situ experiments of a more pertinent conception are needed to precise the actual fluid movement in the Toarcian.

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Entrée sud du tunnel

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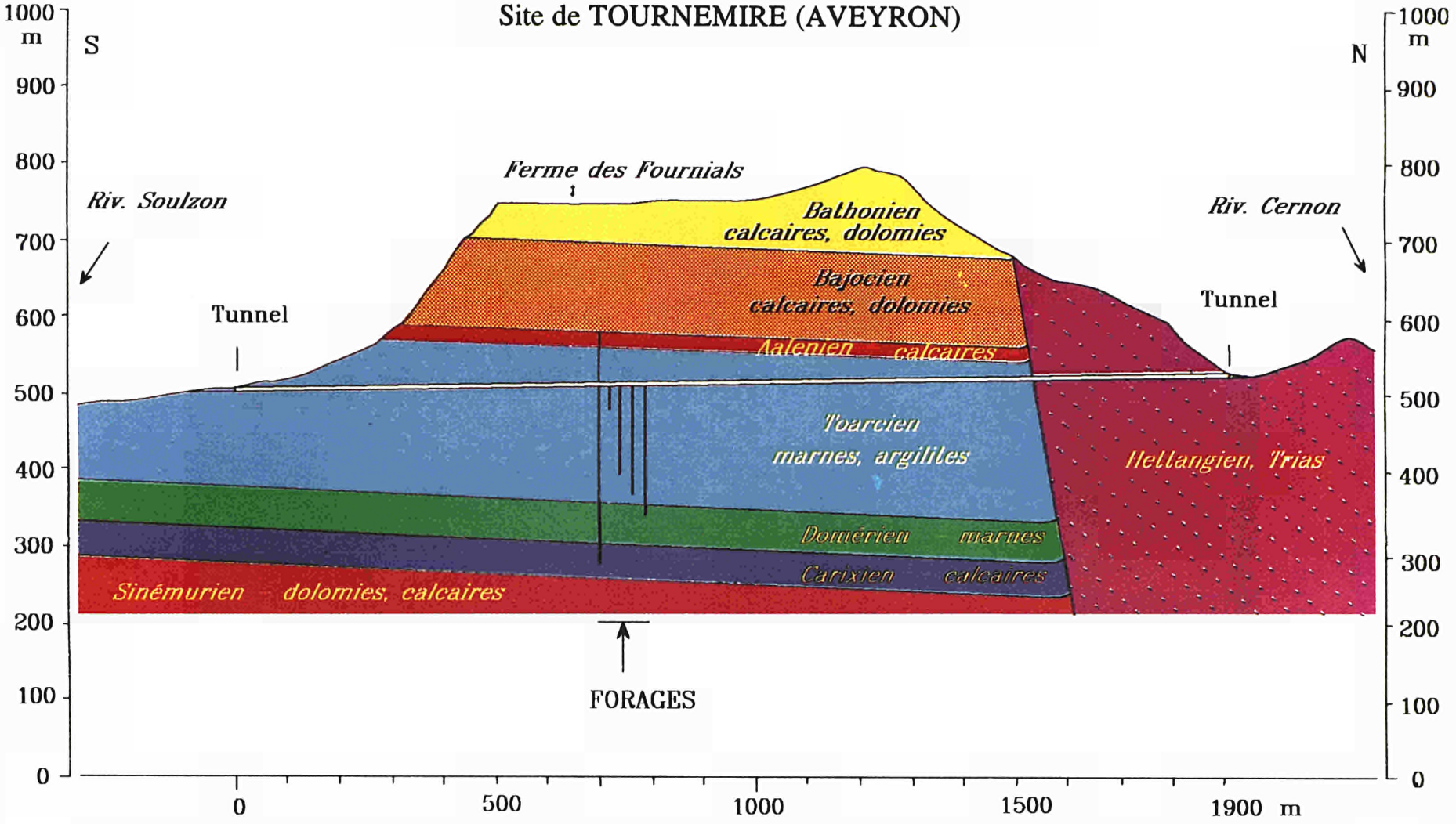

Coupe géologique du plateau traversé par le tunnel et implantation des forages IPSN d'étude des marnes et argilites du toarcien

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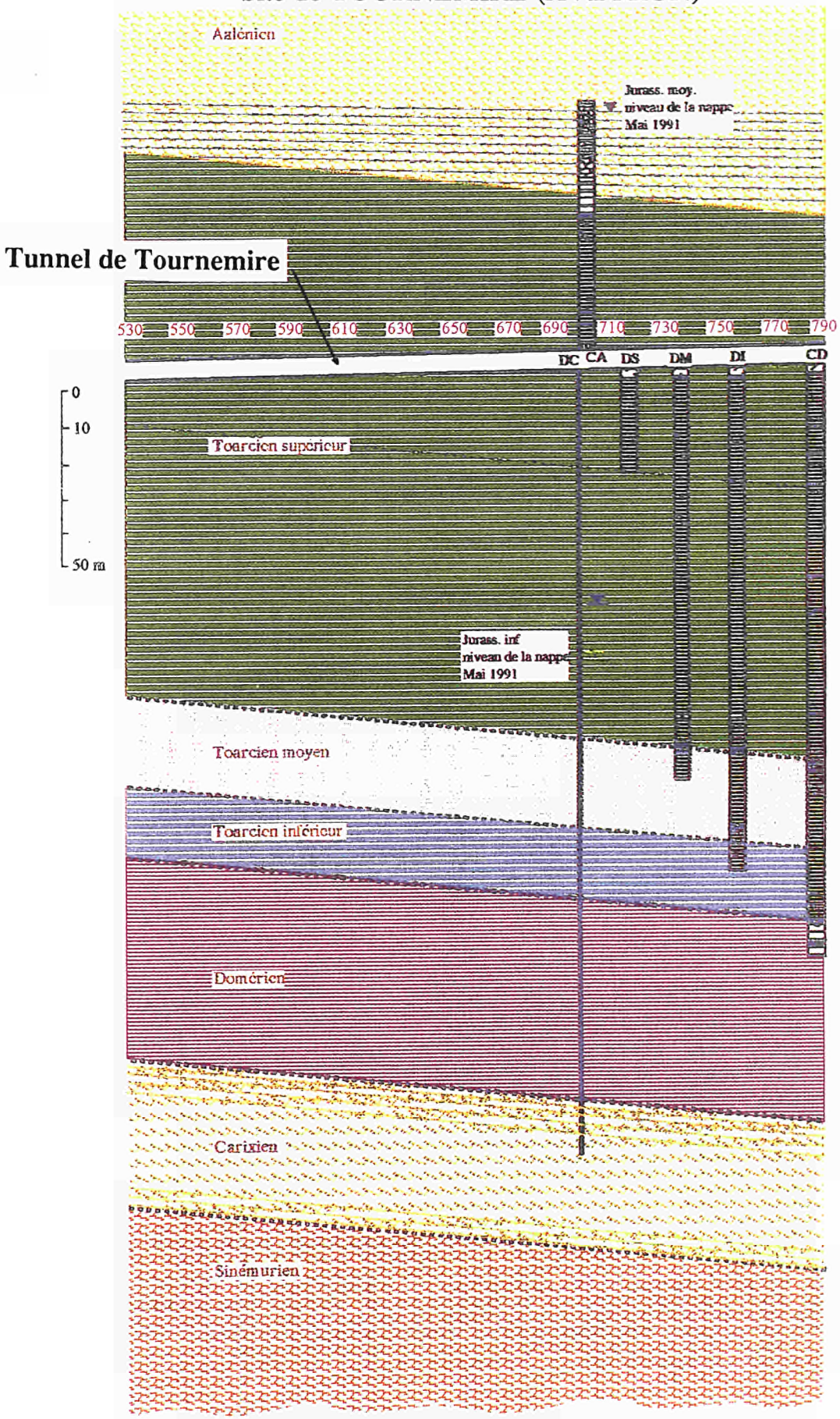

Profil Géologique schématique

10·92

DEVELOPMENT OF BOREHOLE SEALS FOR HIGH-LEVEL RADIOACTIVE WASTE (THE DEBORA-PROJECT)

Contractors: GSF-Institut für Tieflagerung (IfT), Braunschweig, Germany
Stichting Energieonderzoek Centrum Nederland (ECN), Petten, The Netherlands
Contract No.: FI2W-CT90-0048
Duration of Contract: January 1991 - December 1994
Period covered: January 1992 - December 1992
Project Leaders: T. Rothfuchs, J. Prij

A. OBJECTIVES AND SCOPE

The overall objective of a nuclear repository is to protect man and his environment against ionizing radiation from radioactive waste emplaced in this underground repository.

According to section 45 of the German Radiation Protection Ordinance the individual dose to man, caused by radionuclides passing out of the repository, is to be limited to 0.3 mSv/year. In order to achieve this objective within the multiple barrier system of the repository, suitable sealing systems like borehole seals, drift seals and shaft seals are to be developed.

The objective of the DEBORA-project is the "Development of Borehole Seals for High-Level Radioactive Waste".

The DEBORA-project consists of two phases. During the first phase (1991 - 1994) a test plan for a subsequent in situ verification test will be developed in form of a desk study. This study will include an evaluation of literature, a performance of model calculations, and discussions of experts to identify the requirements for and the tasks of HAW-borehole seals under normal repository conditions. Altered repository conditions will be considered at a later stage of the project.

During the second phase, to be started in 1995, in situ tests will be performed and the sealing techniques elaborated during the first phase will be verified.

B. WORK PROGRAMME

B.1 Compilation of the technical boundary conditions important for the design of HAW-borehole seals
B.2 Definition of the tasks of HAW-borehole seals
B.3 Analysis of events affecting the design of the borehole seal
B.4 Performance of model calculations
B.5 Elaboration of sealing techniques
B.6 Development of an in situ test plan

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In 1991 items 1 and 2 of chapter B. were treated and first model calculations were taken up (item 4). The work in 1992 dealt with items 3 to 6.

Fluids which will be released into the borehole and their generation mechanisms have been summarized. Corrosion of steel as packaging material has been studied in the literature and rates of corrosion have been determined as a basis for the estimation of hydrogen production (item 3). The thermomechanical calculations for the region of the seal as well as the calculation of fluid content of the HAW-borehole have been continued (item 4). Their results will be essential to answer questions concerning the importance of events affecting the design of borehole seals (item 3). Concerning the elaboration of sealing techniques (item 5) two literature studies have been conducted. The first dealt with candidate sealing materials and techniques, the second with the consolidational behaviour of crushed salt as one of the moist suitable sealing materials.

Progress and results

3. Analysis of events affecting the design of the borehole seal

The release of liquids and gases into the borehole is of high importance for the seal design because it will increase the pressure inside the borehole. It also promotes corrosion of the waste which, besides radiolysis, is a further source of gas generation.

The different mechanism of fluid generation and release into the borehole and the relevant fluids have been summarized. The more important fluids are different types of brines, water vapour, hydrogen, carbon dioxide and methane. The range of petrophysical parameters of rock salt controlling the migration of fluids have been stated. It turned out that parameters like permeability or parameters describing adsorption and desorption of gases in the rock salt have still to be determined or determined more accurately.

A literature study on the corrosion of steel as the packaging material of the waste has been conducted. Corrosion is an important mechanism of hydrogen generation. Under normal repository conditions ("NaCl-brines" without $MgCl_2$, low amount of water available for corrosion reaction) corrosion rates below 2 µm/year have been found in situ (dose rate 300 Gy/h, temperature 210 °C, various steels mainly consisting of iron). For altered repository conditions rates up to 660 µm/a have been observed in lab experiments. The experiments have been conducted at a temperature of 90 °C and dose rates up to 1 kGy/h. Data at higher temperatures are still missing.

4. Performance of model calculations

a) Thermomechanical calculations

One of the items of the joint GSF/ECN project on HAW borehole seals, DEBORA, is the thermomechanical load on the seal of such a borehole. This thermomechanical load consists of the stresses, deformations, and

temperatures caused by the heat generation of the HAW disposed in the borehole and by the stress redistribution caused by the excavation of the gallery. The waste induced loads depend on amount of waste, the loading tempo of the waste and the heat load. The gallery induced loading depends on the dimension and shape of the gallery, the rock pressure, and the creep properties of the rock salt.

Numerical analyses have been performed to determine the parameters having a large influence on the loading and the parameters having a small influence. Having identified the most sensitive aspects one can concentrate on these items for the further research in this project.
Two types of analyses have been performed:

- Thermal and structural analyses to determine the seal region influenced by the thermal loads of the HAW and the most sensitive parameters with respect to the load in this region.

- Structural analyses to determine the region around the gallery influenced by the gallery induced stress redistribution.

The results of these analyses will shortly be summarized. It will be shown that the seal region influenced by the gallery is much larger than the HAW influenced region. Based on this finding a three dimensional analysis is being performed to determine the complex time dependent interaction between the gallery and the open borehole. Some first results of this analysis will be presented.

Influence of the stack length

The effects of the thermomechanical loading are concentrated in the 10 m above the upper canister but after a period of 10 years the thermal effects are also noticeable in the 20 m above the upper canister. The thermomechanical loading result in changes in the stress state and in deformation of the borehole seal region. The effect on the stresses in the 10 m above the upper canister is limited to 2 MPa for all stack lengths considered, viz. from 0 to 600 m.

It further is concluded that for the first 10 years of heating the thermomechanical loads of the canister at larger distance than 50 m have no influence on the boreholes seal loading in the first 10 m above the upper canister.

In the borehole region at larger distances than 10 m above the upper canister the convergence is only slightly influenced by the thermal loads of the upper 50 m of canisters.

To assess the effect of the convergence more detailed analyses have to be performed. These analyses have to include the compaction of the backfill.

Influence of the gallery

The analyses have shown that two main regions can be distinguished. A relatively small region in which the stresses are influenced by the shape of the gallery and a much larger region where the stresses are only influenced by the size of the gallery but not by the shape.

The quantification of the regions has been performed with finite element analyses, using two different models. A three dimensional model which includes the actual shape of the gallery and an axisymmetric model of a circular gallery. The three dimensional model has been used to analyze the stress redistribution in the direct surrounding of the gallery in the

first 10 years after excavation while the axisymmetrical model has been used to calculate the stress redistribution in the far field and cover a period of 100 years.

From the numerical results it could be concluded that the region where the stress distribution is influenced by the shape of the gallery is limited to 6 times the radius of the gallery (ρ = 6). Within this region a smaller region can be distinguished where the hydrostatic stress is independent of the gallery shape viz. $\rho > 4$. The numerical results also showed that this regions are almost time independent.

The numerical results indicate that the region where the stress distribution is effected by the presence of the gallery depends strongly on time elapsed since its excavation. Ten years after excavation the region where the equivalent stresses are larger than 1 MPa is extended to ρ = 18. For 50 and 100 years the region is extended to ρ = 27 and 32. These results are elucidated with Fig. 1.

The effect of the gallery on the hydrostatic stress component is not so pronounced. The region in which the hydrostatic stress component deviates more than 1 MPa in the time periods 10, 50 and 100 years is limited to ρ = 7, 12 and 15.

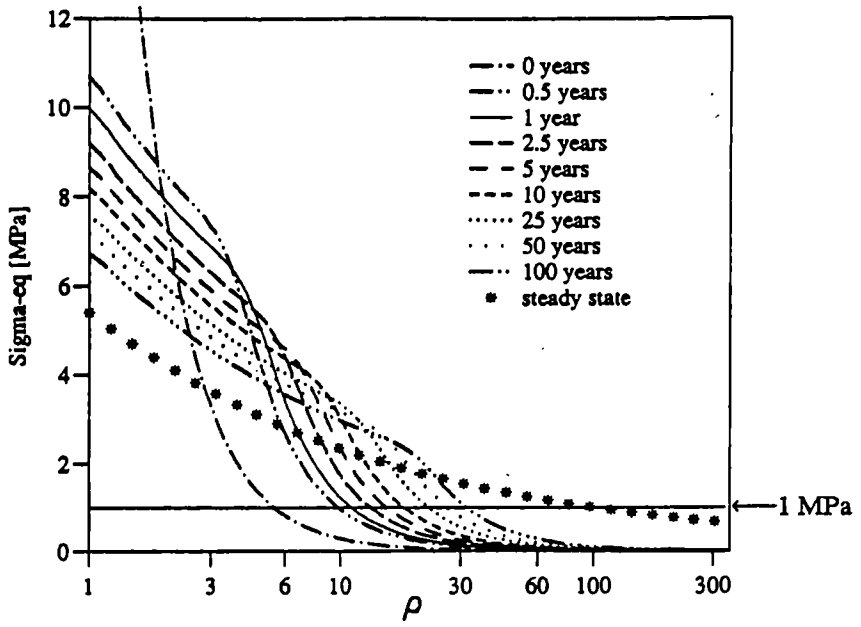

Fig. 1: Equivalent stress as a function of the radial distance ρ (normalized with the radius of the gallery) and time (circular gallery).

These results have some implications for the sealing of a borehole drilled from the gallery. With the gallery dimensions used in DEBORA it can be concluded that in the upper 20 metres of the borehole the stresses and deformations will be influenced by the shape of the gallery. This means that an accurate prediction of the sealing behaviour of the upper 20 m requires a three dimensional model which includes the actual gallery, the borehole and the seal. In the first hundred years after excavation the mechanical loads in the upper 100 m of the borehole will significantly be influenced by the gallery.

The final conclusion therefore must be that an accurate prediction of the behaviour of the seal has to include the three dimensional interaction between the gallery and the borehole.

Interaction of the gallery and the borehole

A three dimensional model has been made for the structural analyses of the upper part of the borehole drilled from the floor of a gallery. Preliminary results indicate that the radial deformation of the upper 20 m of the borehole are disturbed by the presence of the gallery. Due to the actual stress state in this part the model the borehole deformation slightly deviates from the rotational symmetry. It appears that due to creep this non symmetrical deformation vanishes. A further result is that about 5 m below the floor the radial deformation has an extreme value, about twice the deformation in an undisturbed borehole.

b) Estimation of water and hydrogen content in the HAW-borehole

In the first stage of the assessment of water release from the rock salt into HAW-boreholes computations (physical model incorporating an evaporation front model, migration of water vapour in form of Knudsen- and Darcy-flow and migration of liquid inclusions) were compared to measurements in the HAW-test field in Asse mine. The result was a good agreement of theory and experimental data.

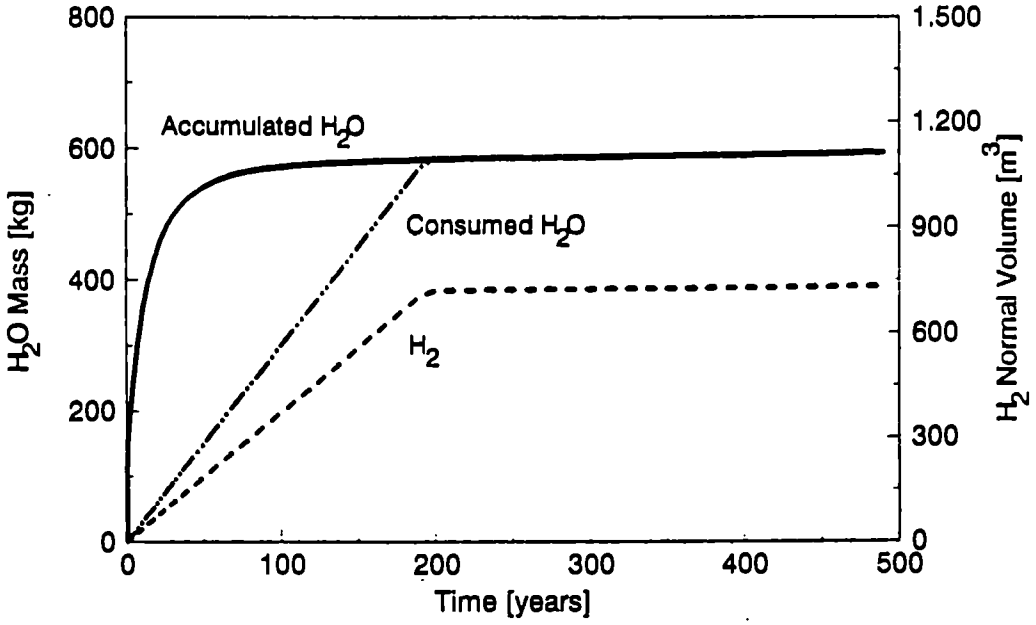

Fig. 2: Calculation of fluid content in a 300 m deep HLW borehole under repository conditions: Accumulated mass of water considering both Knudsen diffusion and liquid inclusion migration (water content of rock salt 0.04 % in mass), mass of water consumed by canister corrosion (corrosion rate 2 μm/a) and produced volume of hydrogen for normal conditions.

Thus, the model of water release could be considered validated and used to compute the water content of 300 m deep HAW-disposal boreholes under repository conditions. As an upper limit a value of 0.04 % water content in the rock salt has been choosen. Fig. 2 displays the accumulated water as a function of time. It can be seen that approximately 2 kg water per metre borehole will be released from the rock salt as an upper estimate under consideration of the high value of water content of rock salt chosen.

The value of 2 µm/year for the corrosion rate of steel as waste packaging material for normal repository conditions was used to calculate the water consumption and hydrogen production. It can be stated from Fig. 2 that all the water in the borehole will be consumed after approximately 200 years due to the corrosion of iron which is the major constituent of the used steel. Consideration of radiolysis of water which is an additional mechanism of water consumption and hydrogen generation may accelerate this process but the total amount of hydrogen will be the same.

5. Elaboration of sealing techniques

a) Evaluation of literature on sealing techniques

It was found that a considerable amount of research on suitable materials and emplacement techniques in rock salt has yet to be performed. Concerned are the material properties and the behaviour of seal constructions under HAW-borehole conditions (elevated temperatures, rapid convergence of the borehole, physical and chemical interaction with fluids).

Suitable materials in the present context are crushed salt (salt grit), salt cement, salt bricks and mixtures of crushed salt and bentonite. Bitumen and asphalt might be used as short-term sealing.

A multi component seal consisting of short- and long-term elements is proposed in many reports.

Emplacement techniques in rock salt as well as quality assurance for seal constructions are rarely considered.

b) Evaluation of literature on the consolidation of crushed salt

Crushed salt is considered as one of the most suitable sealing materials for HAW-boreholes in rock salt. For model calculations its consolidational behaviour has to be described in form of a constitutive law. Studies in this regard became the focus of research very recently so that different formulations are found in the literature.

Usually the constitutive law of the consolidation of crushed salt is expressed as the product of terms seperately describing the effects of stress, deformation and temperature on the rate of deformation. A potential law for the stress effect seems to be generally accepted whereas different terms for the effect of deformation and porosity, respectively, are given. For the influence of temperature an Arrhenius law is used in most suggestions although there is little experimental work considering variations of temperature. Most of the suggested laws do not take into account the effect of the grain size of the crushed salt.

List of publications

GSF-Institut für Tieflagerung and Stichting Energieonderzoek Centrum Nederland (ECN), The DEBORA-Project: Development of borehole seals for high-level radioactive waste, progress report July to December 1991 for the

Commission of the European Communities - Contract-No. FI2W-CT90-0048, Abteilungsbericht IfT 2/92 (1992).

GSF-Institut für Tieflagerung and Stichting Energieonderzoek Centrum Nederland (ECN), The DEBORA-Project: Development of borehole seals for high-level radioactive waste, progress report January to June 1992 for the Commission of the European Communities - Contract-No. FI2W-CT90-0048, Abteilungsbericht IfT 8/92 (1992).

Spies, Th., Prij, J., Rothfuchs, T.: Sealing of HAW-boreholes in salt formations: Objectives and first results of the DEBORA-project, proceedings of the 2. PEGASUS-workshop, June 1992, Brussels, to be published in the EUR-series.

Title: The refinement of soil gas analysis as a geological investigative technique
Contractor: Università "La Sapienza", Rome (Italy)
Contract N°: FI2W-CT91-0064
Duration of contract: from April 1991 to March 1994
Period covered: November 1991 to October 1992
Project Leader: S. Lombardi

A. *OBJECTIVES AND SCOPE*

The present research project consists of a multidisciplinary study aimed to optimize a set of geological investigation methods for the assesment of the safety of sites for operation such as radioactive waste repositories, with high potential for environmental hazard.
The studies are based on the integration of sampling and analyses of soil gases with other investigation techniques. Previous soil gas surveys performed by the participants [1, 2, 3, 4, 5, 6] have demonstrated that the soil gas method has great potential for tracing buried faults and fractures in clayey terrains and has a great flexibility. It is possible in fact to carry out surveys along profiles and/or according regular grids at different scales, i.e. with sampling densities in the range of one to a hundred samples per square kilometre.
The main objectives of the research are:
- the implementation of the analytical and sampling techniques in the soil gas method;
- the study of soil gases as fault tracers and of gas migration within soil and fractured zones by means of in situ tests;
-the comparison (and calibration) of the soil gas approach with other methods in order to test both the soil gas method and different lithotypes as natural barriers to gas migration;
-the creation of a data base in order to give mathematical models on gas generation and migration. The co-participants in the research with Rome University are: ISMES, Italy, coordinator F. GERA; Exeter University, U.K., coordinator P. GRAINGER; INTERA Sciences, U.K., as subcontractor of Rome University.

B. *WORK PROGRAMME*

The present work has been subdivided into seven tasks:

Task 1- Selecting areas in Italian subsiding sedimentary basins as test sites for the soil-gas and geophysical surveys. Laboratory equipments testing and setting up.
Task 2 - Sampling and analysis of soil gas (Rome and Exeter Universities).
Task 3 - Comparison between Rome and Exeter soil gas data.
Task 4 - Study of soil gas variations with depth, using shallow boreholes ranging from 5 to 10 meters (Rome University).
Task 5 - Execution of in situ tests by injection of gases into the soil and subsequent sampling and analysis (Rome University).
Task 6 - Geomorphological and structural research as support to the study of fracture and fault systems (Rome University). Geophysical, geotechnical and pedological studies in order to identify the main geological features and to characterize the soil and subsoil of the study areas (ISMES).
Task 7 - Statistical and mathematical analysis of the distribution of soil gases upon the data collected in the surveys conducted by Rome and Exeter Universities. This task will be carried out with the help of Intera Sciences.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

While tasks 1 and 2 started in 1991, in 1992 the research focused on a further development of tasks 2 (completion of previous surveys and performing of a new one), 3, 6 (geo-structural field surveys) and 7. A soil gas data-base, about a thousand samples, has been made up performing seven field-surveys in five italian sites. The last four surveys were conducted in 1992. All data show a relationship between surface anomalous values of He and Rn and greater fracturing zones, i.e. fault systems, in clayey deposits. The fourth (Siena basin) and the fifth (Ofanto basin) sites have been investigated by both Rome (with grid sampling) and Exeter University (with profiles); Ofanto data processing is still in progress. In the Siena Basin, Rome and Exeter obtained qualitatively the same results, i.e. gas escape signals coincided with a great tectonic lineament. Such results suggest that, in spite of the great thickness of clays, geogas migration through fractured rock occurs. The geophysical and pedological investigations were conducted in the Siena Basin in October 1992. It was decided to wait for the preliminary soil gas results in order to select the best sites for geophysical prospecting. Seismic profiles crossing the major gas anomalies, i.e. along the tectonic "Arbia Line", have been chosen by mutual consent. The data processing is still in progress and the results will be stated in the next report.

Progress and results

ROME UNIVERSITY (Lombardi S., Etiope G.)

A key-point for the studies of clay permeability in respect to endogenous gases lies in the comparison between soil gas data and geological investigations such as the fractured field analysis and photogeologic studies. In 1992 the main effort regarded this point. On the other hand further development have been made in soil gas studies for the refinement of which two methodological research lines have been planned. The first can be based on the acquisition of a wide database, relative to several case histories (in total 771 samples have been collected so far); the second on the comparison between soil gas results obtained with different scale sampling. Gas sampling has been performed using a method which has long been experimented both in the USA and in Italy ([5] and reference therein). It consists of inserting an 8 mm diameter, hollow steel probe into the ground to a depth of 50 cm. Then two 50 cc samples of soil gas are extracted from the probe with a syringe, after purging the probe. The first sample is stored in an evacuated stainless steel cylinder for laboratory analysis: the He content is analyzed by means of a mass spectrometer (Leak Detector VARIAN 938-41), having an instrumental error of about 20 ppb. CO_2 has been analyzed using a "quadrupole" mass spectrometer (VG SX 200). The second sample is used in situ for analyzing radon activity by means of a scintillator counter (EDA RDA 200). Helium results are expressed in part per billion (ppb; v/v) as the difference between helium content in the sample and in the atmosphere (5220 ppb; [7]) taken as reference standard. Radon values are expressed as Bq/l and CO_2 in percent (v/v).

The following sketch summarizes the research line:

Refinement of soil-gas analysis

- *Comparison between soil-gas data, photogeology and mesostructural analysis*
- *Soil-gas data*
  - *acquisition of a wide data-base*
  - *comparison between results from different scale sampling*
  - *mathematical approach (INTERA Sc.)*

The works carried out during the reference period have been:

a) completion of interpretative analysis of previous soil gas survey (performed in the first year) regarding helium, radon and carbon dioxide.

b) Three new soil gas surveys in clayey basins in central Italy

b-1: San Vittorino Valley
b-2: Siena Basin
b-3: Ofanto Basin

where there is no structural evidence of tectonic alignments.
c) a preliminary comparison between the results of different surveys: detailed versus regional survey.
d) mesostructural analysis in the Ofanto valley
e) preliminary photogeologic study in the Siena Basin.

a] The completion of previous analysis regarding the soil gas data partially discussed in the first six-monthly progress report are:
- the He anomalies detected in the first test site, Piano d'Asco (Tarquinia Valley);
- the elaboration of CO_2 and Rn-222, in addition to He-4, sampled in the second test site Pisticci.

An initial detailed soil gas survey, with a sampling density of about 100 samples per square kilometre, was made in the PIANO D'ASCO area (Fig.1), NW of Rome (Latium), where pliocenic blue clays with a thickness of about 150 m outcrop. The substratum is formed by Cretaceous rocks (marly limestones, shales and sandstones). Piano d'Asco has been selected for its low tectonization level and consequently for the lack of important structural lineaments. In this area, helium was detected in order to study its behaviour in a non-fractured clay and therefore to provide a background reference set of data. In spite of the geological features, a certain number of helium positive anomalies were found, however with lower values than those observed in more tectonically active areas in Italy. In Table I some descriptive statistical parameters of helium results are reported. Helium anomalies are distributed in three directions (Fig.2): the first one, NW-SE, seems to be related to regional faultlines, clearly evident where the substratum outcrops (Fig. 1); the other two, having N-S and E-W directions, may be linked to neotectonic lineaments not clearly visible in this zone but quite common in other areas of central Italy.
In the PISTICCI area (Fig. 3) both active tectonics and deep oil reservoirs exist. The pliocenic clayey sequence, more than 1000 m thick and outcropping in the area, is intersected by tectonic elements with preferential NW-SE and NE-SW trends [8]. A soil gas survey, at a regional scale (2-4 samples per square kilometre), was carried out during a seismically quiet period. In all samples ^{4}He and ^{222}Rn were analysed, meanwhile CO_2 was analysed only in about 25% of the samples. In Table II some descriptive statistical parameters are reported. The results show that:
- helium values were found varying in a wide range from -1400 up to + 21010 ppb (v/v) with about 6% of values exceeding + 1000 ppb. Soil gas helium values as high as this were previously observed in Italy only in coincidence of buried helium reservoirs such as geothermal fields [1, 5, 6]. Therefore, it is possible to infer that in the Pisticci area these high helium values are linked to helium migration through fractures from the oil reservoir located at a depth of about 3000 m. Further, positive helium anomalies (Fig. 4) are elongated according mainly to NW-SE and NE-SW trends which coincide with the directions of the most recent fault systems in the Pisticci region (Fig. 3). The highest ^{222}Rn and CO_2 values, even if partially displaced compared to the distribution of positive helium anomalies, show similar trends of helium, i.e. they are elongated according to NW-SE and NE-SW directions (Fig. 5 and 6).

b] *b-1*: A detailed soil gas survey was carried out within Apenninic limestone formations in the SAN VITTORINO VALLEY (Eastern Latium, Central Italy), a restricted basin about 5 km wide, (Fig.7). In this zone, tectonically and seismically very active, a continental sandy-clayey sequence with a thickness ranging from 50 up to 150 m rests directly on the mesozoic carbonate series. In the southern zone of the surveyed area these terranes are covered by gravels, meanwhile travertines occur in the N-W sector. In this restricted area tectonic lineaments can not be recognized, but in the surrounding carbonate chains faults and fractures systems are most evident (Fig.7). Some of these are of regional importance,

such as the N-S Olevano-Antrodoco alignment.
In this survey a sampling density of about 50 samples per square kilometre was used and only Rn and He were analysed (Table III). Helium and radon concentrations in soil gas (Fig. 8 and 9) seem to be influenced by both the regional tectonic and the hydrogeological setting. In particular the radon highest values are elongated according NW-SE and E-W directions, which coincide with those of regional faults clearly recognized on the carbonate outcrop. The highest radon concentrations (up to 16000 pCi/l = 592 Bq/l) have been found corresponding to travertines, that act as a fluid recall area. Positive helium anomalies are widely displaced in respect to radon anomalies. They trend E-W, as with radon, and N-S directions, corresponding with the Micciani master fault, well defined by structural analysis [9]. The different helium and radon distributions may be caused by: different origins, i.e. depth, of these gases; their different solubilities in water; and consequently different paths of migration.

b-2: The soil gas survey in the SIENA BASIN has been planned in order to verify if the local recent clayey deposits can prevent gas upwelling in areas where large and deep faults systems occur. Furthermore, an aerial photo interpretation has been performed in order to define the statistical lineament trends of the area and verify whether links with soil gas anomalies distribution exist. The Neogene Siena basin is a part of a NW-SE 300 Km long tectonic deep extended within the Tuscan graben system. North-east thrusted basement is believed to be present at 1 to 1.5 Km depths beneath a filling of Pliocene sediments (Fig. 10). These are mostly marine deposits formed by clays, sandy-clays and sands with conglomerates. The northern sector is cut by a great transversal tectonic lineament, the Arbia Line, known in literature as supposed because its surface expression is only indirect (alignment of springs and depressions).
Soil gas sampling was conducted in a resticted area (about 9 Kmq) in the northern sector of Siena basin, during a period of stable meteorological conditions, low relative humidity and high barometric pressure. In total 195 samples were collected using a regular grid with a sampling density of 25 samples per Kmq. The results of these analyses are summarized in table IV. Values greater than 1/2 standard deviation above the mean were considered anomalous. Soil gas distribution is showed in Figures 11, 12, 13. Continuous lines represent the main anomalies trends: they have been drawn linking the major soil gas values or following straight countourlines. Dashed lines represent minor anomalies trends. Helium, radon and carbon dioxide anomalies form elongated zones mainly trending SW-NE and NW-SE. These directions are the same of the transversal fault lineaments (i.e. Arbia Line) and of a NW-SE minor fault system, as reported by the geological sketch map (Fig. 10).
In Figure 11 it is possible to observe how both positive and negative values are distributed linearly, as shown by countourline trends. The same distribution occurrs for radon and carbon dioxide. High values of radon, more than 22.2 Bq/l (600 pCi/l) (the standard mean values in soil gas are about 7-11 Bq/l (200-300 pCi/l); [10]) and carbon dioxide (more than 2-3 %) form lineaments SW-NE and NW-SE oriented. The higher value of CO_2 (58 %) lies exactly on the Acqua Borra thermal spring. However it is worth noting the similarity between the three soil gas distributions.
Aerial photo interpretation was performed from 1:13000 scale photos, for the surveyed area. About 50 elements have been recorded and their statistical trend has been computed. The results show two main directions trending SW-NE and subordinately NW-SE (Fig. 14) which are the same directions as the above mentioned fracture zones. A more complete photogeologic study throughout the basin, using 1:70000 scale photos, is actually in progress.
Positive helium anomalies indicate a deep gas (i.e. geogas as suggested by Malmqvist & Kristiansson, [11]), upwelling: therefore they occur over deep fractures that form efficient pathways for He degassing from the earth. It is likely that negative helium anomalies, because of their elongated shape, are produced by water-rich fractures. ΔHe values close to zero suggest conditions of good soil aeration and therefore good drainage, combined with

an absence of gas-conducting fractures.
Therefore the observed soil gas distribution confirms the presence of two fracturing zones which conduct geogas from the basement to the surface. Near the lineaments intersection, greater fracture concentration increases the fluid flux producing thermal springs (Acqua Borra) and the highest CO_2 values.
The directions of soil gas anomalies are the same of those obtained statistically by means of aerial photo interpretation . The affinity of the soil gas anomalies with linear features from the aerial photo is not surprising since photo lineaments commonly represent zones of faulting or intense fracturing. Because fractured rock is more easily weathered and eroded, topographic lows commonly occur over tectonic lineaments. So, lineament-related structures may serve as conduits for gases outgassing from both deep (^4He, CO_2) and shallow (^{222}Rn, CO_2) sources.
Finally a number of conclusions may be drawn:
- The Arbia Line and its perpendicular fault system are tectonic discontinuities that act as preferential avenue for geogas upwelling.
- The Acqua Borra thermal springs and the 58% of CO_2 in soil gas should result from a greater fracturing due to the intersection of the two tectonic lineaments.
-The clay sequence, in spite of its great thickness, if fractured doesn't form an impermeable barrier for geogas.
-Clays prevent gas rising only far from fractured zones.
-The fractures in clays - supposed active until early Pleistocene- are not gas-tight.
Therefore two hypothesis can be put forward: a) fractures are still active; b) clays, despite their plastic behaviour, may not be able to seal the fractures (in contrast with events that seem to occur in other areas where unconsolidated clays exist).
We believe these conclusions (and particularly the last hypothesis) form a key point in the research and for this reason they warrant in-depth studies.
A new survey is going to be performed throughout the basin, using a regional scale (1-2 samples per square kilometre) in order to verify the results obtained and the conclusion drawn.

b-3: In the OFANTO BASIN, located in the southern Apennine, soil gas surveys (110 samples) and mesostructural analyses have been completed but the data processing is still in progress. The results will be explained in the next report.

c] The comparison between results of surveys performed with different densities of sampling allows one to know the sensitivity of the soil gas method for tracing structural features. The data, discussed above, show that high secondary permeability zones, such as faulted and/or fractured rocks, can be detected with any sampling densities. In fact surveys performed by means of 100 samples per square kilometre (Piano d'Asco), by 50 samples per square kilometre (San Vittorino Valley) or 25 (Siena Basin) give qualitatively the same results as those performed by regional sampling i.e. 2-4 samples per square kilometre (Pisticci). The difference in the results lies in the detail of the gas escape anomalies. For a better analysis of results from different sampling scales, the next detailed and regional soil gas surveys will be carried out in the same area. The results described above strongly support the hypothesis that the soil gas method can give useful information on secondary permeability of clayey sequences at any given scale (both regional and detailed). Nevertheless, more geological and geochemical data are necessary for the elaboration of mathematical models on gas generation and migration in soils. In fact, knowledge of these mechanisms in the ground would be useful for interpreting soil gas data at any scale. It is, however, essential both in recognizing preferred channels of gas flow and in monitoring the waste radioactive repositories.

EXETER UNIVERSITY (P. Grainger, G.A. Duddridge)
A mobile laboratory for the analysis of soil gases was commissioned in the first quarter of 1992. Fieldwork then commenced at three sites, one in England and two in Italy with the aim of further testing and improving soil gas measurements as a fault and fracture detection

method. Collection from shallow soil probes, analysis on site and in the laboratory and interpretation are based on methods described in [4] and [12] The main advance in 1992 was the installation of the new and more reliable Helium mass spectrometer, plus a gas chromatograph for major gas analysis. Radon determination remains the same , though scintillation cells await calibration to allow activity in counts per minute to be converted to bequerels per litre.

In the Bovey Basin, Devon, England two out of three sub-projects have been in progress. Firstly, the monitoring of soil gas data against changes in weather at the Twinyeo site, the data from which will help in the understanding of background varitions in soil gas concentrations. Secondly, a regional survey of 49 sqkm with an initial sampling density of 1 site/sqkm, is being made to test for relationships of gases with lithology and major lineaments. The third sub-project will be more detailed work over features revealed by the regional survey.

June 1992 was the date of the first field tests in the Siena Basin, Tuscany, Italy. The basin is one of a number of similar geological structures extending north-west to south-east for 300 km between chains of the Apennines . It has extensional structures and is filled with Pliocene sediments, mostly marine clay deposits with subordinate sands and conglomerates. A number of soil gas samples were taken from around Rapolano Terme, in the vicinity of the basin's north-east side boundary fault.

The fault is very permeable to gases with hydrogen sulphide clearly present in the air in the vicinity of upwelling thermal water at Bagni Freddi and Terme San Giovanni. This area produced high helium values, with some above 2000 ppb, plus CO_2 exceeding 70% at one sample point.

The main study, however, was concentrated over a regional south-west to north-east fault, 'Linea d'Arbia'. Three sections were studied, two within the basin and the third just beyond the north-east basin boundary; The actual position of the fault was predicted from morphological evidence and the hot springs, Site 1, at Bagni Acqua Borra. Here a 17 sample point traverse on 312° showed a zone of anomalous He above 600 ppb and a peak of ^{220}Rn of 219 cpm. These values coupled with high CO_2 from background levels to over 20%, indicates the presence of major permeable feature (Fig. 15)

East north-east along the projected strike of the fault a longer traverse was completed, Site 2, with sample spacing ranging from detailed 10 m spacing at the centre to a wider 40 m reconaissance at either end. Even the highest values of He are 200 ppb lower than at Site 1 and there were no distinct anomalies of this gas or Rn or CO_2

However, it may be that the whole lenght of the traversed line from -200 m to 150 m is anomalous and fault induced to give the He values around 250 ppb, both Rn isotopes at around 150 cpm and CO_2 4%. Outside this trend there are higher or lower values such as at BB7 where dHe is at 311 ppb, ^{222}Rn is 287 cpm and CO_2 5.68% .

Whether or not the sharp increase in gas concentration beyond -400 to -200 metres, followed by a more gradual decline to the 150 m sampling point is a feature of fault geometry is unclear. The fault could dip to the north-north-west and allow fault derived gases to disperse over a wider, but deepening area through hanging wall.

A similar pattern of He and CO_2 was also seen, further along the projected fault strike, at Site 3. Here, though, gas concentrations were higher, with dHe reaching 680 ppb and CO_2 7.81%.

In September-October 1992 soil gas surveys were carried out in the Ofanto clay basin, of the Irpinia region of the southern Italy. Sample spacing was at 20m along single reconaissance traverses, positioned over possible faults identified by Italian geologist from Rome university. Data processing is still in progress.

Of the three work programmes underway in 1992, that in England is still in progress, the first completed tests at the Siena basin site show that this area has great potential for study and is aided by the high gas flux across the area.

INTERA (P. Grindrood, M. Impey)

Automatic identification of soil-gas anomalies and regional faultlines

The interpretation of the spatial distribution of anomalously high gas concentration

(*positive anomalies*) is central to the identification of regional faultine structure, and so forms the focus for Intera's involvement in the HEGAS project. Specifically, one objective has been to quantify the criteria used in the interpretation of positive anomalies, and to incorporate these criteria in a numerical code.

In 1991, Intera developed a methodology for the identification and interpretation of positive gas anomalies based on quantitative criteria. The initial methodology was based on three stages:

1. identification of positive anomalies in the soil-gas data;
2. fitting of straight lines through identified anomalies, using a total least squares algorithm;
3. ranking of the fitted lines by a goodness-of-fit, modified by the geometry of the fitted lines.

In the first step, positive anomalies are identified in the soil-gas data by regarding each soil-gas measurement as defining the elevation of a surface over a two-dimentional region, and then searching for narrow, upward "spikes" in the surface. In the second stage, straight lines are fitted through a number of anomalies. The motivation for this is that faultlines are generally regarded as a piecewise-linear, and so a straight line drawn through a number of anomalies is a possible fault. A total least-squares algorithm is used to fit a straight line through each subset of three positive anomalies: the algotrithm yields a goodness-of-fit parameter Q^*_k which varies from 1, for a perfect straight line fit, to 0, for the poorest possible fit of all the subsets of three positive anomalies in the data set. The derivation of this fit is described in [13], [15].

In the third stage, a ranking parameter, Q_k, is derived for each set of three positive anomalies based on the goodness-of-fit parameter Q^*_k, and taking into account the length of the total least-squares fitted line and the alignment of the fitted line with the user-specified preferred directions.

There are two reasons for considering the geometry of the fitted line. First, it may be that three anomalies that are very far apart lie very close to a straight line, purely by chance , and so the fitted line is unrepresentative of the faultline structure. Secondly, there may be "soft" geological information of the probable length and direction of faultlines. Thus, fitted lines satisfying these "soft" criteria can be thought of as being most representative of the regional faultline structure.

These three stages are described in more detail in [13], [15]. The focus of Intera's work in 1992 has been to further develop the third stage of the quantitative interpretation, by incorporating additional "soft" data information. The approach adopted has been to quantify the variation of the soil-gas data in the neighbourhood of the lines fitted to sets of three positive anomalies. It is expected that if a fitted line corresponds closely to a faultline, then when moving in a direction parallel to the fitted line, the soil-gas measurements will show less variation than when moving in a direction perpendicular to the fitted line. In terms of the surface defined by (x,y,z), where z is the soil-gas measurement defined at point (x,y) in two dimensional Cartesian coordinates, faultlines will correspond to high, narrow "ridges" in the surface. A contour plot of this surface will exhibit narrow elliptical contours, possibly with a number of negative anomalies running parallel to the major axis of the ellipse.

This ridge property has been quantified, and incorporated as a subroutine in the Intera code ROMA which contains the three-step methodology discussed above. The input to the subroutine is the position and value of three positive anomalies, the direction of the total least-squares fitted line, and the other soil-gas measurements in a neighbourhood of the fitted line. Gradients of the soil-gas measurements in the directions parallel and perpendicular to the fitted line are obtained, and used to draw elliptic contours around the fitted line, locally approximating the variation of the soil-gas data (See [15] for details). If the anomalies and local data considerd have the desired "ridge" property, then the ellipse will have its major axis closely aligned with the fitted line, and its minor axis much shorter than major axis and aligned approximately perpendicular to the fitted line. The subroutine outputs a measure, R_k, for each set of three positive anomalies, based on the length and alignment of the major and minor axes. This measure ranges from 1 for the set of three

positive anomalies with the most clearly defined local ridge structure, to zero for the set with the least clearly defined local ridge structure. The measure R_k is combined with the ranking parameter Q_k, to obtain a new ranking parameter, $S_k=QkXR_k$, for each set of three positive anomalies. The set of three anomalies with the largest Sk most closely satisfies the criteria defining a faultline.
Using this revised quantitative ranking procedure further progress can be made towards a robust quantitative methodology for identifying regional faultline structure from soil-gas data.

List of Pubblications

DUDDRIDGE G., GERA F., GRAINGER P., GRINDROD P., LOMBARDI S. , (1991): Gas migration through argillaceous sediments: soil gas analysis as an investigation tool - NEA Workshop on gas gen. and release from rad. waste rep., Aix-en-Provence, 23th-26th September, France.

DUDDRIDGE G.A., GRAINGER P., GRINDROD P., IMPEY M..D, LOMBARDI S. (1991): The refinement of soil gas analysis as a geological investigative techique/ First results. CEC Contract No. F12W-CT91-0064.

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[14]DUDDRIDGE G.A., GRAINGER P., GRINDROD P., IMPEY M..D and LOMBARDI S. (1991): The refinement of soil gas analysis as a geological investigative techique/ First results. CEC Contract No. F12W-CT91-0064 (TSTS)

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TABLES

Table I - Piano d'Asco (Tarquinia Basin)

GAS	Mean	Std.Dev.	Mode	Min.Val.	Max.Val.	N.Samp.
ΔHe (ppb)	30	102	0	-221	242	108

Table II - Pisticci

ΔHe (ppb)	570	3006	0	-1400	21010	264
Rn (Bq/l)	5.36	8.21	0	0	82.51	267
CO_2 (%)	.431	.536	.035	.030	2.825	65

Table III - San Vittorino Valley

ΔHe (ppb)	33	92	0	0	577	91
Rn (Bq/l)	38.14	75.77	8.14	1.48	600	91

Table IV - Siena Basin

ΔHe (ppb)	0	126	0	-460	626	195
Rn (Bq/l)	14.17	18.87	0	0	100.64	195
CO_2 (%)	2.77	4.72	.030	.030	58.25	195

FIGURES

Fig. 1 - Geological scketch map of Tarquinia Valley. Regional faultlines are reported.

Fig. 2 - Helium disribution in soil gas at Piano d'Asco (Tarquinia Valley). This countour map, as well as the following ones, is achieved through creation and interpolation of a grid of values each representing the weighted mean of 8 real values using kriging method. Straight lines represent the alignments of positive anomalies. The NW-SE trend coincides with that of regional fault system. N-W and E-W trends may be coincide with local neotectonic fractures.

Fig. 3 - Geological scketch map of Pisticci area. Dashed lines represent more recent neotectonic alignments.

Fig. 4-5-6 - ΔHe (ppb), ^{222}Rn (pCi/l) and CO_2 (%) soil gas distribution at Pisticci. The observed trends coincide with those of the local fault systems (supposed and outcropping).

Fig. 7 - Geological sketch map of S.Vittorino Valley (Rieti).

Figg. 8 - 9 - ΔHe (ppb) and ^{222}Rn (pCi/l) distribution in soil gas at S.Vittorino.

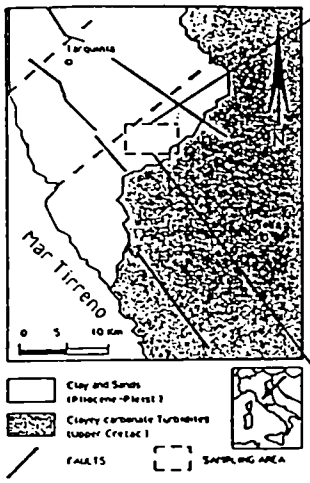
Fig. 10 - Geological skecth map of Siena Basin

Fig. 11-12-13 - ΔHe, ^{222}Rn and CO_2 soil gas distribution in the Siena basin The observed anomalies trends coincide with those of the SW-NE (Arbia Line) and NW-SE fault systems.

Fig. 14 - Statistical lineaments trends from aerial photo interpretation.

Fig. 15 - a) Location of the transverses. b) Soil gas data from site 1 and site 2.

Fig. 1



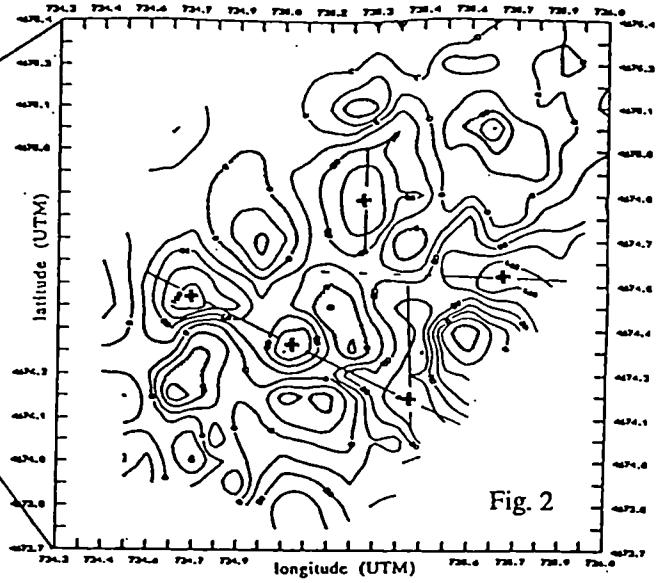
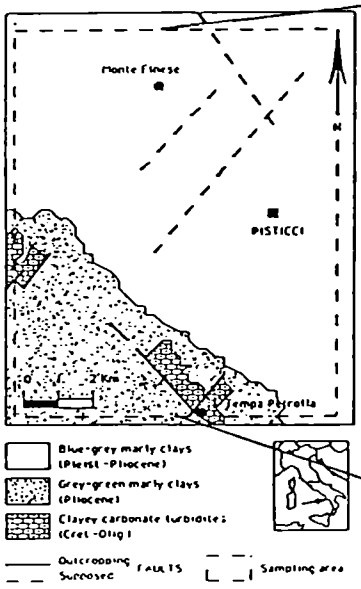
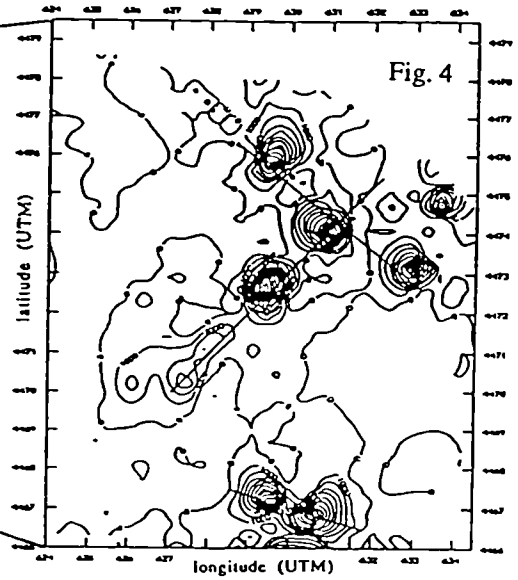


Fig. 2

Fig. 3





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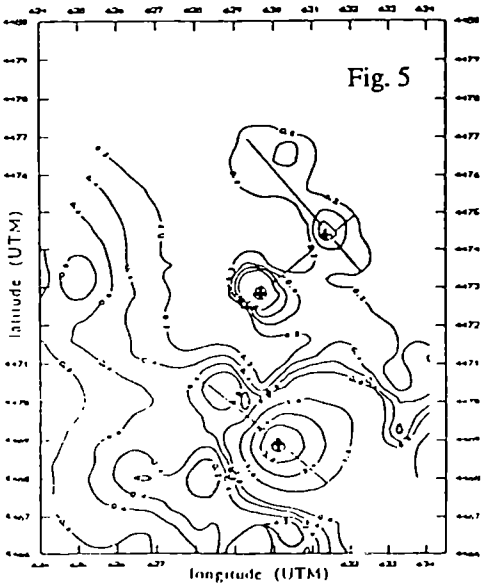

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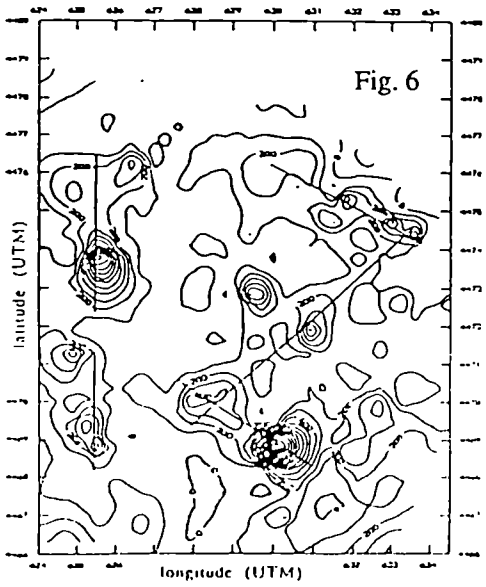

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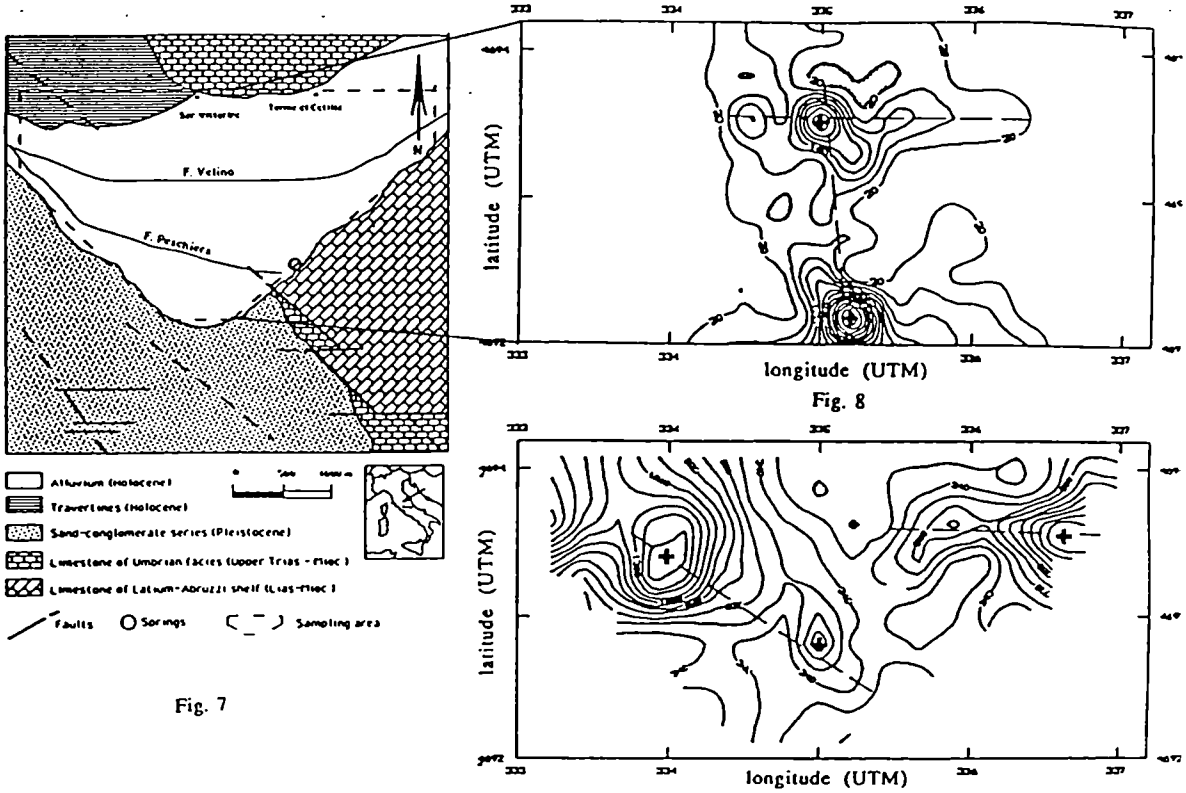


Fig. 7

Fig. 8

Fig. 9

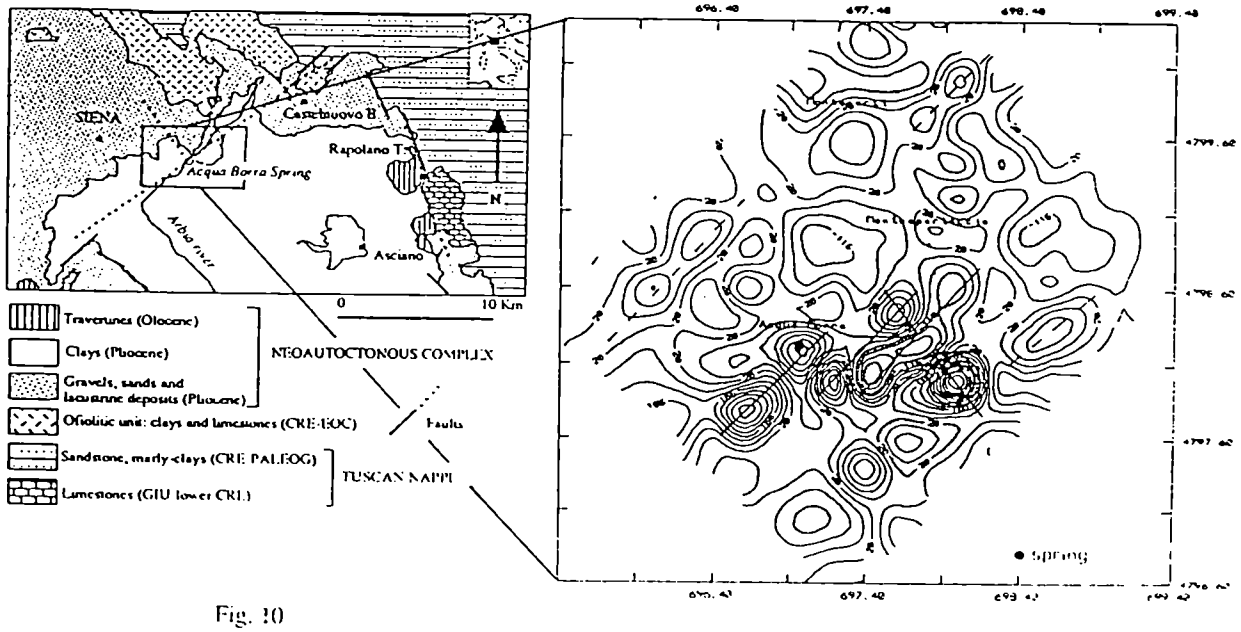


Fig. 10

Fig. 11

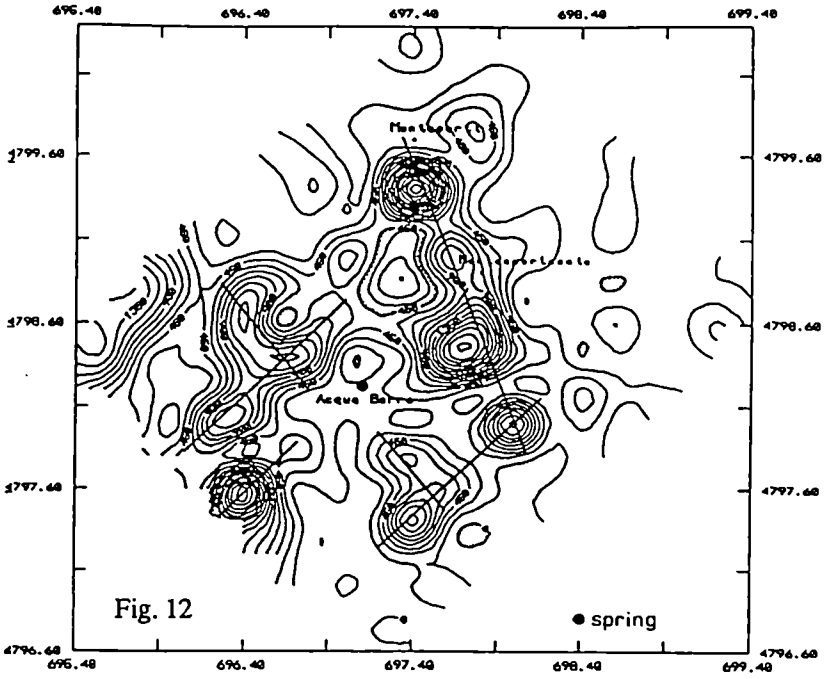


Fig. 12

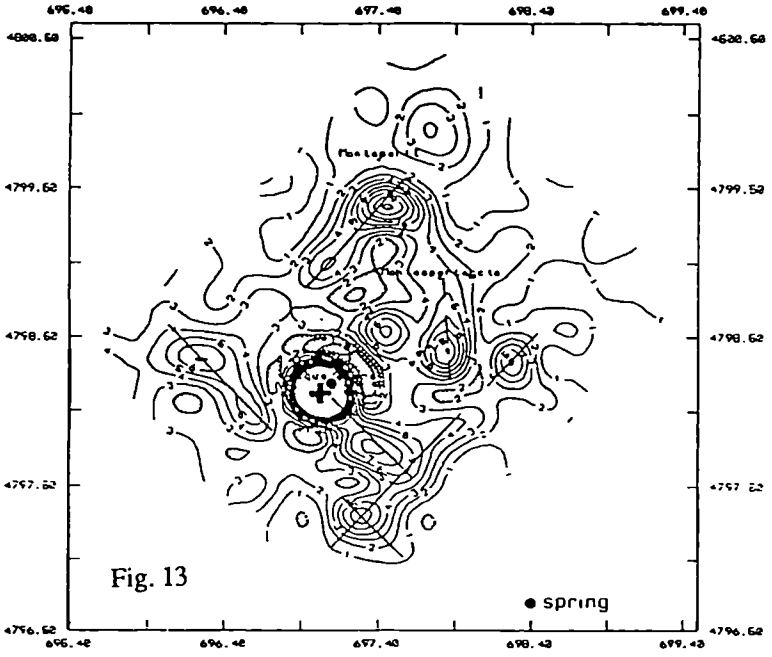


Fig. 13

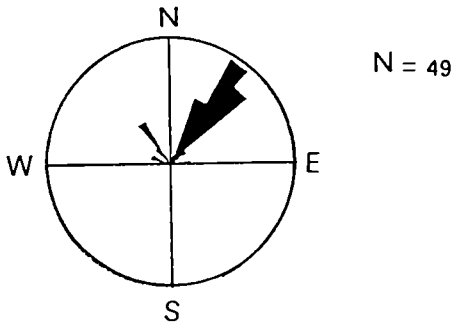


Fig. 14

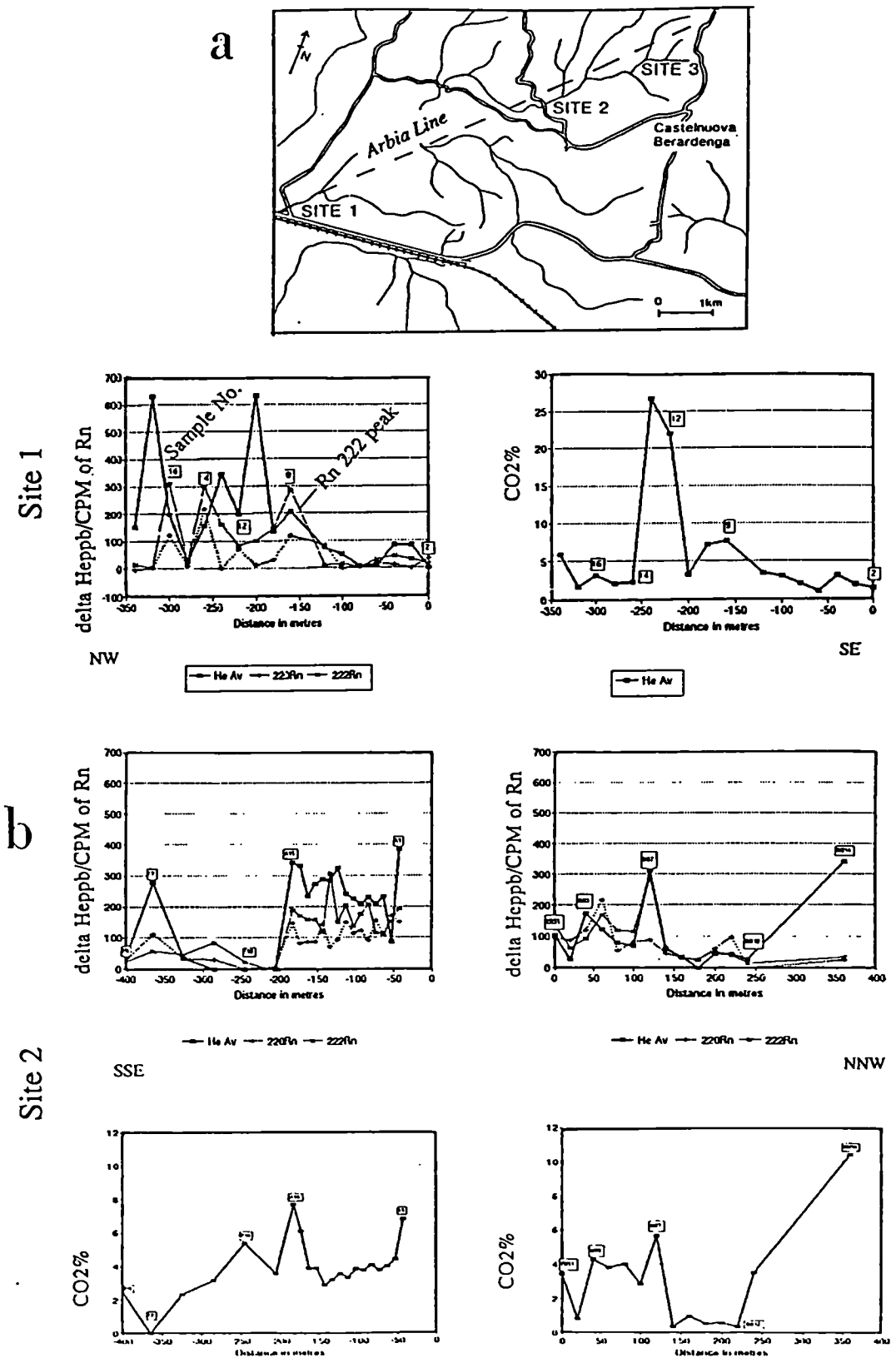

a
SITE 3
SITE 2
Castelnuovo Berardenga
Arbia Line
SITE 1
0 1km
Site 1
delta Heppb/CPM of Rn
Sample No.
Rn 222 peak
Distance in metres
NW
He Av 220Rn 222Rn
CO2%
SE
b
Site 2
SSE
NNW

Fig. 15

MIGRATION AND EXPERIMENTS ON GAS MIGRATION IN REPOSITORY HOST ROCKS

Title :	MEGAS : Modelling and Experiments on GAS migration in repository host rocks
Contractors :	SCK/CEN, INTERA, BGS, ISMES
Contract N° :	FI2W-CT91-0076
Duration of contract :	from 01-03-91 to 28-02-94
Period covered :	from 01-01-92 to 31-12-92
Project leaders :	G. Volckaert (coordinator), M. Impey, P. Hooker, V. Fioravante

A. OBJECTIVES AND SCOPE

For the option of a deep geological disposal facility several potential sources of gases have been identified : i.e. the anaerobic corrosion of iron, degradation of organic materials, the gas present as such in the waste packages. Of those gases hydrogen is certainly the gas which can be released in the potentially largest amount. For the safety evaluation of a repository it is necessary to know the effects of gasses on the host rock.

The primary objective of the MEGAS project is to understand the consequences of gas generation in a clay host rock. The final objective of this project will be to validate a gas migration model and to confirm our understanding using an in situ gas injection experiment.

B. WORK PROGRAMME

1. Chemical reaction and diffusion experiments

The reaction capacity of hydrogen with Boom clay observed in previous experiments will be further investigated by determining the intrinsic reaction rate, the reaction capacity and the diffusion coefficient.

2. Geotechnical experiments : uniaxial

In these experiments the gas permeability (two-phase flow) and the gas breakthrough pressure will be determined.

3. Geotechnical experiments : triaxial

The goal of these experiments will be to define the conditions under which preferential pathways for gas migration might develop and to examine bubble growth and migration. Triaxial experiments will also be performed at elevated temperature.

4. In situ experiments

These will be performed in the HADES underground research facility (Mol, Belgium).

5. Modelling

The following approaches will be utilized : modelling the dynamics of bubble flow and modelling two phase flow. The laboratory experiments will be used to validate and, possibly, calibrate a basic two phase model.

Within this project INTERA will perform the main modelling work. The SCK/CEN will be responsible for the gas reaction, diffusion and uniaxial flow and in situ experiments. BGS will perform geotechnically based triaxial gas flow experiments. ISMES will perform experiments at higher temperature.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

1. Chemical and diffusion experiments

Some blank experiments have been performed using a reactor. It has been shown that the dissolution kinetics of hydrogen in water is fast.

A new improved reactor has been built and is ready for testing.

A first series of in-diffusion tests have been performed. Their interpretation has shown that their is a very small, but on the long term significant, leak which requires minor adaptations and improvements (rubber seals to be replaced by copper).

2. Geotechnical experiments : uniaxial

A X-ray transparent oedometer cell has been constructed and the medical X-ray tomograph of the State University of Ghent has been calibrated for Boom clay. X-ray tomography will be applied next semester to measure in a non-destructive manner the saturation profile during gas breakthrough. Gas breakthrough experiments have been continued and refined. In these experiments the saturation profile after gas breakthrough has been measured destructively. The time between application of the gas pressure and the time of breakthrough has been measured.

3. Geotechnical experiments : triaxial

The equipment has been constructed and tested. A first series of needle injection tests at room temperature have been performed on Pontida and Boom clay.

Next semester 1D gas flow and needle injection experiments at higher temperature will be performed.

4. In situ experiments

The four piezometers for the new in situ injection experiment have been installed successfully in the HADES underground laboratory. Gas injection will only be started in the second half of 1993 after the hydraulic characterisation of the experimental environment.

The gas injection experiment using an existing piezometer is in preparation and will start at the end of January 1993.

5. Modelling

An analytical model for the diffusion in combination with sorption and reaction of a gas in a clay plug is obtained.

The two phase flow code TOPAZ has been further refined. Preliminary calculations for the new in situ experiment have been performed. The spacial configuration of the experiment and the results of the breakthrough experiments were taken into account.

Progress and results

SCK/CEN

H_2 - Boom clay reaction experiments

Using an available simple pressure vessel as reactor a series of blank experiments were performed. These experiments showed that when water and hydrogen are intensively mixed, the dissolution kinetics of hydrogen is fast and that equilibrium is reached in less then 1 hour. The literature value for the solubility of hydrogen at 25 °C namely $1.5\ 10^{-3}$ g/kg water was confirmed. This also shows that all parts of the reactor are inert to hydrogen. Two preliminary experiments with a Boom clay-water slurry were performed. In the first experiment a Boom clay reaction capacity of about

10 μeq/g clay was found. In the second experiment practically no reaction was detected initially but after oxidation with pure oxygen, a clear but slow reaction was observed.

H_2 in-diffusion experiments

Four experiments were performed using the same oedometer as for the breakthrough experiments. The interpretation of the experiments however showed that there is a very small ($1.5\ 10^{-6}$ ml STP/s) but reproducible leak which becomes predominant after about 10 days. A blank experiment showed that the most probable explanation for this leak is the diffusion of hydrogen through the rubber o-rings. Therefore they will be replaced by copper o-rings.

Breakthrough experiments

Three gas breakthrough experiments were performed on fully saturated natural Boom clay plugs of about 9 cm long. Shortly after the gas breakthrough the oedometer cells were dismantled and the clay plugs were cut into slices in order to determine the saturation profile. The results (see Fig. 1) show that the saturation does not decrease below 85 % and that the mean saturation is still above 90 %. Apparently the gas needs to displace the water in the largest pores, to break through the clay plug.

These results will be used by INTERA for a first calibration of their model.

Using three X-ray transparent oedometer cells, the medical X-ray tomograph of the State University of Ghent was calibrated for volumetric water content changes in Boom clay at its natural density. The following calibration curve was obtained :

$$HU = 1188 + 10.12 w_v$$

with : HU = measured radiological density in Hounsfield units

w_v = volumetric water content

In situ experiments

The design and actual configuration of the new in situ gas injection experiment is shown in Fig. 2. The four piezometer nests have been installed successfully on the 22-10-92 for the central injection filter and the 27-11-92, 30-11-92 and 01-12-92 for the surrounding detection filters. For the small diameter detection filters the drilling and installation was performed on the same day which lead to a sooner pressure equilibrium. The larger injection filter was installed in two days.

BGS

Theoretical development and basic studies on gas migration

Early 1993 the report on the theory will become available and will contain a literature search, a description of gas migration mechanisms, and evaluation of key parameters for the Boom clay and a new scanning electron microscopy (SEM) study of selected Boom clay samples, including fresh samples provided by SCK/CEN.

The new SEM study of the Boom clay was carried out in order to define the texture and microstructure of the Boom clay in different hydration states. These new data help to understand the effects of dried and wetted increasing gas pressure on the Boom clay.

The examination of micro-structures of Boom clay in dehydrated and hydrated conditions was made possible through using the "environmental scanning electron microscope (ESEM) at the University of Manchester. The ESEM was used not only to identify the mineralogical details but also the sizes of the pore radii and the presence and sizes of microfractures and their apertures. Parallel to the bedding, pores exhibited laminar shapes.

The interparticulate distances between clay flakes could be observed directly on undisturbed hydrated samples to be <0.1 micron. The role of water saturation in controlling fracture density and aperture sizes and therefore permeability has been a key outcome of the ESEM study; the profound effects of different water contents on clay swelling and pyrite oxidation can be seen directly. The results of this work have been incorporated in the interim report on the theory of gas migration.

Experimental design

A simple apparatus has been designed for the helium migration experiments on 50 mm diameter specimens of the Boom clay. All core samples will be produced to a high standard using proven geotechnical methods utilising a soil lathe to provide the necessary tolerances. A water saturated helium gas will be introduced in a gas flood operation at a constant flow rate at one end of the core. Each core will be resaturated using standard techniques. An in situ confining pressure is likely to be maintained throughout, though in the first experiment a stepped profile will be used to observe the interaction of diffuse and fracture flow. This will help to direct future experiments. The pressure at the other end of the core to the point of injection (during experimentation) will be kept constant, so that any volumetric changes will be recorded and indicate gas breakthrough and or diffusion flow. Fracture orientation will be investigated post experimentally using SEM techniques. A sweep of tests will be run using core samples taken in orthogonal directions with flow rate, back pressure, and confining pressure range to find the conditions most likely to promote a gas fracture. If there are sufficient samples, needle point injection experiments will be made to view the effects of gas production at a single point and its relative migration in an initially hydrostatic stress state.

ISMES

Triaxial experiments

Needle gas injection system has been fully developed and implemented in the HITEP apparatus. To test the equipment a series of experiments was performed at room temperature using Pontida and Boom clay. As Pontida clay is more permeable than Boom clay the system could first be tested at relative low pressure. The experiments were performed using different initial gas injection pressures and different vertical effective pressures. A summary of experimental conditions is given in Table 1.

In these experiments the evolution of the gas pressure in the injection chamber and in the outlet chamber is measured as function of time. An example of this evolution for Pontida and Boom clay is given in Fig. 3 and Fig. 4. As expected the gas pressure dispersion is a lot faster for Pontida clay than for Boom clay. The breakthrough pressures for Boom clay in these experiment are within the same range as those measured by SCK/CEN.

Due to difficulties with the temperature control system, it was not yet possible to perform the same kind of experiments at higher temperature. A new temperature control system has been installed on the HITEP apparatus. The new system has been tested and showed to be reliable so that the high temperature experiment will probably start early 1993.

INTERA

Two-phase flow modelling

The two-phase flow code TOPAZ has been further refined and has now become completely operational. With the TOPAZ code, some preliminary calculations were performed in advance of the new in situ test. The main goal of the calculations was to estimate gas breakthrough time and flow rates and their sensitivity to a number of parameters such as gas injection pressure, hydraulic conductivity, critical gas saturation, gas threshold capillary pressure. Such calculations are also an important help for the experimenters for the design of the injection equipment and choice of data acquisition system for the test. The TOPAZ code calculates the evolution of the gas inlet flux and the evolution of the gas and water pressure field. Also the changes in saturation as function of time and space can be calculated.

For the case of a 3-D spherical geometry with a gas inlet pressure of 3.5 Mpa and a threshold capillary pressure of 1 Mpa the results are shown in Fig. 5 to 8.

The preliminary calculation show that a flux of about 1 mg/hour can be expected and that the breakthrough time to the 0.75 m position appears to be of the order of several weeks to several months. These travel times depend strongly on the critical gas saturation.

Table 1 : Experimental conditions of the needle gas injection experiments

TEST	USED CLAY	vertical effective pressure [kPa]	initial pressure [kPa]
1	PONTIDA	400	90
		600	87; 105
		800	109
		1200	137; 172
2	BOOM	2500	1490; 1600
		1360	1140
3	BOOM	2500	1700

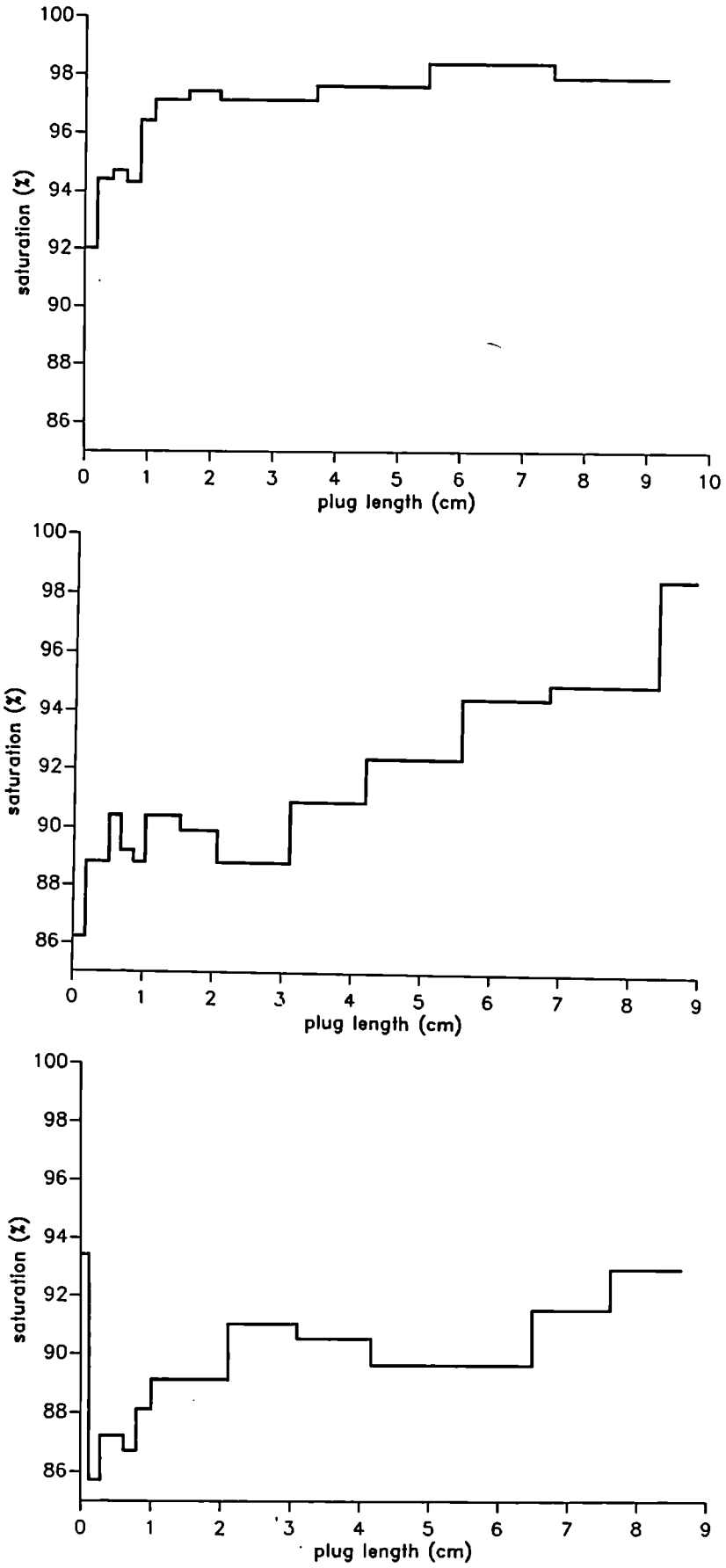
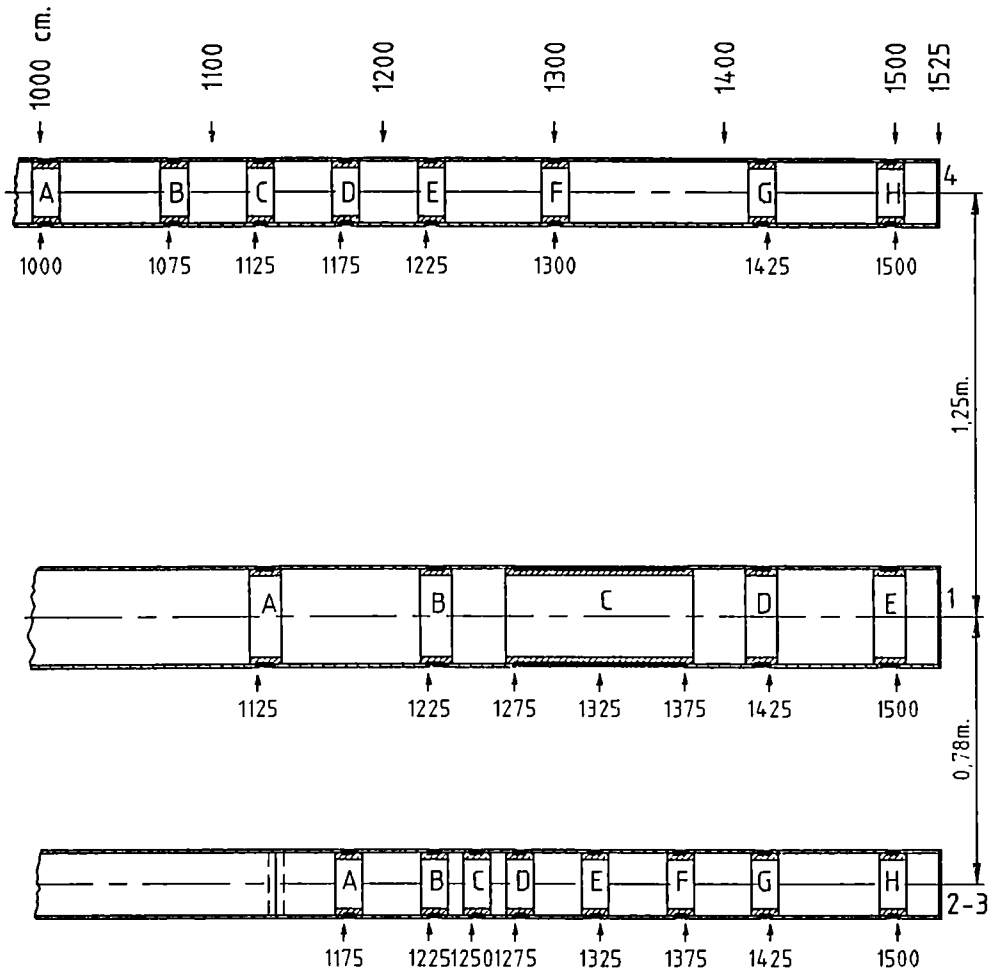


Figure 1 : Saturation profiles on three Boom clay plugs after gas breakthrough



(2-3) Filters Ø55,6/50 van 11,75 tot 15 m.
(4) Filters Ø55,6/50 van 10,5 tot 15 m.
(1) Filters Ø89/79 van 11 tot 15 m.

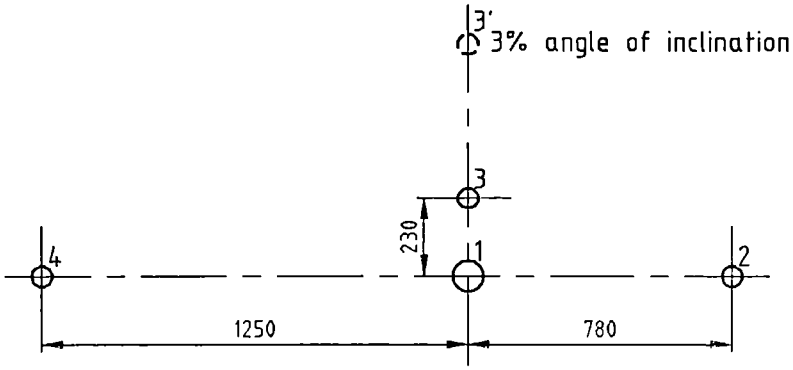


Figure 2 : Design of the MEGAS in situ gas injection experiment

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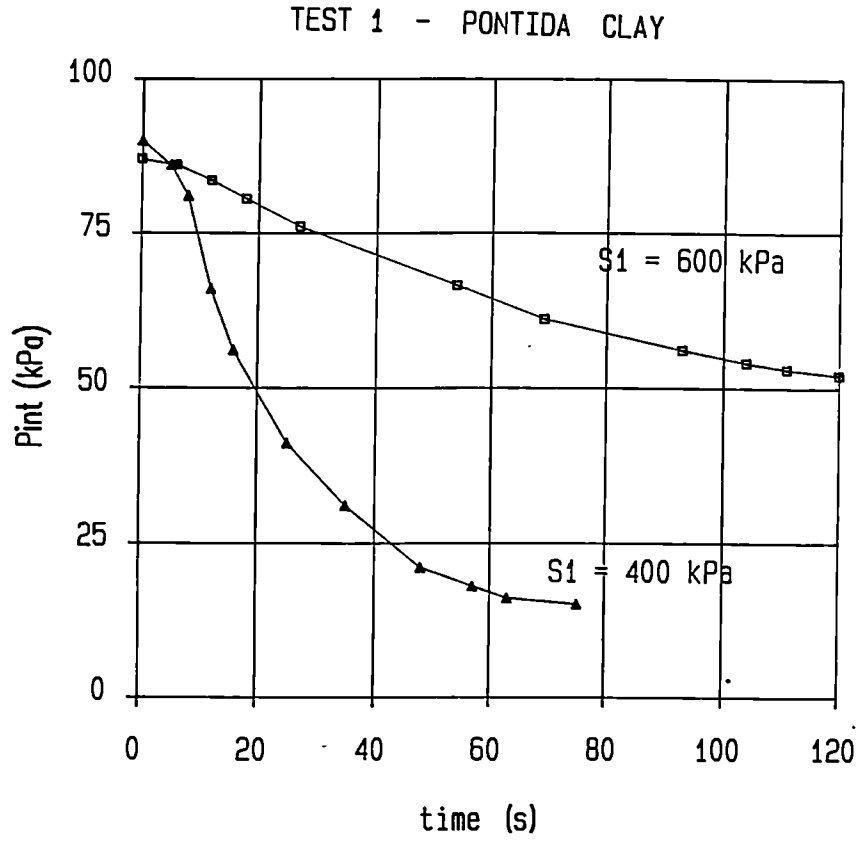

Figure 3 : Inlet pressure evolution for the needle gas injection on Pontida clay (Pint = internal pressure; S1 = vertical effective pressure)

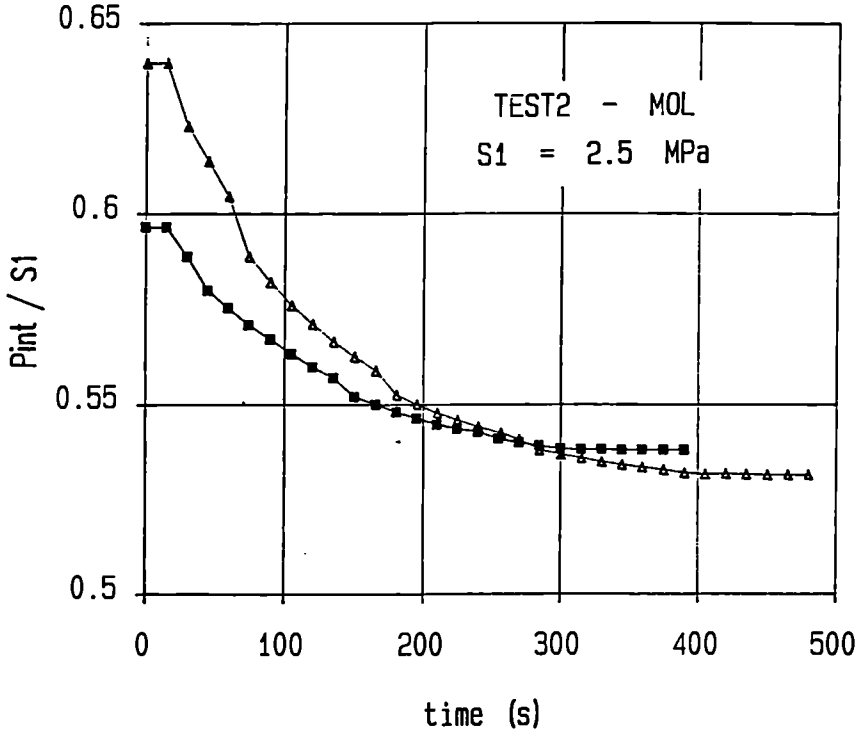

Figure 4 : Inlet pressure evolution for needle gas injection on Boom clay (Pint = internal pressure; S1 = vertical effective pressure)

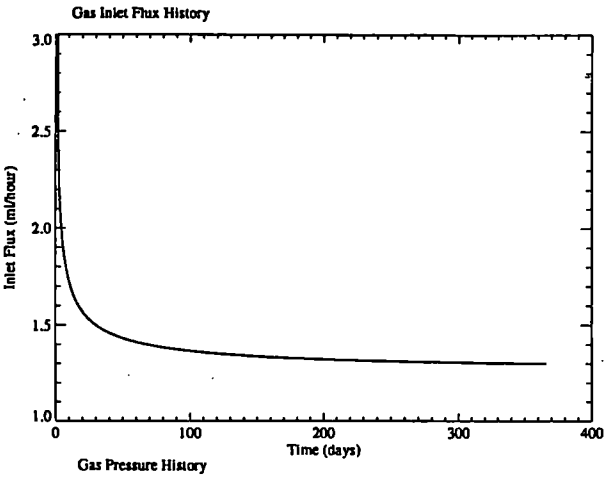

Figure 5 : History of Gas flux Entering the Clay

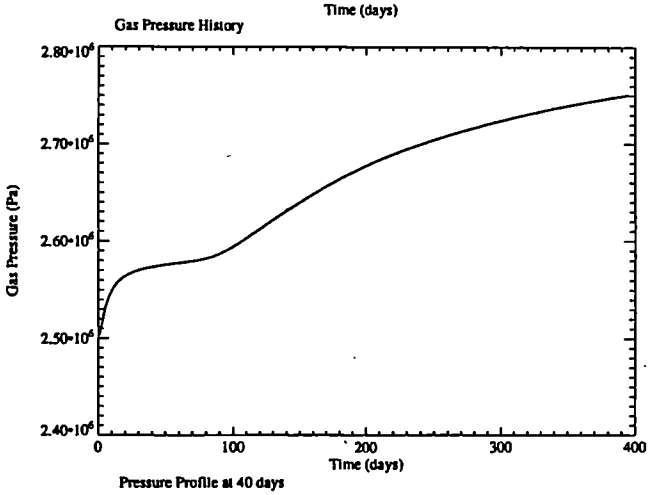

Figure 6 : History of Total (Gas) Pressure in Clay, 0.75 m from the Gas Inlet, with Critical Gas Saturation of Zero

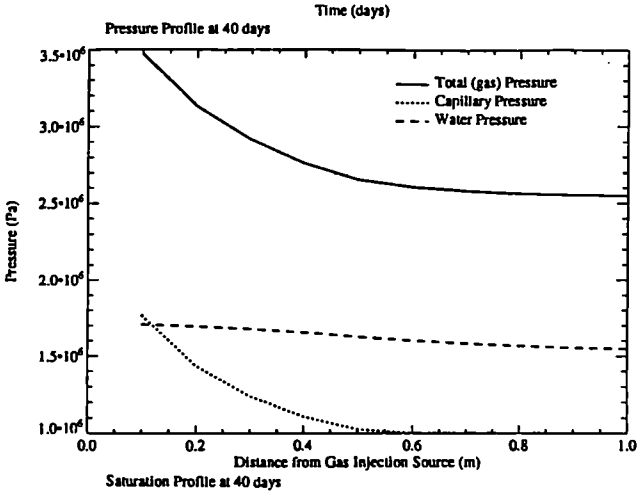

Figure 7 : Pressure Profiles in the Clay when Gas has Migrated 0.75 m, with Critical Gas Saturation of Zero

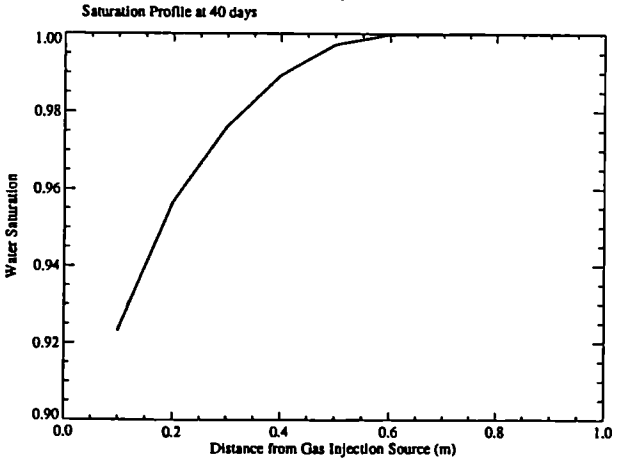

Figure 8 : Profile of Water Saturation in the Clay when Gas has Migrated 0.75 m, with Critical Gas Saturation of Zero

GAS PRESSURE BUILD-UP IN RADIOACTIVE WASTE DISPOSAL : HYDRAULIC AND MECHANICAL EFFECTS

Contractor:	GEOSTOCK, France
Contract N° :	FI2W/0093
Duration of contract:	July 1 1991 - June 30 1995
Period covered:	July 1991 - December 1991
Project Leader:	P. COLIN

A. Objectives and scope

The specific aim of this study is to evaluate the consequences of gas generation from a radioactive waste repository. The evaluation will be carried out in terms of gas migration in the backfill and the host rock and in terms of mechanical effects.

The phenomenology of the physical process involved in gas transport will be reviewed; then some selected numerical codes taking into account two phase flow will be presented. The gas pressure build up will be simulated for different designs of repositories, different host rock characteristics using numerical two phase flow models such as reservoir simulators used in the oil industry. A sensitivity study will then be performed. The mechanical modelling using new theoretical developments for fracture initiation and propagation through the bifurcation theories will be carried out with the cooperation of the French Institute of Petroleum (IFP); the scientific adviser is Pr Dragon from ENSMA in Poitiers (France).

B. Work programme

1. Phenomenology review : inventory of two phase flow phenomenology applied to gas migration from a radioactive wastes repository.
2. Laboratory experiments : limited number of investigations (threshold pressure, capillary pressure, relative permeability, etc) on some representative host rock core samples.
3. Two phase flow modelling : suitability of existing reservoir codes, simulation of gas pressure build up (isothermal flow, and in thermal conditions), in porous and fissured medium.
4. Mechanical developments and modelling : theoretical works for the elaboration of a new criteria for fracture initiation and propagation.
5. Conclusions.

C. Progress of work and results obtained

State of advancement

NOT SUBMITTED

SALT PERMEABILITY
IN SITU TEST
(Amélie Mine France)

Contractors CEA/ANDRA - Fontenay-aux-Roses - France
G.3S (Groupement pour l'étude des structures souterraines de stockage) - Palaiseau - Fance

Contrat n° FI2W-CT91-0101

Duration of contract from January 92 to June 95

Project leaders M. RAYNAL, JF. LAURENS

A/ OBJECTIVES AND SCOPE

The purpose of the in situ tests that will be performed in MDPA mines is to measure the gas permeability of a rock salt bed previously submitted to a brine percolation.

This is of major importance for predicting the becoming of the gases present in the repository (gases comming from radiolysis, corrosion, bacteriological activity, trapped air ...).

The experiment is planed to include two tests in separate boreholes at Amelie underground facilities.

As the measured quantities will be very low, the choice of experimental parameters will allow to eliminate or minimize or quantify all the undesirable effects in order to facilitate the datas interpretation.

The scientific interpretation of the results will be made by the G.3S.

B/ WORK PROGRAM

1. Prefeasability tests in order to validate the experimental device (tightness of the borehole system, accuracy of the measurements).

2. Pilot test in borehole n° 1, with brine, increasing the pressure up to fracture the rocksalt.

3. Test in borehole n° 2 including :

   - measurement of gas permeability ;
   - injection of brine and measurement of brine permeability ;
   - emptying of the borehole and measurement of gas permeability.

C/ PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

A theorical study using on analytical model has allowed to dimension the tests. The sensibility to different parameters has been tested.

The test site has been selected.

The feasability tests of the device inside the borehole have been made.

Progress and results

1) Theorical studies

Theorical studies have been conducted. The main hypothesis are :

- Two geometries of cavity have been investigated ; spherical and cylindrical with an infinite length, the reality being beetween these two cases.
- The rock salt is considered as an isotropic, saturated porous medium with an elastic, viscous, plastic behaviour.
- The flows through the rock salt are governed by Darcy's law (this last hypothesis being arguable).

Two cases have been investigated :

- constant pressure test,
- variable pressure test (pulse test)

General disturbing phenomena have been evaluated :

- creeping of the cavity,
- thermal effects,
- solution cristallization of halite.

The table 1 shows the orders of magnitude of the different phenomena.

The two solutions : constant and variable pressure have been compared, the table 2, shows their advantages and disadvantages.

The results of that study allow to recommend the constant pressure hydraulic test which offers to have a better control over the disturbing effects : creep and solution. Other recommendations are as follows :

Phenomenon	ΔV (cm3)	ΔP (MPa)
Permeability	- 150	- 45
Creep	- 6	- 1,8
Thermal expansion	+ 3	- 1,5
Salt solution	+ 3	- 0,3

Table 1 - Orders of magnitude of the different phenomena
(The sign + means an increase of volume or pressure. The sign - means a decrease of volume or pressure)

Experimental process	Advantages	Disadvantages
Constant Pressure test	- Solution-crytallisation Effects partially controlled, - Better estimation of creep.	- Critical measures of flow rate and volum, - small characteristic times.
Variable Pressure test	- Easy measurement of presure, - Higher charcteristic times possibly.	- Disturbing effect (creep, solution-crystallization) not controlled.

Table 2 - Advantages and disadvantages of the different experimental processes

- the borehole diameter has to be as large as possible to allow a reasonable duration of measuring data (large characteristic times),
- the distance between the pressurized zone and the gallery has to be long enough to prevent the mechanical disturbance induced by the gallery. According to the results of the W.I.P.P. tests (1985,1991) a distance between 10 and 20m seems to be enough,
- in order to reduce the thermal effects, thermoregulated brine injection should be used.

According to these recommendations the test site has been selected. The cavity will be bored vertically from a gallery in a 1.80 meters thick pure salt bed. The site will be located in the neighbourhood of the CPPS, DAM, and CRUSHED SALT test. The cavity will be far enough from openings to neglect their mechanical influence.

The main characteristics of the experimental procedure have been defined.

The temperature of the fluids will be constant. The pressure will be kept constant step after step, each step being approximately 2.5 MPa and from 15 to 30 days in order to minimize the undesirable effects.

The helium gas will be used for three reasons :
- Its behaviour is similar to the hydrogene (foreseen under repository conditions).
- Its use is not dangerous.
- Its detection is easy in case of leakage.

2) Shutter tests

Two types of shutters have been envisaged and compared.
- The first type consists of a classical system of inflatable packers already used in Asse Salt Mine and WIPP site.
- The second type consists of a new concept of inflatable packers using soft rubber (latex) and allowing to provide a good tightness on a short distance. As this distance is small there is the need to inject a sealant in order to avoid the skirting of the packer via the rocksalt (see figure 3).

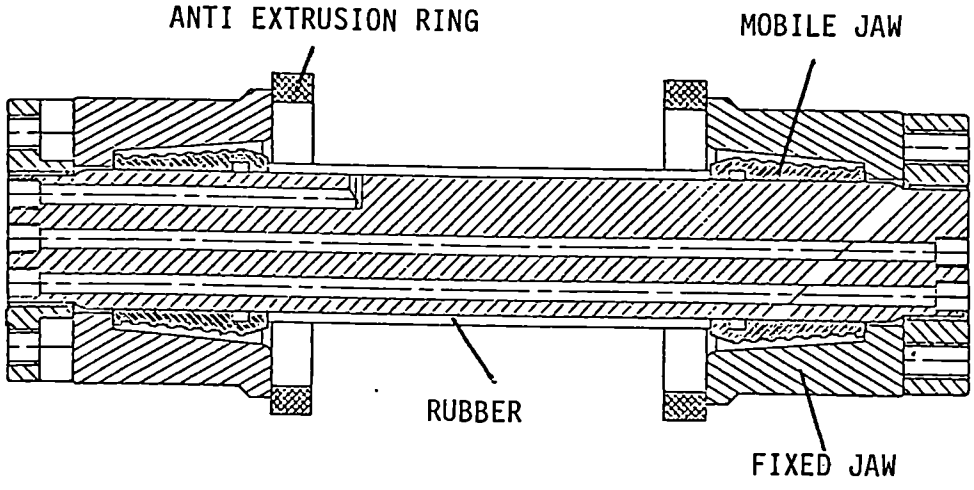

Figure 3 : Shutter Tested

2.1. Laboratory tests

A cell has been built (see figure 4) in order to test the second type of shutter. The system could withstand a pressure of 15 MPa during 12 hours. Surface faults have been put in order to simulate what could happen in a borehole. It has been proved that the system can allow them if they are not too sharp.

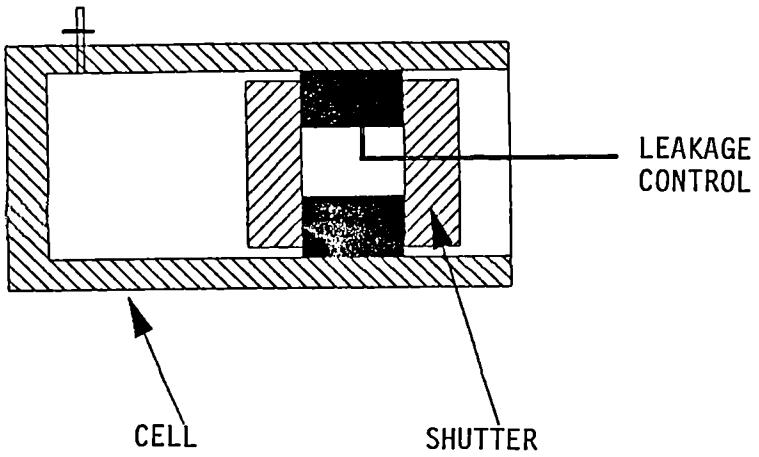

Figure 4 : Laboratory cell test

2.2. In situ tests

The tests of the second type of shutters have been performed in MDPA Amélie Mine in a borehole (diameter 116mm, length 4.80m) (see figure 5).

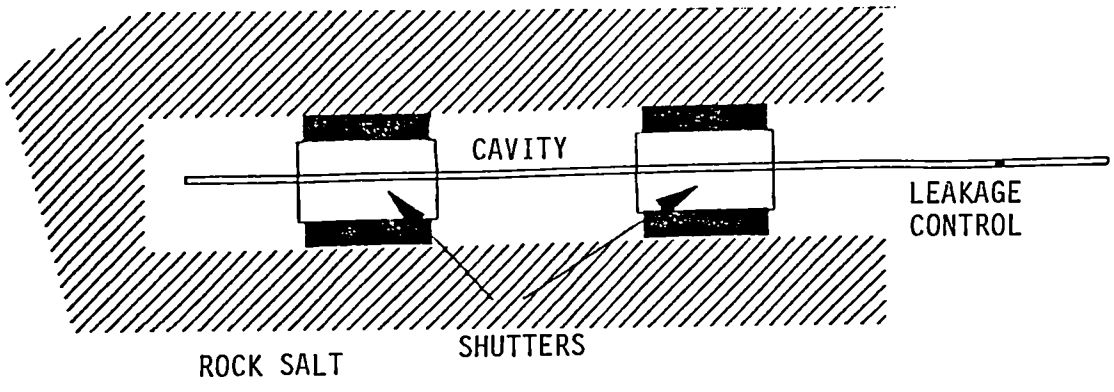

Figure 5 : In situ shutter test

The tightness of the system has been very good (pressure of the packers 7.5 MPa, pressure of the gas in the cavity 2.5 MPa and 5 MPa). From this test it has been possible to confirm the order of magnitude of the MDPA rocksalt permeability : 10^{-4} m Darcy.

3) Sealant specifications

The criteria for the choice of the sealant are :

- low initial viscosity,
- polymerization not too much heat generating,
- polymerization not too fast,
- sealant must remain supple enough in order to keep in contact with the rocksalt,
- sealant should not react with the rock salt or the fluid.

Polyacrilic sealants are under test.

4) Tender specifications for the borehole and the cavity

- The salt layer in which the test will be performed being 1.80 meters thick the cavity will be 1.20 meters long.

- The diameter of the cavity will be 146mm.

- The quality parameters of the borehole : rugosity, verticality, faults ... have been defined. A conventional drilling equipement used with care will be sufficient to fulfill these specifications.

Publications

COSENZA Ph, BAZARGAN B.
Conception et dimensionnement d'un essai in situ de perméabilité du sel au gaz et à la saumure.
Rapport interne ANDRA - 695 RP G.3S 92.001

TELANDRO S., BAZARGAN B.
Essai de perméabilité dans le sel.
Etude sur l'équipement du puits.
Rapport interne ANDRA - 695 RP G.3S 93-001

Continuation of the migration experiments in Boom clay (laboratory and in situ)

Contractor : ONDRAF/NIRAS, Brussels, Belgium

Contract N° : FI2W/0039

Duration of contract : September 1991 - Augustus 1995

Period covered : January 1992 - December 1992

Project leader : J. Van Miegroet

A. OBJECTIVES AND SCOPE

As the PAGIS /1/ and PACOMA /2/ safety studies have indicated, the migration of the critical radionuclides in the Boom clay is one of the key factors in the overall HLW disposal concept in Belgium. For this reason this programme aims at identifying the relevant migration mechanisms and at quantifying the migration parameters for these radionuclides.

This programme, a continuation of ongoing research, involves both percolation/diffusion experiments in the laboratory and in situ (underground lab).

The experimental work is performed by CEN/SCK.

B. WORK PROGRAMME

1. Migration experiments in the lab

For a selected list of critical (^{14}C, ^{99}Tc, ^{135}Cs, ^{237}Np) and possibly critical radionuclides (^{79}Se, ^{93}Zr, ^{107}Pd, U-, Am- and Cm-isotopes) as well as for dissolved organic molecules migration experiments in clay cores will be executed.

2. In situ migration experiments

In situ migration tests with HTO (tritiated water) and ^{134}Cs were started previously and are regularly monitored.

Additional tests with Am, Tc and HTO are planned.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

1. Lab-experiments

New experimental results were obtained for C (as HCO_3^-), I (as I^-) and Se (probably as HSe^-). The four C experiments, of which 3 were actually with a mixed $^{14}C/^{131}I$ label, provided a coherent ηR and D data set. No retardation of HCO_3^- due to sorption, precipitation or isotopic exchange could be evidenced.
The interpretation and modelling of the Se migration experiments were complicated for reasons that are not yet understood. Two widely differing migration profiles in the labelled and contacted clay plugs are possibly due to Se precipitation in the labelled clay plug.

2. In situ experiments

For the new 3D migration experiment 3 multiple piezometers were installed in the Boom clay and the actual start of the HTO migration experiment is foreseen in the second half of 1993.
^{125}I was injected in two different piezometers, one oriented horizontally and one vertically. The first ^{125}I concentrations were measured in the neighbouring filters and in the injection filter itself. The obtained results were compared to the MICOF predictions.
The HTO migration experiment in CP1, which was started in January 1988, still runs as planned. New experimental data have become available.

Progress and results

1. Lab experiments

The experimental results of one $H^{14}CO_3^-$ and three $H^{14}CO_3^-/^{131}I^-$ flow-through tests on reconsolidated clay plugs were analysed and the ηR and D values derived (Table I). The possibility of a chemical reaction between HCO_3^- and the Boom clay was also considered by including a first order reaction in the mathematical model. As in all four cases the first order rate constant was found to be zero, this chemical reaction seems to be negligible.

The ηR values for I^- and HCO_3^- are almost equal (mean value is 0.11) which strongly indicates that, as R = 1 for the non-sorbed I^-, HCO_3^- is not retarded by sorption or isotopic exchange. The observed ratio of about 2 between the D values of HCO_3^- and I^- is in agreement with the ratio of their diffusion constants in pure water /3/. If we discard the test 1 results because of the obvious deviation with the other results, we obtain for HCO_3^- a mean ηR value of 0.11 and a mean D value of $1.8\ 10^{-10}\ m^2.s^{-1}$.

For the four ^{75}Se migration experiments mentioned in the Annual Progress Report 1991, the ^{75}Se migration profiles in the clay plugs were measured. A first attempt to interpret the obtained diffusion profile of the Boom clay reduced Se(*) diffusion experiment failed as a pronounced difference between the Se diffusion behaviour in the labelled (i.e. disturbed) clay plug and in the unlabelled contacted clay plug was observed. This difference between the two D values amounts to 4 orders of magnitude, with the smallest D ($\pm\ 5.10^{-16}\ m^2.s^{-1}$) calculated for the labelled clay plug. A possible explanation may be given by a precipitation of Se, e.g. as metallic Se or $FeSe_2$, in the labelled clay plug. Further interpretation of the Se experiments will also include precipitation phenomena in the mathematical migration model.

Three new percolation experiments were started to study the migration behaviour of the Boom clay organic molecules. These experiments should confirm and refine the previously obtained results /4/. First new results are expected in the course of 1993.
Finally, 3 percolation experiments were set up to assess the effect of the ionic strength on the diffusion accessible porosity η for I^-. NaCl solutions of different ionic strength (1N, 0.1 N and 0.01 N) will be percolated through the clay cores until an equilibrium with the NaCl solutions is attained. The migration of $^{131}I^-$ and HTO in the equilibrated clay will be studied by a percolation experiment with impulse injection.

(*) Two experiments (one diffusion and one percolation) were conducted with a ^{75}Se label which had been equilibrated with a Boom clay suspension for 40 days while in the other two experiments (also one diffusion and one percolation) a metallic ^{75}Se label was used.

2. In situ experiments

The 3 multiple piezometers for the new 3D HTO migration experiment were successfully installed in January 1992 and the hydrostatic pressure build-up in the neighbourhood of the different filters is continuously monitored. When the hydrostatic and mechanical disturbances of the clay, caused by the installation of the piezometers, have dissipated, HTO will be injected in the central piezometer. This is planned in the second half of 1993. The configuration of the 3 piezometers will allow a measurement of the HTO migration in both horizontal and vertical direction.

Two new I^- migration experiments in the underground laboratory were started. A $^{125}I^-$ labelled solution was introduced in the filters nr. 8 of one horizontally and one vertically oriented multiple piezometer, both located at Test Drift ring 41. The predicted concentration histories in the adjacent and injection filters were earlierly reported /5/. Since the start-up of these experiments two sampling campaigns were performed in the adjacent filters and in the injection filter itself of both experiments. The measured $^{125}I^-$ concentrations and the predicted time functions of the $^{125}I^-$ concentrations in the different filters are given in Figure 1 and 2.
Comments on the results of these experiments will be postponed till more experimental results are available. Given the relatively short half-life time of ^{125}I (60.1 d), both migration tests will run for 2-3 years.

For the HTO migration experiment in the CP1 piezometer (started February 1988), the initially injected quantity Q_o (Bq) was recalibrated with the same method (liquid scintillation, external standard) as used for the HTO concentration measurements in the filters. In this way errors introduced by different measurement techniques can be avoided. The new value for Q_o is 1.25 GBq instead of 0.925 GBq as reported before. With this new Q_o value the best estimate parameter values were calculated and compared to the "base case" (i.e. a priori) values. The results are given in Table II. It should be emphasized that the "base case" values were derived a priori and from independent lab and in situ experiments. At the end of 1992 26 experimental measurements were available for a total migration period of almost 5 years.
The experimental data and the predictive MICOF calculations using the "base case" values are given in Figure 3.

List_of publications

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- Put M.J., De Cannière P., Moors H., Fonteyne A. and De Preter P. "Validation of performance assessment model by large scale in-situ migration experiments". Paper presented at the "International symposium on geologic disposal of spent fuel, high-level and alpha-bearing wastes", Antwerp, October 1992.

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/3/ Yuam-Hui L. and Gregory S., Geochimica and Cosmochimica Acta, 38, 703-714 (1974).

/4/ Put M.J., Monsecour M. and Fonteyne A., Radiochimica Acta, 58/59, 315-317 (1992).

/5/ Put M.J., De Cannière P., Moors H., Fonteyne A. and De Preter P. Paper presented at the "International symposium on geologic disposal of spent fuel, high-level and alpha-bearing wastes" Antwerp, October 1992.

Table I : $\eta R(-)$ and D $(m^2.s^{-1})$ values for HCO_3^- and I^- as obtained by flow-through diffusion tests on reconsolidated clay plugs

Test nr.	Species	P_{con} (MPa)	ηR (-)	D $(m^2.s^{-1})$	ηRD $(m^2.s^{-1})$
1	HCO_3^-	4.41	0.18	$7.5\ 10^{-11}$	$1.4\ 10^{-11}$
2	HCO_3^-	2.00	0.12	$1.5\ 10^{-10}$	$1.8\ 10^{-11}$
	I^-	2.00	0.10	$3.7\ 10^{-10}$	$3.7\ 10^{-11}$
3	HCO_3^-	2.00	0.10	$1.8\ 10^{-10}$	$1.8\ 10^{-11}$
	I^-	2.00	0.12	$3.5\ 10^{-10}$	$4.2\ 10^{-11}$
4	HCO_3^-	1.98	0.11	$2.2\ 10^{-10}$	$2.4\ 10^{-11}$
	I^-	1.98	0.11	$4.3\ 10^{-10}$	$4.7\ 10^{-11}$

Table II : Large scale in situ injection of HTO (CP1 experiment) : Comparison of the "base case" and "best estimate" parameter values for Q_o = 1.25 Bq HTO

Parameters (*)		"Base case"	"Best estimate"
D_x	$(m^2.s^{-1})$	4.1×10^{-10}	4.05×10^{-10}
V_x	$(m.s^{-1})$	1.7×10^{-10}	1.7×10^{-10}
D_z	$(m^2.s^{-1})$	2.0×10^{-10}	2.17×10^{-10}
ηR	(-)	0.35	0.34
D_x/D_z	(-)	2.05	1.88

(*) D_x = apparent diffusion coefficient in horizontal direction
D_z = apparent diffusion coefficient in vertical direction
V_x = apparent velocity
η = diffusion accessible porosity
R = retardation factor = 1

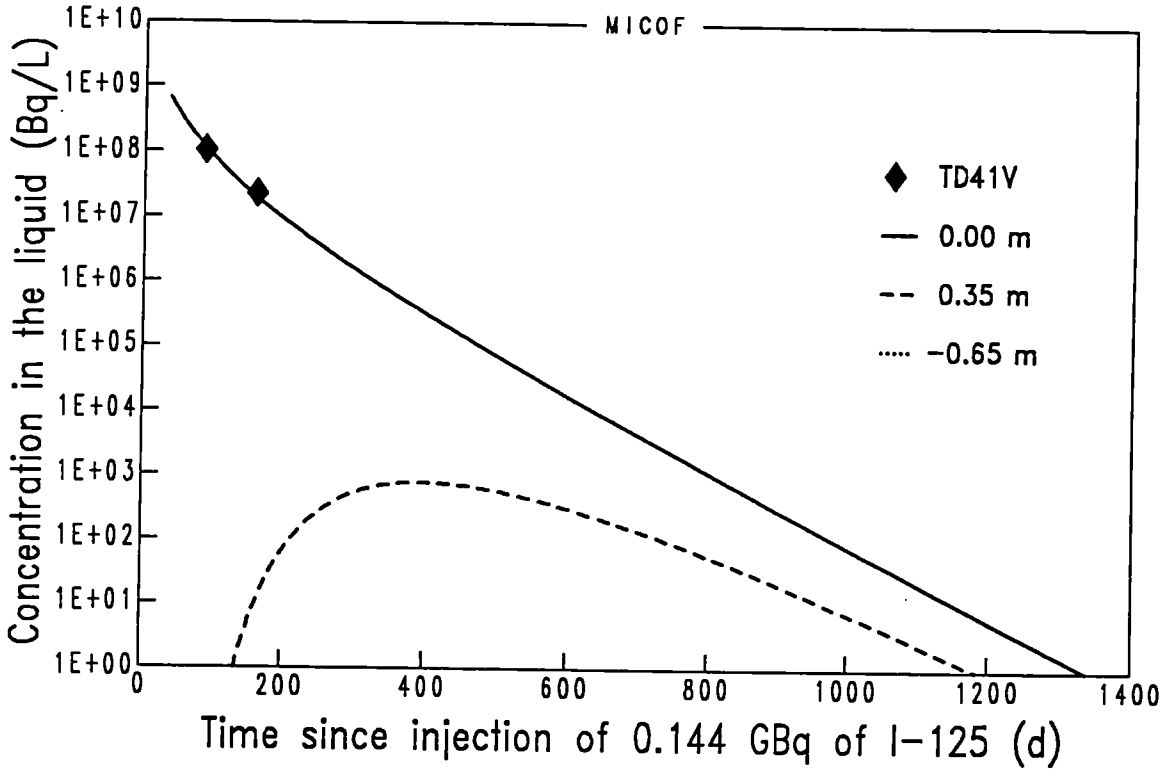

Figure 1 : Predictive model calculations of the ^{125}I concentration evolution in the liquid of the injection filter (0.00 m) and the neighbouring filter (0.35 m) for the vertical piezometernest. First experimental measurements are also shown.

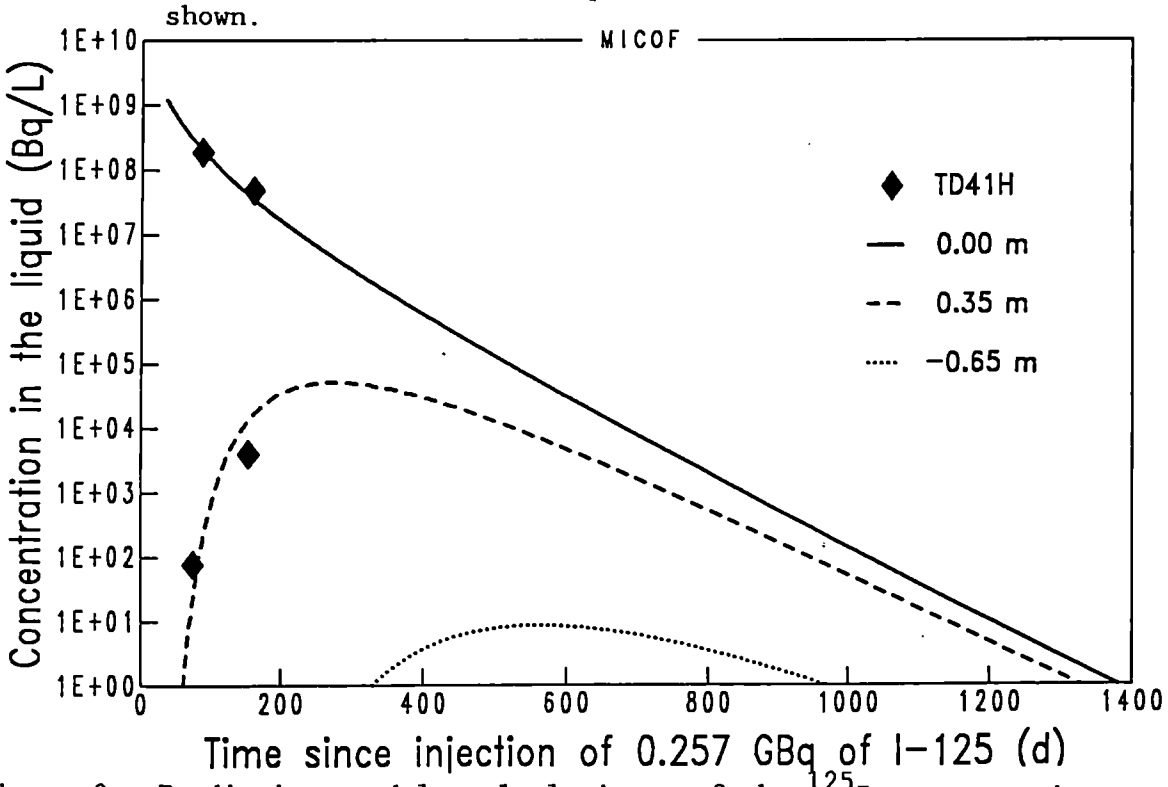

Figure 2 : Predictive model calculations of the ^{125}I concentrations evolution in the liquid of the injection filter (0.00 m) and the neighbouring filter (0.35 m) for the horizontal piezometer. First data points are also given.

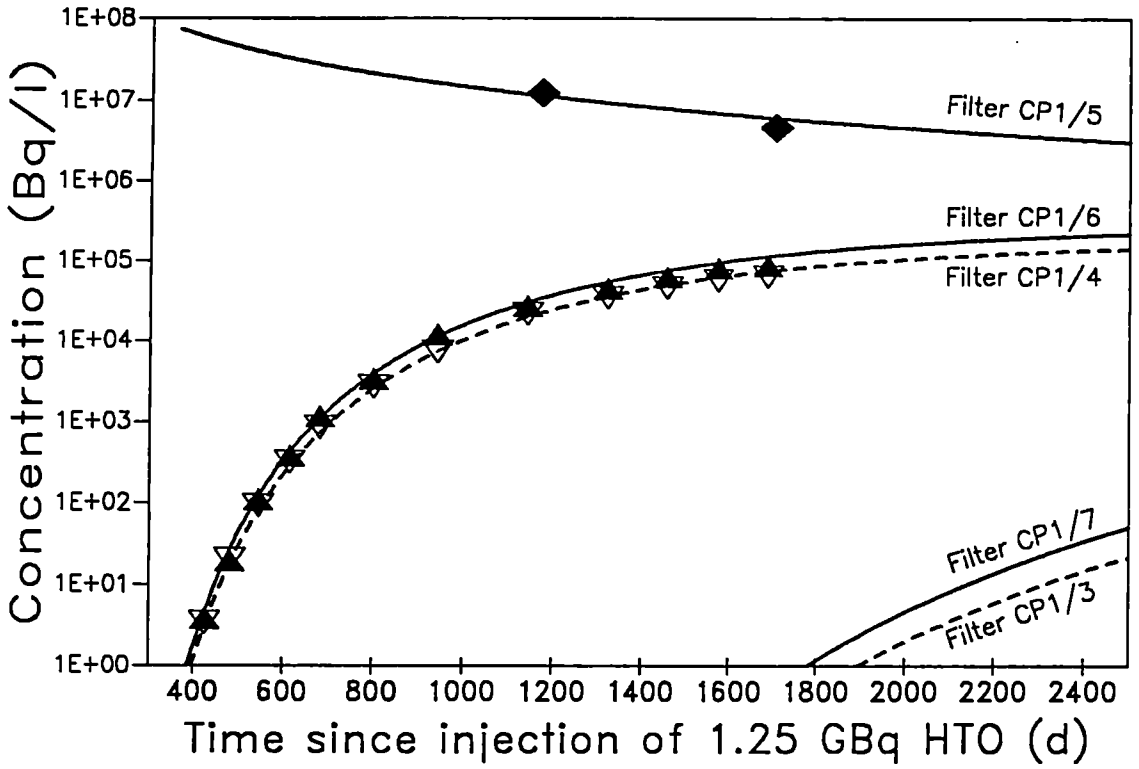

Figure 3 : Predictive model calculations (lines) and measured HTO concentrations (markers) in the liquid for the large scale in-situ injection experiment with tritiated water. Results for injection filter (nr. 5) and filters at distance of 1 m (nr. 4 and 6) and 2 m (nr. 3 and 7) from the injection filter.

CHEMVAL2: A COORDINATED RESEARCH INITIATIVE FOR EVALUATING AND ENHANCING CHEMICAL MODELS USED IN RADIOLOGICAL RISK ASSESSMENT

Contractor/Coordinator: WS Atkins Engineering Sciences, Epsom, UK

Contract Nos: FI2W/0065;

Duration of Contract: May 1991 - December 1994; September 1992 - December 1994

Period Covered: January 1992 - December 1992

Project Leader: D Read

A. OBJECTIVES AND SCOPE

The international CHEMVAL Project, initiated in 1987, has been assessing the validity of computer-based models used to describe the geochemistry of radioactive waste disposal systems. The original project /1/2/3/ was concerned, primarily, with the verification of equilibrium models though a number of attempts were made at a priori predictive validation. CHEMVAL2 aims to build on this earlier study by targeting specific areas shown to be of particular concern in radiological assessment. Eighteen organisations in nine countries currently participate in CHEMVAL and, of these, seven have direct responsibility for technical coordination, as outlined below:

a) Temperature Effects: BRGM/ANDRA, France (R Fabriol, G Ouzounian)
b) Ionic Strength Effects: GSF-IfH, Germany (H Lang)
c) Organic Complexation: LUT/Atkins ES, UK (P Warwick, D Read)
d) Sorption Processes: AEA Harwell/BGS, UK (C Tweed, M Crawford)
e) Co-precipitation: MBT/ENRESA, Spain (J Bruno)
f) Coupled Modelling: EMP/CEA, France (Ph Jamet, D Stammose)

B. WORK PROGRAMME

1. Definition and initiation of programme, production of status reviews.
2. Execution of research programmes for each technical area encompassing data review, model development, code verification and model validation.
3. Comparison with experimental studies and reporting.

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of Advancement

During the early part of 1992, the coordinating groups for each of the main technical areas undertook status reviews of current modelling capabilities and data availability of relevance to their particular research programmes. From these, a schedule of tasks was defined following discussions amongst participants. For each area a preferred modelling approach was adopted and, where suitable data were available, the broad outline of verification and or validation test cases defined. These status reviews and work programmes have been combined and submitted for publication as an EUR series report.

In addition the need for continued development and maintenance of a standardized thermodynamic database, both within this project, and for studies of radioactive waste management in general, has been recognised and is being undertaken in parallel with the CHEMVAL2 programme under the related CEC Contract FI2W/CT92/0122.

Progress and Results

The structure of the CHEMVAL2 Project is shown in Figure 1. Atkins ES together with the two main funding organisations, CEC and HMIP, provide a secretariat acting as a contact point for the technical coordinators. The role of Atkins ES encompasses organisation of meetings, preparation of reports and dissemination of data in addition to modelling and review activities. Progress within each research area is summarised below.

a) Temperature Effects

BRGM, under contract to ANDRA, are responsible for a programme of work aimed at assessing the effects of elevated temperatures on the speciation and solubility of radioelements in groundwaters /4/. In order to make this assessment, improvements to a number of computer programs used previously in CHEMVAL will be required. Implementation of code changes is the responsibility of individual participants but formal verification of the enhanced programs will be addressed within CHEMVAL.

The thermodynamic database will also need to be extended to account for changes in formation constants (log β) and solubility products (K_{sp}) as temperature rises in the range of 5-200°C. On the basis of available data, BRGM/ANDRA have recommended use of the Van't Hoff equation for all temperature corrections in view of its simplicity and the potential to compile a comprehensive, consistent data set. Data collation is largely complete and a series of verification tests have been distributed amongst the participants.

b) Ionic Strength Effects

The existing CHEMVAL Database accounts for activity coefficient (γ) corrections using a modified form of the Davies Equation. This was deemed essential during the previous CHEMVAL contract owing to the limited timescale available and the need to adopt a consistent method throughout. Extension of CHEMVAL modelling activities to more saline waters is the responsibility of GSF-IfH who have carried out a brief review of available methods /5/. The latter range from the idealised Debye-Hückel theory for very dilute solutions to the heavily-fitted Pitzer virial expansion algorithms which have been applied to fused salts. Within CHEMVAL2, emphasis is being placed on salt concentrations up to 1 moldm^{-3},

encompassing seawater and most natural groundwaters. Direct comparison of several alternative γ correction methods on a limited number of well defined experimental data sets has been carried out and preliminary interpretation suggests that the Specific Ion Interaction Theory (SIT) is most suitable for adoption within the CHEMVAL2 programme.

c) Organic Complexation

The problems associated with quantifying complexation of trace elements by high molecular weight organic matter were highlighted during the original CHEMVAL Project. The theoretical basis for most extant models is weak and few if any have a real predictive capability. Essentially, therefore, CHEMVAL2 is aiming to develop a practical modelling approach which can be independently tested and, further, be used in conjunction with conventional inorganic speciation models. The work is being coordinated jointly by LUT and Atkins ES. Following a detailed review of the literature /6/, three approaches have been advanced as meriting more detailed consideration; the simple ligand-binding model of Sposito and Mattigod, as incorporated in the GEOCHEM code, the continuous distribution (statistical) approach of Perdue and Lytle and the electrostatic site-binding models of Tipping and Falck. Both of the electrostatic models have been incorporated within the PHREEQE code. In association with this model development work, an experimental programme is underway at LUT to provide data for model testing.

d) Sorption Processes

The objectives of work on sorption processes within CHEMVAL2 are to compare the various models which have been incorporated into geochemical speciation codes and to assess their usefulness for simulating observed behaviour in the laboratory and the field. A review of sorption models of varying complexity has been undertaken /7/, with emphasis on data availability and the applicability of each approach to predictive modelling studies. The current status of eight computer programs has also been addressed though it is unlikely that all will feature in verification/validation exercises.

A three stage work programme is underway comprising:

- code verification using standardized data
- predictive modelling of uptake onto pure (monomineralic) phases
- modelling uptake onto natural substrates.

Verification and validation tests have been distributed to the participating groups and the results collated by the coordinators. These will be presented at the forthcoming plenary meeting early in 1993.

e) Co-precipitation

Solubility limits based on equilibrium precipitation-dissolution are often used to establish source term concentrations for radiological assessment and also to estimate maximum concentrations of transported radioelements in geological media. Calculations based on pure solid phases may be grossly in error, however, as trace elements in nature tend to occur as substituted "impurities" in mineral phases. The aim of work within CHEMVAL2, coordinated by MBT/ENRESA, is to develop viable models of trace element co-precipitation on ubiquitous minerals such as calcite and amorphous iron oxides /8/. Progress to date has included a systematic literature review of available data on coprecipitation, experimental work at the Polytechnical University of Catalonia into the co-precipitation of uranium on iron oxides, and preliminary calculations for model testing. More detailed model validation exercises are to be distributed amongst the participants in February 1993.

f) Coupled Chemical Transport Processes

A limited verification of six coupled codes was completed successfully during the first CHEMVAL Project /3/. However, no predictive validation studies were feasible within available timescales and comparisons with experiment were restricted to back-fitting published column data. A more exhaustive verification has been proposed for CHEMVAL2 whereby eight codes will be evaluated against analytical solutions and/or experimental data /9/. Problems encountered previously with poorly specified experimental data have been addressed by commissioning column studies designed specifically for testing coupled models. Two separate column investigations are already underway dealing with, respectively; uranium migration through intact sandstone cores (at AEA Winfrith) and Cs, Sr transport through packed sediments (at CEA-Grenoble). A review of the available computer codes has highlighted development priorities and five verification tests have been defined and circulated amongst the participants. Results from these are currently being collated for presentation at the forthcoming plenary meeting. A number of possible validation cases have also been identified and their distribution will follow early in 1993.

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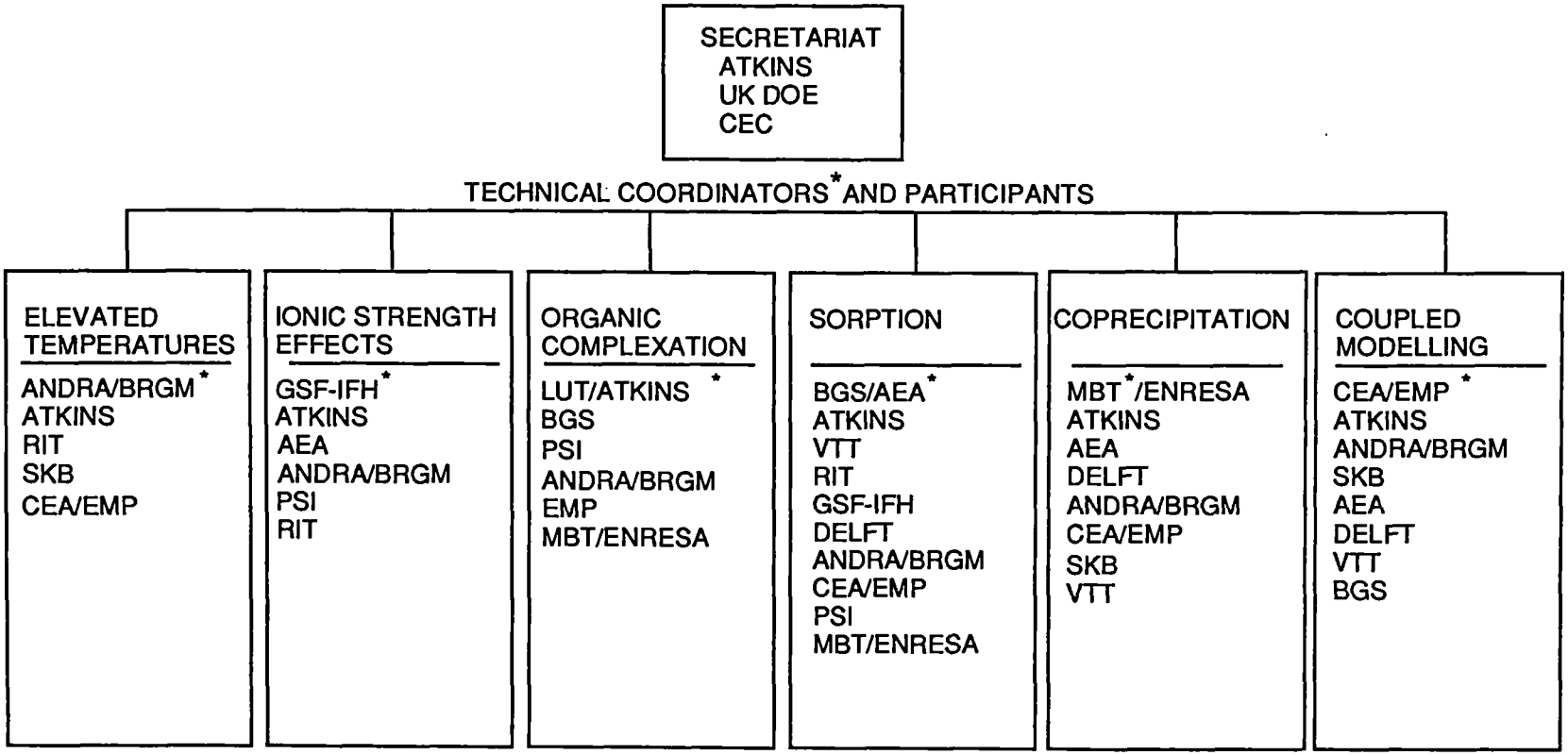
SECRETARIAT
ATKINS
UK DOE
CEC
TECHNICAL COORDINATORS* AND PARTICIPANTS
ELEVATED TEMPERATURES
ANDRA/BRGM*
ATKINS
RIT
SKB
CEA/EMP
IONIC STRENGTH EFFECTS
GSF-IFH*
ATKINS
AEA
ANDRA/BRGM
PSI
RIT
ORGANIC COMPLEXATION
LUT/ATKINS*
BGS
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ANDRA/BRGM
EMP
MBT/ENRESA
SORPTION
BGS/AEA*
ATKINS
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COUPLED MODELLING
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SKB
AEA
DELFT
VTT
BGS

Title : Oklo, natural analogue for transfer processes in a geological repository.

Contractor : C.E.A./ I.P.S.N.

Contract : N° FI 2 W CT 0071

Duration of contract : 4 years (January 1st, 1991 to December 31st, 1994)

Period : 1992 (2nd year of contract)

Project leader : Mrs Chapuis

A.- OBJECTIVE AND SCOPE

The Uranium ore body in Oklo is a unique subject in the world, as natural fission reactions occurred there two billion years ago. It provides opportunities for the study of natural analogy with deep radioactive waste disposal, specially radionuclide mass transfer processes to the surface. However the peculiarities of this uranium ore deposit imply a thorough assessment of the radionuclides and daughters as well as ancient and recent geochemistry and hydrodynamics.

B.- WORK PROGRAM

This program involves several different tasks :

1°- *In situ* sampling, in close collaboration with the mining company (C.O.M.U.F., COMPAGNIE DES MINES D' URANIUM DE FRANCEVILLE, Mounana, Gabon). To this part of the program can be added the collecting of new data on the general setting of the Oklo mining area and deposits.

2°- Study and characterization of the source term (mostly in CEA laboratories).

3°- Studies on the geochemical systems ruling the migrations can in turn be divided into studies on the ancient migrations, contemporaneous to the rock diagenesis, to the nuclear reactions and to the general geological history of the basin, and on the recent to present migrations (tertiary to present?).

3.A.- The studies of the ancient migrations will encompass several subjects, and imply collaboration between CEA laboratories and other institutions :

3.A.a.- CEA laboratories (DCC/DSD/SECTION DE GEOCHIMIE) cooperate with all other institutions in the program to assess the petrography and elemental chemistry of the deposits.

3.A.b.- The retention properties of the clays towards radionuclides is the main topic of the investigations of the CENTRE DE GEOCHIMIE DE LA SURFACE (CNRS, Strasbourg).

3.A.c.- The contribution of CREGU (CENTRE DE RECHERCHES SUR LA GEOLOGIE DES MATIERES PREMIERES MINERALES ET ENERGETIQUES, formerly "DE L'URANIUM", Nancy) will be to investigate the thermal history of the deposits in and around the reactor zones.

3.A.d.- Reconstructing the chemical characteristics of the hydrothermal fluids which left their chemical imprint in tracer mineral when they were circulated through the deposits has been undertaken by the CENTRE DE GEOLOGIE GENERALE ET MINIERE of the ECOLE NATIONALE SUPERIEURE DES MINES DE PARIS (ENSMP, Fontainebleau).

3.B.- The study of the recent migrations also imply collaboration between CEA laboratories and other institutions :

3.B.a.- The CENTRE D'INFORMATIQUE GEOLOGIQUE (ENSMP, Fontainebleau) is responsible for the understanding of the hydrogeological.conditions.

3.B.b.- The SECTION DE GEOCHIMIE of CEA/DCC/DSD is in charge of the hydrochemistry.

(Conterra A.B. on behalf of SKB from Sweden collaborates to part 3.B., particularly on the Bangombé area.)

4°- Modelling : Part of the modelling will take place in each laboratory involved, but the final integrated hydrodynamical-geochemical models will be the responsibility of ENSMP and CEA/IPSN.

C.- *PROGRESS OF WORK AND RESULTS OBTAINED*

State of advancement

At mid term of this contract, we can summarize the advancement of work as follows :

*Task 1, **field sampling**, can be considered as terminated, and the last solid rock samples are on their way to France and will be distributed to the laboratories as soon as possible.*

*Task 2, **source term** studies : the analytical phase can be considered as finished for R.Z. 10 and 13. The next step for these R.Z. is to obtain a general balance of fissiogenic materials. As new samples from the BA 145 and OK 84bis R.Z. were only obtained in 1992, the analytical work will be limited to the level needed as a source term to the hydrochemistry program.*

*Task 3.A, **Ancient migrations** : a wealth of data has already been obtained on the general petrography and geochemistry, on the reactor-clay and on the reconstruction of the fluids. The interpretation of the results on fluid inclusions only needs editing, and the fission tracks results have not been obtained yet.*

*Task 3.B, **Recent migrations**, is very much linked to task 4, **integrated modelling**. It does not appear as advanced as the other tasks, but this is mainly due to the fact that it benefited from previous scientific programs in Oklo to a much lesser extent that tasks 2 and 3 .However as the heavy part (drilling campain) has been done, we can expect to make up for this apparent delay.*

Progress and results

1°- FIELD SURVEY, SAMPLING, AND GEOLOGICAL SETTING

The Oklo uranium ore body lies on the south-western margin of the precambrian sedimentary basin of Franceville.

The age of the basement (the Chaillu granite) was already known from Ru/Sr and K/Ar dating : it is close to 2.696-2.680 Ga.

The uranium deposits are sedimentary, in a sandstone layer 3 to 6 meters thick, at the top of the conglomerate and sanstone basal formation (FA) of the Francevillian series (Palaeoproterozoic). They are overlain by the mudstones, shales, dolomites and organic-rich shales ("ampélites") of the FB formation : the early diagenesis of the clays in these levels has been dated at 2.065 Ga by the Sm/Nd radiochronometer.

The uranium originates from erosion of the Chaillu basement to the south-west, and maybe from the leaching of overlying volcanic ashes inter bedded in the FB levels. The uranium precipitated in hydraulic fracturation corridors, at a reduction front determined by the presence of mature organic matter, probably at the same time as the early diagenesis of the clay minerals took place..

There is at present no specific mining of the remaining reactors, as there is no market for depleted uranium. The present accessibility of the reactors is thus as follows :

- Reactor 10, is situated in the center of the bearing, 70 to 80 m north of the dolerite dyke, downhill from the quarry, between the 120 and 150 m elevations (slices D65 to D81). It has been estimated to about 300 tonnes of depleted uranium, of which 40 % have already been taken. In february 1992, a new circulation drift has been mined into the lower levels of this reactor (D81). The trace of borehole SF 29 and the lower closure of the reactor have been directly observed and extensively sampled. Unfortunately, owing to the structural conditions, it has been necessary to wall out the drift soon afterwards.

- Reactor 13 was also situated downhill from the quarry, but about 35 m to the south of the dolerite dyke, at an elevation of 230 to 218 m. Very little of this reactor, if any at all, may remain at level SD38.

- Reactor 16 was discovered in may 1991, in slice D75N, *i.e.* at mid-level of reactor n°10, but about 150 m to the north. No indication of the presence of a reactor was known there. As drift D75N is intended for ventilation, an easy access to the reactor will remain for some time.

- The "OK 84" reactor lies 500 m to the south-east of the quarry, at an elevation of about 60 m. Several drifts come close to it, but none did actually cut through it up to now. The hydrology drilling campain has provided a new opportunity for sampling anew this zone last fall.

- The "Bangombé" (rather than "Bagombé") reactor is located a few kilometers to the south-east of the town of Moanda, itself 20 kilometers south of Mounana and the Oklo deposit. This reactor is very shallow, as the "reactor facies" was met less than 12 meters from surface. The hydrology campain there also provided us with new cores through this zone.

2°- THE SOURCE-TERM

The main points which allow the characterization of reactor zones 10 and 13 during the geochemical history of the bearings from the time of the reactions to the present are :

- the age of the nuclear reactions in R.Z 10, which has been measured accurately with the U/Pb chronometer to 1970 Mega-annum (Ma), thanks to the discovery of cubic uraninite crystals, contemporaneous to the fission reactions. This age fits perfectly to the one derived from the fission products ; it makes it possible to recalculate an uranium-235 enrichment ratio at the time of divergency of 3.68 %, *i.e.* five times the present value.

- The uranium grains in the so-called "sanstone reactor" in R.Z. 10 have remarkably preserved their fission products and their original isotopic composition. The same applies to the uraninite grains in R.Z. 13, despite an almost complete loss of their radiogenic lead 750 Ma ago. In these samples we find an excellent *in situ* correlation between the uranium depletion and the neodymium, samarium, zirconium and thorium amount, four fissiogenic elements on which bore our choice.

- Metallic aggregates containing fission platinoïd elements (gold, rhodium and palladium) to which lead, bismuth, antimony, tellurium, arsenic and sulfur are associated, have been observed in the silica and in the joints of some uranium oxide grains.

3.A.- THE GEOCHEMICAL SYSTEMS : ANCIENT MIGRATIONS

3.A.a.- PETROGRAPHY AND ELEMENTAL CHEMISTRY

The rock facies observed in and around the deep reactor zones are similar to those known from the previously studied reactor zones. However they exhibit some peculiar features, such as a high mechanical coherency, related to the absence of supergene weathering.

The sandstones surrounding the reactors are made up of detrital mineral grains (quartz, biotite little feldspar and accessory minerals, mainly zircon, uranium oxides, sphene and organic matter). These sandstones were deposited as layers (or lenses) with thickness ranging from a few centimeters to the meter, and the grains ranges from fine sand to conglomerate. The clay fraction is made of ferrous chlorite and illite, and calcite is present as fissure infillings.

The "reactor-clay" facies generally surrounds the reactor proper. In this facies, magnesian chlorite is interspersed with corroded quartz grains and less-soluble primary minerals (zircon, sphene, uranium oxydes). Some secondary minerals develop at the expense of primary accessory minerals : coffinite, cryptocristalline zircon, sphene and variable amount of apatite.

In the "reactor-core" facies, the main mineral phases are uranium oxide and white micas.

All these facies can be run through by fissures, with a width ranging from micrometers to a few millimeters. They are generally filled with fibrous calcite.

Silica accounts for 95 % of the total rock in the sandstones, and decreases drastically towards the reactor-core facies. This is interpreted as the result of silica dissolution by the intense hydrothermal ciculation triggered by the heat from the nuclear reactions. The other major elements, Al_2O_3, Fe_2O_3, MgO, Na_2O, K_2O, MnO, and TiO_2, clearly increase from the sanstone to the reactor. These elements are clearly linked to the phyllitic component of the different facies, either primary or secondary. A good correlation between CaO and CO_2 shows that they are linked together as carbonate.

The trace elements can have two origins : some come from the initial sandstones (accessory phase and clay fraction) : apart from uranium, the sandstone contain Ba, Sc, Ga, Sr, V, Zn, and Zr. The second possible origin is the formation of trace elements in the course of the nuclear reactions and radioactive decay. This is the case not only for Zr, Nb, Ba, Nd, Sm, Eu and Gd, but also for Pb, Ru, Ag, Cd and Te. All trace elements have much higher concentrations in the reactors than in the surroundings.

3.A.b.- RETENTION BY CLAYS

It has been attempted to reproduce the isotopic analysis of the sample enriched in uranium-235, and to search for other similar samples.

The analysis of this enriched sample has been shown to be reproducible, but it has not been possible up to now to find any other with a similar enrichment. A very low amount of total uranium seems to be the determinant factor to make it possible to detect such an enrichment.

Oxygen isotopic analyses have been performed on the reactor clay and on Uraninite from the core of reactor zones 10 and 13. The interpretation of these data in term of thermal history of the clays, and of the physical and chemical conditions necessary to fission products retention is now under way.

Careful x-ray diffractometry analyses performed on four chlorites from reactor zone 10 have made it possible to characterize the presence of Sudoïte, an aluminous and magnesian di-trioctahedral chlorite known from rocks submitted to a hydrothermal regime. Sudoïte is the only clay mineral in the enriched-uranium sample, thus demonstrating an hydrothermal phase at the reactor edge.

3.A.c.- THERMAL HISTORY OF THE REACTOR ZONES

A microthermal study has been conducted on sandstone and quartz samples by observing the phase changes with temperature in the fluid inclusions, in a temperature range of -180°C to 600°C. The samples were taken from R.Z. 10 and from Okélobondo, and come from sandstones, from quartz veins and from the contact between sandstone and reactor-clay.

The fluids so investigated are distributed into three types :

- The diagenetic fluids yelded melting temperatures of -2 to -6° C, (3 to 8 % NaCl wt equ.), and temperature of homogeneization of 160 to 200° C.

- The fluids associated to circulation around the reactors (fissures infillings) gave melting temperatures of -10 to -15° C (14 to 24 % NaCl wt equ.) and homogeneization temperatures of 110 to 150 °C in calcite or 190 to 270 °C in apatite grains.

- Nearest to reactor 10, in the nourishment zone of quartz grains within contact of the reactor-clay, melting temperatures of -6 to -10 °C (9 to 14 % NaCl wt equ.) and homogeneization temperatures from 280 °C up to 480 °C have been observed.

These temperature are low estimates which will need correction according to the local pressures assumed at the time of trapping of the inclusions.

3.A.d.- RECONSTRUCTION OF ANCIENT FLUIDS

During hydrothermal circulation, mineral precipitation occurs either at the walls of open cracks, as vein lining, or as isolated crystals within percolated rocks. Authigenic minerals act as traps for trace elements in solution, thus supplying efficient concentration mechanims for elements specific to the mineral species considered. Apatite [$Ca_5(PO_4)_3F$], and sulphides [galena (PbS) and pyrite (FeS_2)] are efficient geochemical traps for REE, and for Ag, As, Sb and Mo, respectively.

Several fluids or fluid stages have been identified, and mixing processes between some of these have been argumented, on the basis of heterogeneous mineral populations in some samples. By contrast, some samples, though close from each other, have shown quite different mineral populations, and have thus been in contact with quite different fluids, without any evidence for interaction : this suggest a rather large time-span between the circulation of these fluids.

At least one stage is very late in the history of the deposit, and is related to the dolerite intrusion around 750 Ma ago. One fluid at least could be directly related to the nuclear reactions 1.97 Ga ago : this fluid seems to have had a very low content in most elements, except in fission products, as shown by the light rare earth elements (L.R.E.E.) content of the associated apatites. Another fluid apparently contributed to the dilution of the fluids escaping from the reactor zones. A fourth type is related to the reworking of the sedimentary metal stock present in the FA sandstone formation, and shows no relation to the reactor zone.

3.B.- THE PRESENT MASS-TRANSFERS

3.B.a.- HYDROGEOLOGY

The drilling programme, aiming at the hydrogeological fitting of the sites, set down in 1991 and during the first half of 1992, has been conducted during two field missions from september to december 1992.

3.B.b.- HYDROGEOCHEMISTRY

At the same time, the existence of a natural tracer of the reaction zones in the present groundwaters has been investigated. Depleted uranium was considered the best, as uranium is soluble in oxidizing environment and as the $^{235}U/^{238}U$ ratio is the clearest and most conservative tracer of nuclear reactions. Among six preliminary groundwaters samples, two have shown significant deviation from natural uranium isotopic composition : $^{235}U/^{238}U = 0.006872 \pm 0.000010$ for a sample taken from a short drill-hole in the mineralized level in Okélobondo, not close to any known reactor zone, and $^{235}U/^{238}U = 0.007095 \pm 0.000010$ for a sample taken from borehole Ba 145, thanks to which a reactor zone was indeed discovered there.

The samples needed for the hydrochemical and isotopical analyses of the waters, and the *in situ* test and measurements, both necessary to the validation of the hydrogeological diagramatic model proposed and to the development of the hydrodynamical model, will take place late February and March 1993.

List of publications

BLANC, P.-L., 1992 : Oklo as a natural analogue for radionuclide transfer processes in a waste geological repository : present status of the program. 5TH CEC NATURAL ANALOGUE WORKING GROUP MEETING AND ALLIGATOR RIVER ANALOGUE PROJECT FINAL WORKSHOP. 5-9th October, Toledo, Spain (to be published in the EUR-SERIES).

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BROS R., L. Turpin, F. Gauthier-Lafaye, Ph. Holliger & P. Stille, 1992 : Occurrence of naturally enriched 235-uranium : Implications for Pu behaviour in natural environments. (submitted to GEOCHEMICA ET COSMOCHEMICA ACTA).

CHAPUIS, A.-M. & P.-L. BLANC, 1992 : Oklo, natural analogue for transfer processes in a geological repository : present status of the program. MIGRATION OF RADIONUCLIDES IN THE GEOSPHERE (MIRAGE PROJECT-3RD PHASE). Proc. of prog. meet., 127-132 (to be published in the EUR-SERIES).

HEMOND C, C. Menet & M.-T.Ménager, 1992 : U and Nd isotopes from the new reactor 10 : Evidence for radioelements migration. MAT. RES. SOC. SYMP. PROC. Vol. 257, 489-496.

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DEVELOPMENT OF A MODEL FOR RADIONUCLIDE TRANSPORT BY COLLOIDS IN GEOSPHERE.

Contractors	ARMINES / INTAKTA / RIVM / CNRS-LSGC / ENRESA
Contract n°	FI2W - CT91 - 0079
Duration of the contract	from 01/10/91 to 30/09/95
Period covered	01/10/92 - 31/12/92
Project leader	E. LEDOUX

A. OBJECTIVES AND SCOPE

The objective is the development of mathematical models for radionuclide migration from underground repositories for radioactive waste to the accessible environment by colloids in groundwater. The model development is to be supported by migration experiments in laboratory, its validity will be evaluated against field data.

The model must be able to interprete laboratory and field experiments, and also to be included in geosphere transport code for safety assessment. For this reason a series of codes, from detailed to simplified, must be developed and validated successively, at different scales.

B. WORK PROGRAMME

1 Literature survey.

2 Formulation of a first conceptual model. Screening of phenomena to be included in the model by performing simple calculations of test cases.

3 Planning of laboratory migration experiments with a simplified fixed solid phase. Research of optimal experimental conditions with the help of task2.

4 Laboratory migration experiments focusing on the study of mechanisms for advection-dispersion of particles, on the interaction between particles and fixed solid phase, and agglomeration and sedimentation of particles.

5 Formulation of a second conceptual model, computer programming, numerical verification of the computer code and tests against the laboratory experiments (task 4 and 6).

6 Planning and performing laboratory experiments using field material as fixed solid phase. Verification of the relevance of the second conceptual model. Compilation of a field data base for model verification.

7 Development of a model for simulating field experiments. Application of this computer code to field experiments and to the compiled data base.

8 Development of a colloid migration model for performance assessment. Application of the code to some relevant performance assessment scenarios.

9 Project management.

C. PROGRESS OF WORK AND OBTAINED RESULTS

STATE OF ADVANCEMENT

The scientific work carried out during year 1992 concerns mainly the model development and the laboratory experiments (tasks 2, 3 and 4) :

- Partner 01 (ARMINES [F]) has proposed first microscopic model concepts including three different levels : hydrogeological flow model, solid surface-particle interaction model, surface complexation and chemical equilibrium model. Programming of these models has started.

- Partners 02 and 03 (resp. INTAKTA [F], RIVM [NL]) have proposed macroscopic model concepts, which have been tested against some data available in the literature.

- Partner 04 (LSGC/CNRS, [F]) has started with laboratory experiments, developing a first model to design experiments and performing both column experiments with hydrodynamic chromatographic apparatus and batch experiments.

- Partner 05 (ENRESA - CIEMAT, [SP]) provided information about El Berrocal samples.

1. Macroscopic approaches

1.1 INTAKTA

Within this stage of the study, it has been found that the code **TRUMP,** developed by the Lawrence Berkeley Laboratory and Department of Mineral Sciences and Mineral Engineering within the University of California [*Narashiman et al.* 1986] is a possible choice to implement a special module to represent the colloid migration within fractured or porous medium. The case of a porous medium has first been investigated.

This code is very flexible and allows to perform calculations for a large variety of porous and fractured media. Furthermore, it involves several characteristics which are of interest for this study : consideration of solubility limits, simultaneous migration of several chemical constituents, possibility of a constant or variable flow field which can be easily calculated for both saturated or unsaturated conditions with the help of the numerical code TRUST using the same discretization principles [*Neretnieks and Rasmuson*, 1984] as TRUMP. The code has been tested against some available column experiments involving the injection of either tracers or low given concentration of clay particle suspension within a column filled with glass beads, with a constant water rate, in saturated conditions [*de Cayeux*, 1988 ; *de Cayeux et al.*, 1990]. Pulses and steps injections had been numerically tested with **TRUMP.** The results are both concentration profiles within the column, and breakthrough curves. They provide information in three main areas :

- quantity of tracers or suspension which has exited the column,
- mean residence time within the column, corresponding to the porous volume experienced by the fluid,
- hydrodynamic dispersion, corresponding to the geometry of the porous space.

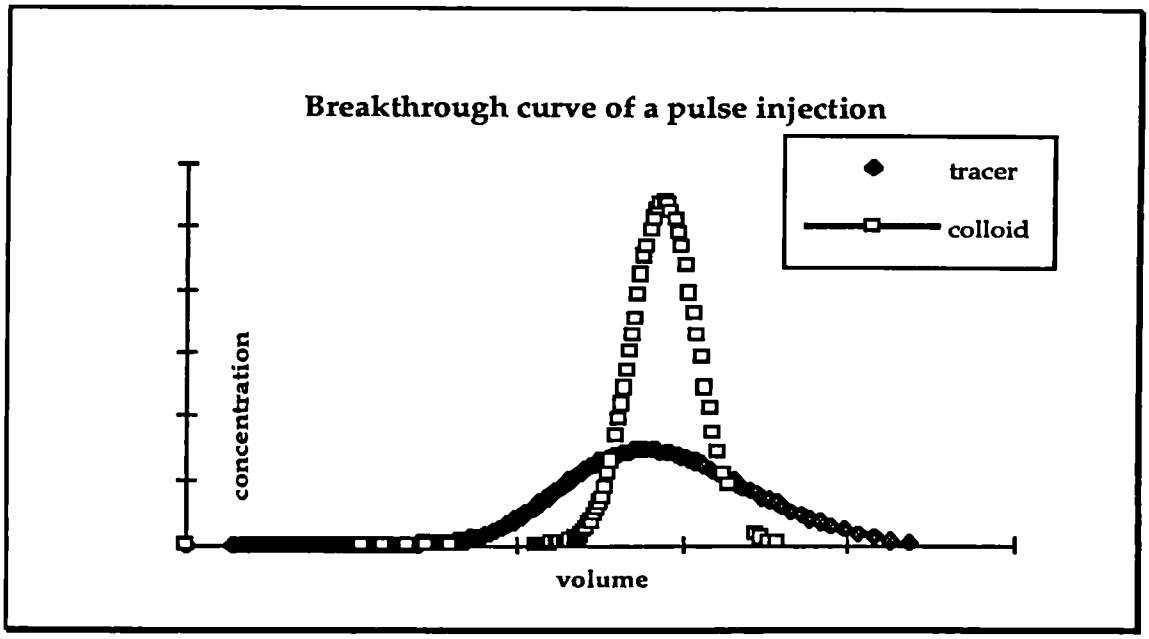

Figure 1 *Calculated breakthrough curves for a pulse of water (tracer) and for a pulse of retarded suspension (colloid).*

Figure 1 gives an example of the calculated breakthrough curves : a pulse injection of a tracer and a suspension of colloid has been modelled. *Figure* 1 shows the differences between both the mean residence time which is less important for the suspension than for the tracer and the quantity which has exited the column, which is equal to the quantity entered for the tracer and less than the inlet quantity for the colloid suspension. These two calculated curves can be respectively compared to experimental curves. An example of available experimental curves is represented in *figure* 2.

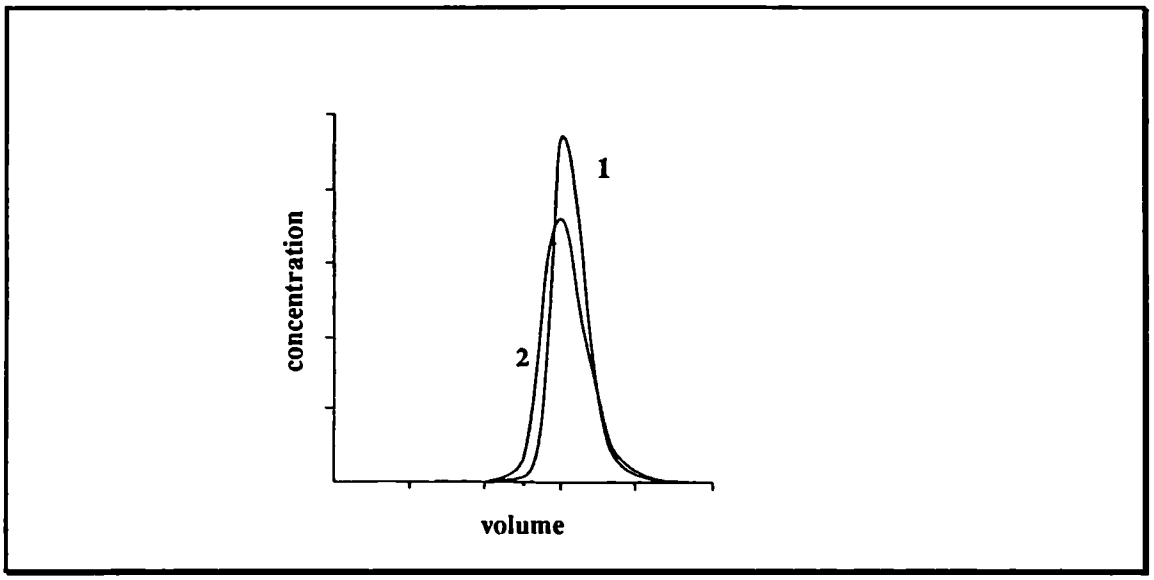

Figure 2 *Response of the porous bed before filtration. 1 : breakthrough curve of a tracer pulse . 2 : breakthrough curve of colloidal suspension . From de Cayeux et al., 1990.*

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CAYEUX M.D. DE, GAUTHIER C., LEVY Y.E., TRAN N.L., DELYON F., Assessing some aspects of deep bed filtration of clay suspensions via transport properties, Powder Tech., 62, pp 183-188, 1990.

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NERETNIEKS I. AND RASMUSON A. : An approach to modelling radionuclide migration in a medium with strongly varying velocity and block sizes along the flow path. Water Resources Research, vol. 20, n°12, pp 1823-1836, dec. 1984.

1.2 RIVM

A simple one-dimensional model has been developed, describing the transport of a radionuclide through a "saturated porous medium - groundwater - colloid" system with stationary groundwater flow. The colloid concentration can be varied in time and space and also the mass per colloid can be specified. Both non-linear and linear sorption of radionuclides can be included. The following model assumptions are made:

- one type of colloid / one type of radionuclide.
- no speciation of the contaminant (sorption excluded).
- dispersion/diffusion coefficients are different for colloids and radionuclides,
- radionuclides do not distinguish between mobile and immobile colloids; their sorption is described by the same sorption isotherm.
- attachment and detachment of colloids to/from the solid phase can be described by a first order reversible equation.

Calculations were carried out using data from a column experiment with bacteria [*Hornberger et al.*, 1992] : input colloid concentration, flow velocity, density of the solid phase, porosity and ratio between the specific surface area of colloids and solid phase. The model results described the experimental data reasonably well. The best fit for the association and dissociation constant and the diffusion/dispersion coefficient for the colloids were derived from model calculations. Further, sensitivity analyses for different parameters were performed. It can be concluded from *figure* 3 that flow velocity is very important in cases where colloid association/dissociation can be described by a kinetic equation. Sorption of radionuclide to colloids and to the solid phase is described by a Langmuir isotherm with different combinations of the Langmuir constants and capacity constants for colloids and radionuclides.

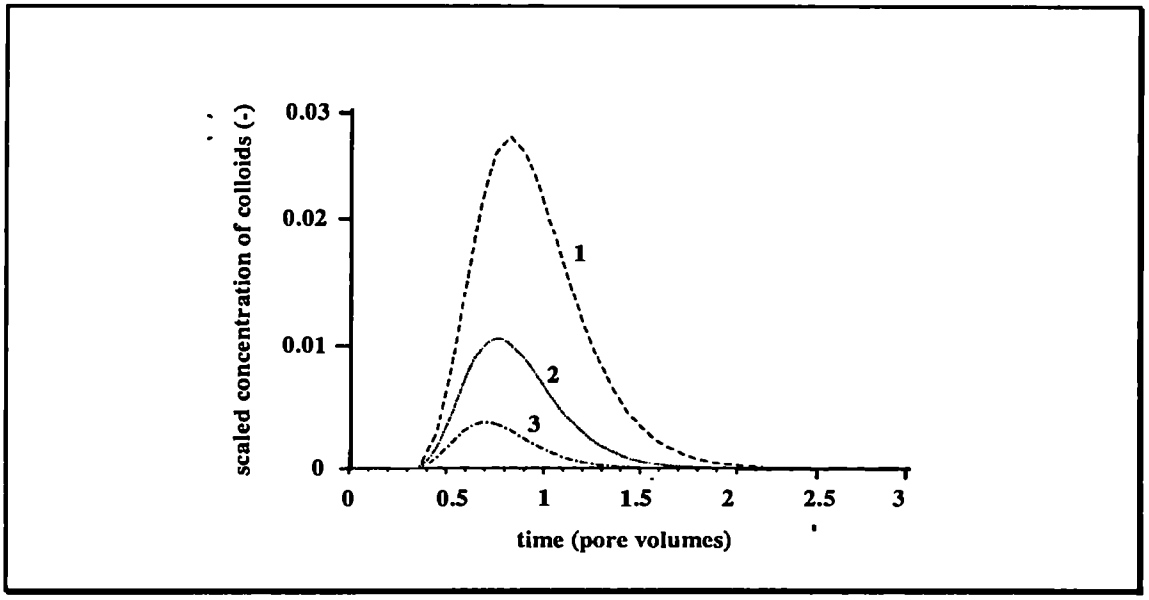

Figure 3 *Calculated colloid breakthrough curves (puls input) using different flow velocities :1 : 70 cm/h, 2 : 14 cm/h, 3 : 7 cm/h.*

Radionuclide breakthrough curves for model calculations with and without a step input of colloids are also available from the model. For example, the following case has been performed : an equal Langmuir constant for sorption of radionuclides to colloids and to the solid phase, ratio of the specific sorption capacity values for the two sorbing species (colloids and solid phase) assumed to be equal to the ratio of their specific surface area.

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2. Microscopic approach : ARMINES

2.1 The hydrogeological flow model

A single fracture and a column filled with homogeneous porous medium will be considered at this stage of model development. A constant head boundary condition at inlet and outlet of the system induces a linear pressure drop, resulting in a constant flow profile throughout the column length. The porosity of the medium could change as colloids block part of the pores and consequently a non-linear pressure drop will provoke a variable flow field. The transport problem is determined by the interactive behaviour of the colloids and solutes with the medium, and consequently, the flux from the inner pore-space towards the surface of the medium has to be calculated. In the single fracture system, the flux towards the solid surface is dominated by diffusion, gravitation and, close to the solid surface, electrostatical interaction. In a tortile pore system, the flux towards the surface should be corrected for hydrodynamical interception as well.

2.2 The solid surface - particle interaction model

Once the colloids approach closely the solid surface, interaction is dominated by electrostatical and eventually chemical forces. As colloids are assumed to enter an initially "clean" system, interaction will be dominated by clean surface colloid interaction. Interaction energy distributions as a function of separation distance at different ionic strengths can be calculated, and model refinement has been incorporated by including an interdependency between surface potential of the solid medium and concentration of adsorbed colloids.

2.3 Surface complexation and chemical equilibrium model

A new equilibrium model has been designed which includes electrostatic interaction phenomena for colloidal matter. The model could then deal colloid stability and metal complexation. An extended surface complexation approach is adopted, based on classical equilibrium chemistry and electrostatic surface interaction processes.

The bases of chemical modelling consist of the chemical equilibrium model, equipped with a reliable actinide speciation database. The model has been constructed in such a way that complexation of metals with organic or inorganic colloids can be incorporated easily. The new model named *CHESS*, which stands for *CHemical Equilibrium Speciation with Solids*, is specially designed for coupling purposes, and allows validation with existing models. The database is for the moment taken from the literature.

There remains, at least in our opinion, an important unknown factor in complex modelling : we do not know what complexes are formed. An attempt to evaluate the probability of complexation reactions has been presented at a meeting of the TUM, CEA-FAR, UM, KUL and JRC-Ispra in Gorleben June, 1992 [*Van der Lee*, 1992].

The surface complexation model will be extended to deal with the formation of different complexes, and to take into account the problem of colloid stability after complex forming. The necessity of such an extension is illustrated by the example of Cm(III) complexation with humic acids [*Wimmer et al.*, 1992] : six different species are considered. *Wimmer et al.* conclude that (at least) two different complexes are formed, although no qualification of these complexes appears possible at the moment. Theoretically, however, it is possible to calculate which possible complexes will be formed. Moreover, it is impossible to generate an "average" complex built of a humic or fulvic acid and an "average" Cm-species. Many complexes are possible, and only a posteriori an averaging is possible. We conclude that chemical speciation and knowledge of complexes is essential for complexation modelling, and further concept development for complexation reactions is necessary.

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WIMMER H., KIM J.I., KLENZE R. A direct speciation of Cm(III) in Natural aquatic systems by time resolved laser-induced fluorescence spectroscopy. Radiochemica Acta 58/59 p.165-171 (1992)

3. Experiments : CNRS - LSGC

3.1 Experimental systems

The experimental study is performed using a chromatographic technique, and concerns the distribution coefficients measurement. Modelling work aims to evaluate the orders of magnitude of interaction phenomena from literature data, and to design laboratory experiments. Transport and capture of well defined colloids in well defined porous media is being studied.

Physico-chemical and hydrodynamic conditions imposed are well known, constant and can be changed at will, the aim being to examine the relative importance of the measurable parameters [*Elimelech,* 1991]. Impulse injections of small quantities of colloidal suspensions are made into a flow of constant composition carrier solution passing through a porous medium, to determine the amount of colloids passing through and hence the amount of colloids retained in the bed. The standard liquid chromatography equipment is shown in *figure* 4.

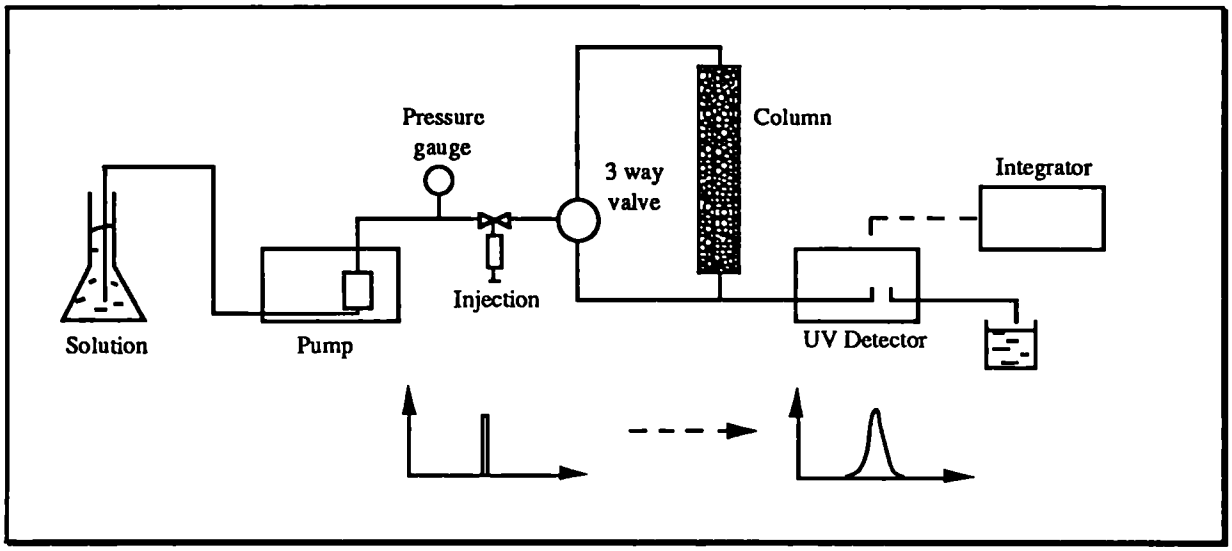

Figure 4 Experimental equipment.

Impulse experiments were made to determine the number percentage of particles passing through the bed for the three different latex samples at four different values of ionic strengths, two different values of pH, and for a range of flow rates. As an example of the available results, *Figure* 5 shows the proportion of particles passing through the porous medium as a function of particle size at a given flow rate. Due to surface reaction with the glass beads [*Elimelech,* 1991] the pH of the outlet solutions was always higher than the inlet pH. It can be seen that the higher the ionic strength and the lower the pH the greater the possibility for a given size of latex to be captured. In addition, extensive static batch experiments failed to show any detectable adsorption of latexes on glass beads. Another available result is the percentage of the particles passing through the bed as a function of ionic strength and flow rate : it confirms that the capture of colloids is increased by increasing the ionic strength.

Another result is that, in a given column, an increase in the flow rate reduces the capture of the colloids, *figure* 6 shows such results. To examine this hydrodynamic effect, similar to that predicted by conventional mass transfer correlations, we present our results as Sherwood numbers versus Reynolds numbers. It can be seen that that the higher the flow velocity the higher the Sherwood number : the lower the ionic strength and the higher the pH the lower is the Sherwood number with respect to that which would be expected. This may be understood by the corresponding increase in the repulsive barrier which hinders capture.

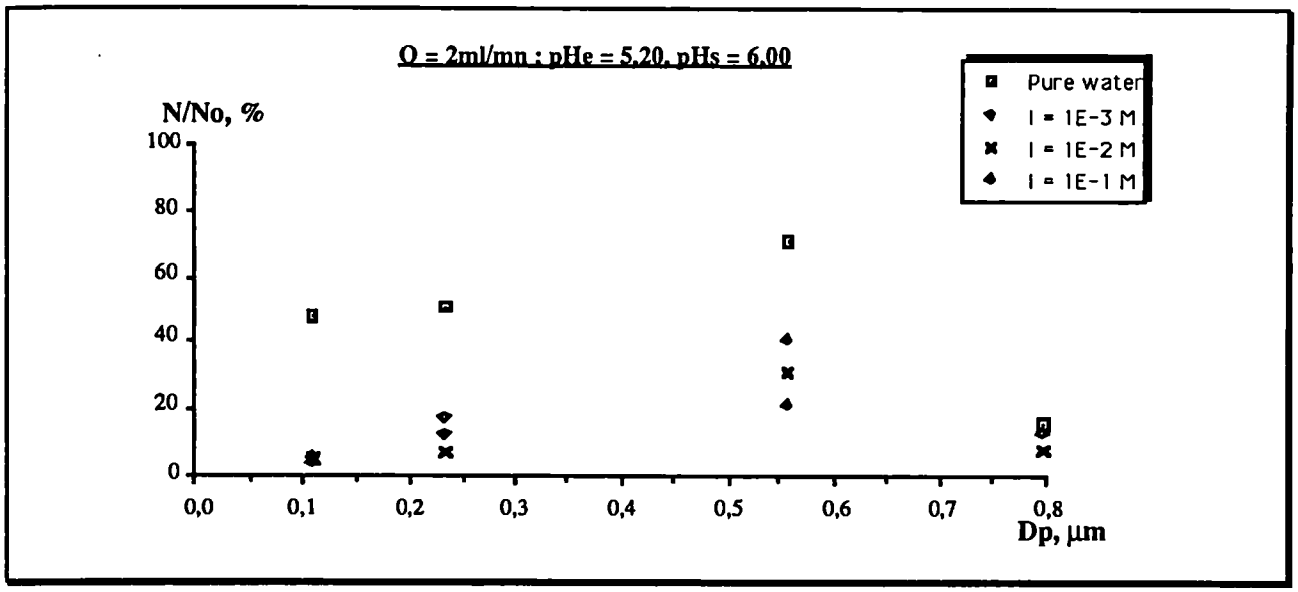

Figure 5 *Number percentage of latex particles passing through the bed as a function of particle size .*

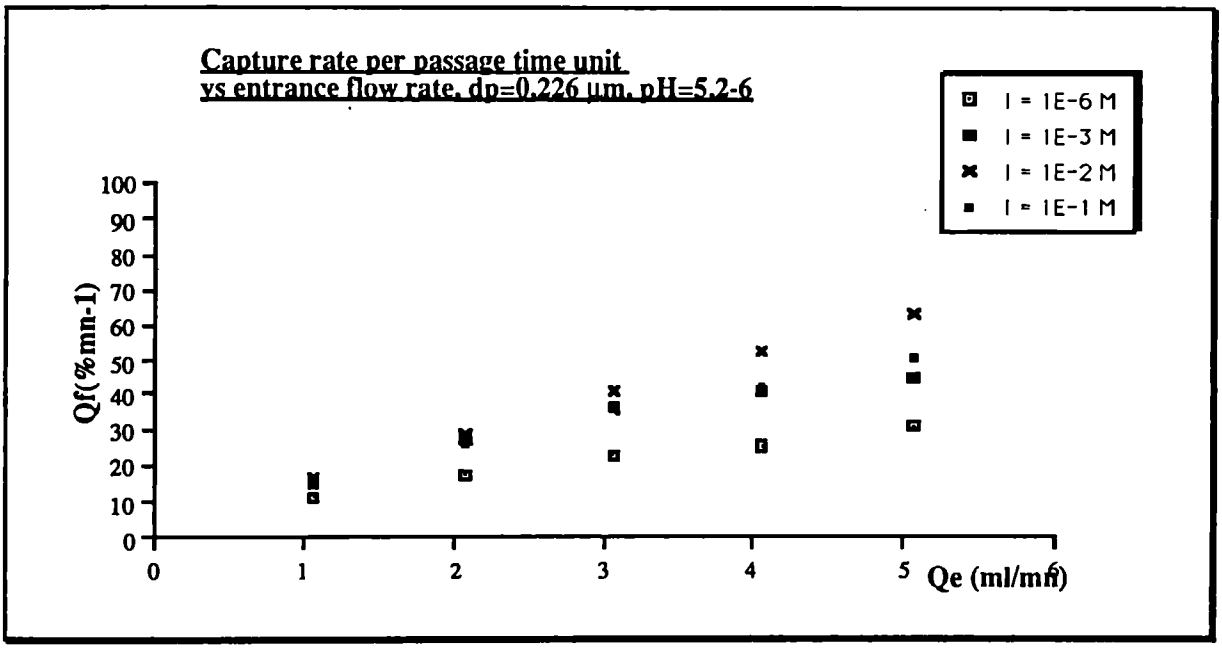

Figure 6 *Capture flux (% number of particles captured / residence time in bed) as function of flow rate and ionic strength.*

The main features of this investigation are that, as expected, capture is reduced when there is a potential barrier between colloid and capture surface. However it seems that hydrodynamic flow is necessary to help the colloids to overcome the repulsive barrier. This is confirmed by the lack of detectable adsorption in batch experiments and is in agreement with the mass transfer theory predicting that an increase in flow velocity improves the capture efficiency.

3.2 Development of an Equilibrium Flow Model

Facing the problem of the transport of radionuclides in porous media, the first approach was to obtain an order of magnitude of the retention capacities of natural porous media from literature data. With this aim a simple transport model has been formulated to evaluate the migration of pollutant and colloids in a fracture [*Smith and Degueldre*, 1992]. It takes into account three phases : a solute phase containing radionuclides, a colloidal phase, and a porous medium as solid phase. The kinetics are not included in this model.

The physical model is viewed as a single fracture system, divided in three zones (*figure* 7): the mobile zone, in which transport is governed by advection and dispersion, the immobile zone is a coating zone in which colloids in equilibrium with radionuclides are sorbed, the porous matrix in which radionuclides in solution are transported by diffusion and are sorbed on the surfaces. Colloids are assumed to be excluded from the matrix pores due to their size. Corresponding fractions f_m, f_{im} and f_s of total volume are defined.

Furthermore, we set that particles are in a given ionic environment controlled by concentrations of major species in solution and the pollutant is at very low concentration. The convective dispersive flow is assumed to be dominant in the mobile fraction, and is modelled by mixing cells in series, the two parameters being the number of cells and the mobile fraction on the aqueous flow. No adsorption of radionuclides on the external surface of the porous matrix has been considered. Local equilibrium is always assumed to be established : interaction colloid-surface can be accounted for by a linear distribution coefficient, K_c, distribution of radionuclides between colloids and solution by a linear interaction, K_{Nc}, concentration of radionuclides in porous matrix and in solution by a distribution coefficient, K_a.

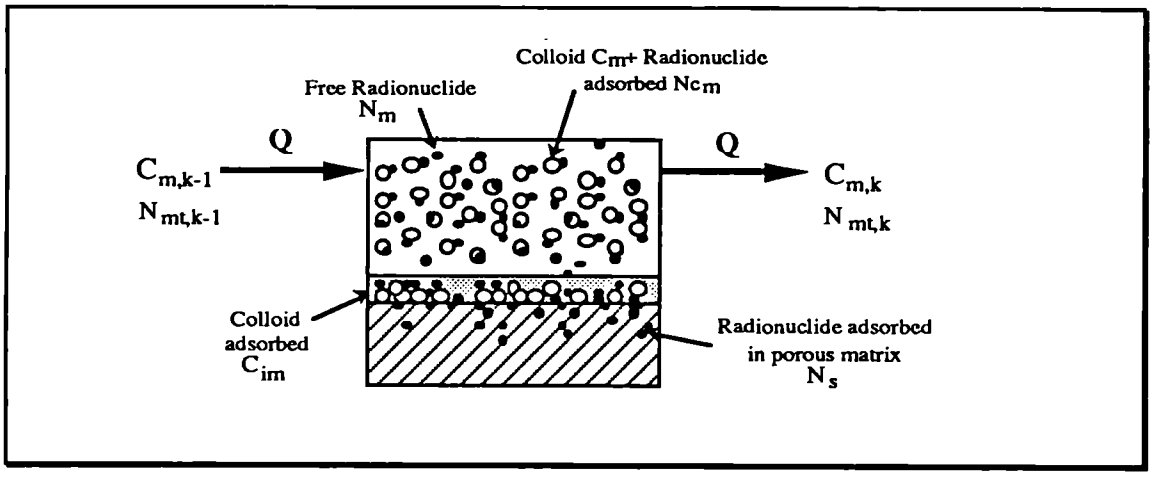

Figure 7 Description of a mixing cell k

The model is based on 2 types of equations : the equilibrium relationships, linking concentration of radionuclides, radionuclides adsorbed on colloids and radionuclides adsorbed in the porous matrix, and the mass balance equations [*Sardin et al.* 1991]. This model leads to a non-linear system. To get a linear model and to determine the retention time of radionuclides, the colloid concentration is assumed to be constant. This assumption allows

one to formulate a transfer function and to express the concentration of dissolved radionuclides, N_m.

To obtain an order of magnitude for the retention capacities of natural porous media, data from natural experimental sites have been collected from the literature [*Commission of the European Communities*, 1990-1991], they are summarized in the following table which highlights the large incertitude in the determinations. In particular the partition of colloids between the solution and the coating is generally not measured.

Experimental site	**C_0 (g/l)** colloid concentration in solution	**K_{Nc} (l/g)** distribution coefficient between solutes and colloids	**K_a (-)** distribution coefficient between solutes in the 3 fractions	**K_c (-)** distribution coefficient between colloids in mobile and immobile zones
Gorleben (D)	1.6 to 8.10^{-2}	12 to 56	no direct value	$K_c >> K_a$
Fanay Augères (F)	2.10^{-3} organic colloids	390 (U)	no direct value	
Grimsel (CH)	2.10^{-4}	10 to 650 (U) (Th)		
Markham Clinton (UK)	$\approx 10^{-3}$	1 to 110 (U) (Th)		

The variation of the residence time as a function of the concentration of colloids is very large because a small increase of concentration does not only induce an important adsorption of colloids on surfaces, but also an adsorption of radionuclides on colloids. Colloids being less retained in the medium than radionuclides, the output of radionuclides increases.

3.3 Experimental work

The first experimental work focuses on the measure of the distribution coefficients between colloidal, solute and solid phases [*Chenevière et al.*, 1991]. The three materials are: the sand of Entraygues (South of FRANCE), monosized latexes and strontium chloride for which interactions and ion exchange properties on charged surfaces are known. To gain access to the distribution coefficients, three types of experiments has started : batch experiments to study the interactions sand-latex and latex-strontium, column experiments to follow the output of strontium flowing through sand or granitic material, dialysis experiments with small volumes of strontium and latex. The variations of the concentration of colloids are measured by optical density. The first results are presented on the following table for batch experiments with sand and latex.

Concentration of Latex (mg/l)	Mass of sand (g)	NaCl (mol.l-1)	Sedimentation duration	% of latex fixed
2	0.5	-	3 days	6.6
20	0.5	10^{-3}	5 hours	2.3
20	0.3	10^{-1}	24 hours	4.5
20	0.3	1	24 hours	55
50	0.5	10^{-3}	5 hours	8.5

It was proved afterwards that the high result (55% of fixed latex) is due to the floculation of latexes and to the sedimentation of the flocs and not to an adsorption of latexes on sand.

These results show the influence of the ionic environment on the retention of colloids on the sand : the higher the ionic force, the higher the adsorption. Batch experiments between latex and strontium within NaCl express the competition between Na^+ and Sr^{2+} and the K_{Nc} calculated is 0.2. The first dialysis experiment shows that it is possible to use this method and to titrate strontium in good conditions.

The parameters which effectively control the transport are found to be the colloid concentration in mobile phase and the values of the linear coefficients, the main part of research must then deal with the knowledge of colloid distribution between surface and solution as a function of the speciation of major cations. When the behaviour of colloids in porous media is truly and quantitatively described, it will be possible to predict the concentration of colloids in solution.

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Title: Characterization and validation of natural radionuclide migration processes under real conditions on the fissured granitic environment
Contractor: ENRESA (Coordinator)/CIEMAT, CIMNE, AEA, BGS and CEA/IPSN
Contract n°:FI2W-CT91-0080(RZJE)
Duration of contract: 24 months from March 1st, 1991 to February 28, 1993
Period covered: January 1992 to December 1992
Project leader: Julio Astudillo (ENRESA)

A. OBJECTIVES AND SCOPE

The objective of the project is the characterisation of natural radionuclide (U, Th, and their decay products) migration processes in a fractured granitic environment and validation of models describing these processes.

In situ studies will be developed at the "El Berrocal" site, a post-tectonic batholith, taking into account:

- The characteristics of the rock fissures and discontinuities
- The hydrodynamic and hydrogeological conditions, and
- The variation of the physico-chemical characteristics with depth.

In parallel to these in situ activities, a series of laboratory experiments have been planned to study the same phenomena under controlled conditions.

Finally, the identified processes will be modelled and validated.

The project is managed and co-ordinated by ENRESA (Spain), with the technical assistance of Intera Environmental Division (United Kingdom). Participating organisations include CIEMAT (Spain), CIMNE (Spain), CEA/IPSN-Cadarache (France), AEA Technology (United Kingdom) and BGS (United Kingdom). Partial funding is provided by the CEC-Brussels, and JRC/CEC-Ispra co-operates with the Project participants. The Project is scheduled to run for four years, in two two-year phases. Phase 1 was initiated on 1st March 1991, and is the subject of this contract.

B. WORK PROGRAMME

I. Characterization of the physical environment: Geotectonic characterisation from the surface. Underground characterisation from boreholes. Geochemical and petrographic fissural filling studies. Litho-structural model of the site

II. Geochemical characterisation: Hydrogeochemistry (physicochemical and ionic phases). Groundwater colloidal phases studies (sampling, characterisation and transport). Groundwater mixing and circulation patterns. Fissure filling characterization. Hydrothermal and weathered transformations.

III. Migration studies: Natural radionuclide distribution.
Mobilization/retention processes (laboratory). In situ migration experiments

IV. Hydrogeological characterisation: Assessment of borehole conditions. Design and construct wirelines straddle packer testing system. Transmissivity and head measurements. Define numerical models. Design crosshole interference tests in selected fractured zones.

V. Modelling studies: Development of computer code (flow and transport, 2-D fractures in 3-D medium). Prediction of uncertainties caused by spatial heterogeneity. Flow and solute transport in a single fracture.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

A major portion of the planned Phase 1 field work was completed in this reporting period, and the supporting laboratory work has begun to yield its initial results. Highlights over the period are summarised below.

- One of the five boreholes (No. 16) drilled in the first year of the Project was deepened to 600 m for Phase 2 work. In addition, two further boreholes were sited and percussion drilled.

- An extensive hydrogeological measurement programme in the Phase 1 boreholes was completed and preliminary analysis and modelling of the results accomplhised.

- A preliminary three-dimensional structural model of the site was completed.

- Preliminary laboratory results of the colloid and hydrochemical sampling campaign in boreholes S1 and S7 were obtained and interpreted, and reference sampling zones in the new boreholes were identified.

- Interpretation and in situ crosshole tracer test performed between boreholes S1 and S7 using a conservative, non-radioactive bromide tracer was completed, and the conceptual design of a second in situ test formulated.

- A substantial field campaign involving full-scale testing of a suite of novel downhole tools for site characterisation-CHROMATOLAB, AUTOLAB and FORALAB - was undertaken, and supporting laboratory analyses initiated.

- Development and reporting of the TRANSIN-II code was completed, and a first version of its successor, the three-dimensional groundwater flow/radionuclide transport code TRANSIN-III, was implemented.

Progress and results

I. Characterization of the physical environment

Drilling activities: The five boreholes up to 250 m depth planned for the Phase 1 of the projects was completed. Two further boreholes have been drilled, using percussion techniques and, one of the first phase boreholes (S-16) was redrilled up to 600 m to be used during the Phase 2.

Geophysical activities: Three different geophysical tools have been applied at the Berrocal site. Combined helicopter borne magnetic, electromagnetic and VLF survey; surface gravimetric method and borehole geophysical testing.

The two first methods have been used to obtain information of the regional structure of the batholit. The other tools have been applied to obtain detailed information of the litho-structural characterisation of the study area on the site.

All the boreholes (except 17) were fully logged using downhole geophysical equipment and, in addition, a televiewer system was used to provide detailed information on fracture orientations. Additional geophysical studies were performed in borehole 17 by CEA/IPSN.

Lithostructural and petrographic characterization

During the drilling activities the borehole cores obtained were studied in a field office. The fractures and the mineral distribution were studied and described in relation with depth. Number of fractures, petrological description of the rock matrix, and alteration products (magnesium and iron oxides and hydroxides, sericite, moscovite, chlorite, quartz, sulphides, carbonates, kaolinites, clay, uranium minerals, etc.) are described for each borehole.

The litho-structural studies have been performed at different scales, considering Landsat and Spot images, aerial photography and field studies (outcrops and gallery). A general agreement is observed between remote sensing data analysis and field measurements.

At a regional scale 8 fracture families have been established related with the Hercinian and Alpine movements. At the local scale, three main fractures namely F1, F3 and F4 divide the site in four morphotectonic blocks.

The mineralogy of the fissural fillings is related to the fracture family, but more precise data are under consideration. The most important structural feature of the El Berrocal site is the fracture F-1 (N70-75W) named "Berrocal Fissure". The uranium dyke is associated with this fissure. A 3-D structural preliminary model has been constructed (Figure 1).

At a regional scale four granitic facies have been distinguished (Fig. 9): Porphyritic biotitic San Vicente granites, leucogranites, quartz dykes and Berrocal granites (two mica granite and pegmoaplites).

The two mica granite, muscovite predominating over biotite, is the main facies of El Berrocal pluton. This granite has a typical berrocal morphology, this term being the origin of the name. This facies can be classified as an alkaline feldspar, highly evolved, SiO_2-rich, peraluminous, hypocalcic granite, with an evolutive tendency from a potassic to a more sodic end. The granite is enriched in incompatible elements, including Li, F and Sn, with a K/Rb ratio ranging between 80 and 89 like in pegmatites, and U/Th > 2, like in U fertile granites, most of the U being enclosed in uraninite. The two mica "El Berrocal" granite is the only unfertile facies found up to now.

II. Geochemical characterization

Groundwater hydrogeochemistry

To perform the groundwater characterisation the Geochemical Transport Working Group (GTWG) of the El Berrocal Project, decided to establish a set of Referenced Zones for groundwater sampling, colloidal studies and fissure filling characterisation and radionuclide distribution.

Preliminary investigations on the study of the number of open and close fractures, nature of fracture filling, geophysical parameters as resistivity in cores: 13, 14, 15 and 17 and the compiled data of the hydraulic conductivity carried out by BGS staff in 13, 14 and 15 were discussed in the GTWG and the most important hydraulic fractures (higher permeability were selected).

Prior to sampling analysis of new boreholes, the pre-existing boreholes were sampled and analyzed from groundwater and colloid to obtain information of the geochemical processes between the surface and a depth of 60 m.

Before sampling the groundwater it is necessary to establish whether the groundwater is in equilibrium or not. Every selected zone needs to be pumped several times controlling the concentration of the tracer (Br^- and I^-). When the concentration reaches the background level of the zone, the sample is considered to be representative. Some measurements will be made in the field in a closed line flow through cell flushed with an inert gas to avoid chemical changes in the sample. These parameters include pH, two measures of Eh, temperature, electric conductivity and dissolved oxygen. Groundwater samples will be filtered by an in line cartrigde filter 0.45 microns prior to all the measurements. At this moment Br^- content in groundwater is between 5-15% and for this reason the sampling will be delayed.

Colloids Study

The colloidal studies are performed using different methodologies.

The colloidal sampling will be performed in the reference zone of the boreholes. In each borehole the reference zone will be isolated with packers and flushed for many hours before colloid collection. To characterize particle size and number, photon correlation spectroscopic (PCS) and transmission electron microscopy (TEM) techniques, were used.

Regarding this subject two different teams were encharged of laboratory work.

The preliminary results obtained by both teams are similar. The data obtained for boreholes S-7 and S-2 indicate that the colloidal populations are relatively low (10^{12} particles per litre) and the size distribution is broad with a lot of large particles.

U and Th partition calculations indicate that more than 88% of total U and more than 92% of total Th are in true solution; there is virtually no loading of colloids in these boreholes. The $^{234}U/^{238}U$ activity ratios for colloid, solution and particulate phases are similar (about 2 to 2.5) confirming that these phases are in chemical equilibrium with respect to U.

Natural radionuclide distribution

One of the aims of the "El Berrocal" Project is to establish the natural radionuclide distribution in the pluton. Further the radionuclide contents on the mobile phases (colloidal and groundwater) the distribution in rock matrix and fissural infill material has been considered.

Uranium and thorium distribution in Berrocal fresh granite

According to the data obtained, it is concluded that approximately 63% of the U and between 25 and 30% of the Th would remain undistributed. However, the presence of frequent uraninite and thorite-auerlite crystals would account for those high U and Th percentages.

The U in essential and accessory minerals represents 20.5% of the total U in El Berrocal granite, so the remaining 79.5% is shared between uraninite ($\approx$ 63%) and labile U ($\approx$ 16.5%). The latter comes from the oxidation of uraninite and the partial remobilization of U from the mineral.

Uranium and thorium distribution in clayey materials associated with fractures

The natural radionuclide migration/retention processes in the clayey materials, fractions $< 60\mu m$ and $> 2\mu m$, associated with the N100°-110°E fractures, in El Berrocal U mine, have been studied. These fractures are critical because the uranium mineralization dyke exhibits the same direction. A very detailed study of this system is included in an internal project of natural analogues performed by CIEMAT and ENRESA, considering the hydrothermal granite alteration and the behaviour of uranium in these processes.

The clayey materials associated with N110°-100°E fractures, in the El Berrocal mine, were originated by the hydrothermal alteration of the crushed granite, as a consequence of the same fracturation phase. Therefore, they should not be considered as fracture filling "senso strictu".

The neoformed clay minerals and accessory minerals and mineraloids play an important role in the retention, either by adsorption or precipitation of the radioactive (U and Th), heavy elements, P and organic C, released during the hydrothermal alteration of the granite and weathering of the sulfide and uraniferous mineralizations. The organic C could either be due to present biological activity in the clays or to organic acids transported, from the topographic surface, by the percolating water. In the latter case, organic-clay complexes would probably be formed.

Among the natural radionuclides, U is precipitated as UO_2^{++} phosphates, mainly autunite and torbernite, as UO_2^{++} sulfates, like uranopilite, and adsorbed by the clay minerals and Fe, Al and Si gels. Th can be found in the minerals inherited from the granite and mainly adsorbed by the clay minerals and/or precipitated as Th hydroxides and/or cryptocrystalline silicates. The heavy metals have also been studied.

Uranium series isotopic analysis of fractures infill materials

In order to establish the natural radionuclide distribution in the mineral phases of the fracture infill materials in the El Berrocal batholith, a number of water-bearing horizons have been selected and core material from these sampled. The radiometric data base currently being set up should serve as the data base for planned rock/water interaction modelling at El Berrocal. Some of the data obtained are shown in table 1.

The fracture infill materials so far analysed indicate high uranium content ranging from 20 to 400 ppm. Thorium concentrations are typical of near surface cystalline rocks with a range of 5 to 15 ppm. The $^{234}U/^{238}U$ activity ratios greater than unity are indicative of recent uranium uptake from the fracture fluids by these fracture wall mineral assemblages. However, judging by the $^{230}Th/^{234}U$ activity ratios most of which are within 2σ uncertainty of unity, the observed uptake may have occurred on the timescales of many thousand of years allowing ^{230}Th to grow into secular equilibrium with its parent ^{234}U, or alternatively the U uptake has been slow allowing ^{230}Th daughter to maintain itself in secular radioactive equilibrium. The type of fractures infill have been characterized.

III. Migration studies

In the Berrocal Project the activities in relation with the migration experiments include:

. Application of borehole tools, cross-hole migration test with conservative tracer, and laboratory experiments on column migration

The objective of applying the borehole tools is to obtain the chemical parameter, in situ, in relation with the strategy to be used for geological barrier characterisation.

A substantial field campaign involving full-scale testing of a suite of novel downhole tools for site characterisation was undertaken by CEA/IPSN in borehole 17, and supporting laboratory analysis were inititated. The main tools tested in this period were AUTOLAB and CHROMATOLAB. Furthermore, in situ radar measurements were obtained toward the end of the reporting period. In addition, other more standard downhole measurements in boreholes 14 and 17 were undertaken, in particular, Eh and pH.

The AUTOLAB experimentation included a tracer diffusion along a clay column, under natural conditions in the borehole n° 17. The column has been prepared, using the clay fissured filling of the El Berrocal, and the hydrodinamic and geotechnic characteristics are tested before the AUTOLAB experiment. Nd, Eu, Sr and Se will be the tracers.

The cross-hole migration test has not been concluded and no specific data can be presented now.

Laboratory experiments

The objective of the migration studies is to compare the field and laboratory data in relation with the uranium migration.

Two granitic columns have been selected from core borehole 17. These two columns included a longitudinal fracture, and will be used to study migration of ^{75}Se, ^{137}Cs, ^{60}Co and ^{233}U, in the fracture and in the altered rock adjacent to the fracture.

In addition, initial sorption-desorption studies using the same isotopes have begun in batch experiment on crushed fresh granite and fracture infilling material from the site.

After the chemical stabilisation and control of 6 columns in the lab the hydrodinamic characterisation has been initiated. Two columns are of big dimensions (50 mm lenght and 84 mm diameter. The other four columns are 9 cm length and 38 cm diameter.

For the hydrodynamic characterisation, tritium is injected using four different flow injection rates. Different breakthrough curves have been obtained, indicating different phenomena of dispersion-diffusion in relation with the speed. The data are under study.

IV. Hydrogeological characterization

The objective of the hydrogeological program is to use the hydrogeological measurements to characterise groundwater flow in the hillside especially around the mine cavity and associated dyke. Information on heads and permeabilities is used to construct a conceptual model of flow to be used in generating mathematical models. It is essential to understand the groundwater regime in order to design experiments and collect water samples enabling colloid movement to be understood.

Single borehole testing of boreholes S13, S14, S15, T1 and T2 has been performed using the straddle packer system designed for the site. Each borehole was tested using an 11 metre overlapping straddle interval. Great care was used to identify and eliminate leakage around packers. Zones with a significant transmissivity were re-tested using a shorter straddle interval, usually 3 meters, in an attempt to identify particular flowing features. Results for the single borehole testing are shown in diagrammatic form in figure 2.

Preliminary crosshole measurements have been made between boreholes on the site. During the testing of both S13 and S15, the pressure in S2 (a sub-horizontal borehole drilled into the hill from the end of the mine gallery) was monitored. Hydraulic signals generated in S13 and S15 arrive at S2 within several hours. A 30 metre increase in water level in S13 generated a 2 metre pressure increase in S2. It is likely that the zones at 36 meters in S13 and 40 meters in S15 are the points of connection. Some small connection was identified between S16 and S14.

Preliminary modelling

At the beginning of phase I of the Project, three conceptual groundwater flow model possibilities were considered. Now a preliminary modelling, using the first hydraulic testing data, has been performed.

This preliminary hydrogeological modelling, was done in two dimensions, using a section perpendicular to the hill, i.e., parallel to the access gallery to the mine, and a constant value of hydraulic conductivity. The hydrogeological measurements suggest that the dyke has a major influence on the groundwater flow system, effectively acting as a drain. Groundwater flow rates, pathlines, and travel times were estimated (Figure 3). Typical conductivity is 10^{-9} m/s.

Preliminary conclusions from the field-work suggest that the site comprises a series of poorly permeable blocks. A small amount of recharge is able to maintain steep hydraulic gradients in both the horizontal and vertical directions. The distribution of hydraulic conductivity is non-uniform, appearing to be higher in the upper 100 m than at depth, and higher within specific features, such as the main quartz dyke. Groundwater flow is generally from the top of the hill towards the bottom, with some groundwater being intercepted by the dyke, an extensive feature which, as noted above, drains water through the rock mass. Excavations in the dyke complicate the natural head conditions. The head in the dyke at depth (where penetrated by borehole 15) is lower than in the gallery. This indicates that the dyke drains the mine, rather than the dyke carrying water to the mine. The outflow point of the dyke is unknown.

Boreholes connect transmissive zones (usually associated with faults or dykes), which tend to have different water levels and act as conduits, transporting groundwater from zones of high head to zones of low head. As the conductivity is generally low, flows from or into such zones are relatively small.

V. Groundwater flow and radionuclide transport modelling

The work has been organised into four tasks:

1. flow and solute transport inversion,
2. flow and transport through isolated fractures,
3. flow and transport through fracture networks, and
4. hydrogeology of the site, focussed on hydraulic test interpretation.

The modeller now has a preliminary version of TRANSIN-III running, and work is underway to improve the numerical algorithms employed. As more data from the site become available over the next months, the preliminary hydrogeological conceptual models of the site will be refined. In addition, the TRANSIN-II code will be fully documented and the TRANSIN-III code further refined.

In relation with task 2, the research was foccussed on the effects that heterogeneity, as associated parameter involved in hydrogeology, causes in flow and transport. The approach used has been mainly numerical development in the program FAITH, a finite element computer code capable of solving the basic flow and transport equations in highly heterogeneous aquifers and for a very large number of nodes. The program solves the steady-state flow and transient transport equation. FAITH is designed to work in supercomputers to take advantage of vectorization.

3. LIST OF PUBLICATIONS

[1] Migration Radionuclides on Fissured Granitic Environment 1989-90 (Preliminary Draft), CIEMAT, 1991 - Madrid.

[2] L. Pérez del Villar, B. de la Cruz, J. Pardillo and J.S. Cózar, (1991). An approach to the calculation of U (Th) mineralogical distribution in the fresh granite from "El Berrocal" pluton (Toledo, Province, Spain). El Berrocal Project Topical Report (EB-CIEMAT-(91)26) CIEMAT - Madrid.

[3] "El Berrocal Project" Phase 1. First Six-Monthly Progress Report. 1-3-91 to 31-8-91 ENRESA, 1991

[4] "El Berrocal Project" Phase 1. Second Six-Monthly Progress Report. 1-9-91 to 29-2-92 ENRESA, 1992

[5] "El Berrocal Project" Phase 1. Third Six-Monthly Progress Report. 1-3-91 to 31-8-92. ENRESA, 1991

[6] L. Pérez del Villar, B. de la Cruz, J. Cózar, J. Pardillo, P. Gómez, Mª Jesús Turrero (1992). Characterisation of clayey materials associated with N100-110E fractures in El Berrocal site (Gredos, Spain). Genesis and U, Th and other elements retention capacity. El Berrocal Project Topical Report (EB-CIEMAT-(92)-34)

[7] J. Astudillo, "El Berrocal Project" 5th CEC Natural Analogue Working Group Meeting (NAWG). Alligator River Analogue Project (ARAP). Toledo, Spain, October, 1992.

TABLE 1
RADIOMETRIC DATA FOR TOTAL FRACTURE INFILL MATERIALS

SAMPLE (Harwell Code)	[U] (ppm)	[Th] (ppm)	[Th/U] (MR#)	$^{234}U/^{238}U$ (Activity Ratios)	$^{230}Th/^{234}U$ (Activity Ratios)	$^{228}Th/^{232}Th$ (Activity Ratios)
S7(44.75 m) (6741)	30.0 ±0.8*	8.51 ±0.98	0.28 ±0.03	1.02 ±0.02	0.95 ±0.06	0.70 0.14
S7 (44.35 m) (6722)	20.3 ±0.4	7.14 ±0.22	0.35 ±0.01	1.00 ±0.03	0.95 ±0.04	–
S7 (45.45 m) (6721)	114.4 ±4.6	13.70 ±1.39	0.12 ±0.01	0.89 ±0.02	1.02 ±0.06	±0.16
S1 (48.52 m) (6723)	105.3 ±4.8	11.5 ±1.3	0.11 ±0.01	1.38 ±0.03	0.95 ±0.06	0.86 0.21
S14 (216.30-216.5 m) (Fracture A) (6724)	404.6 ±20.0	9.69 ±1.21	0.024 ±0.003	1.32 ±0.02	0.88 ±0.06	0.95 ±0.20
S14(216.30-216.51 m) (Fracture B) (6725)	209.1 ±12.4	7.16 ±1.21	0.034 ±0.006	1.14 ±0.03	0.92 ±0.08	0.60 ±0.34
S14 (216.30-216.51 m) (Fracture C) (6724)	154.2 ±7.2	5.29 ±0.82	0.034 ±0.006	1.20 ±0.03	0.86 ±0.05	1.17 ±0.42

* All quoted errors are 1σ uncertainties due to nuclear counting statistics only
#MR = Mass Ratio

FIGURE 1
3-D MODEL

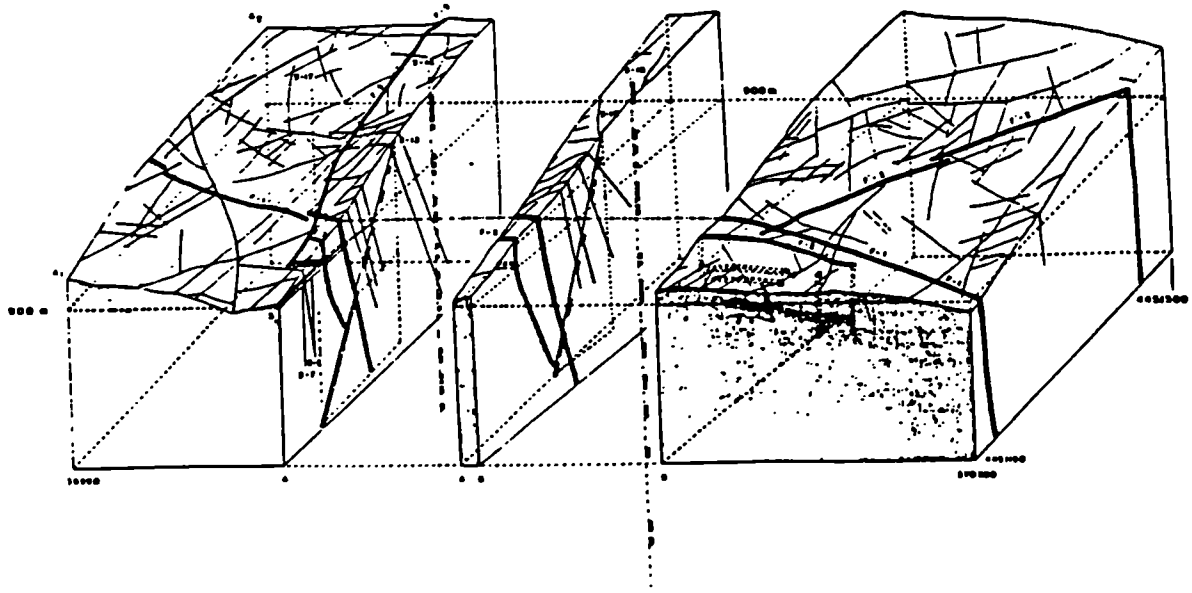


FIGURE 2

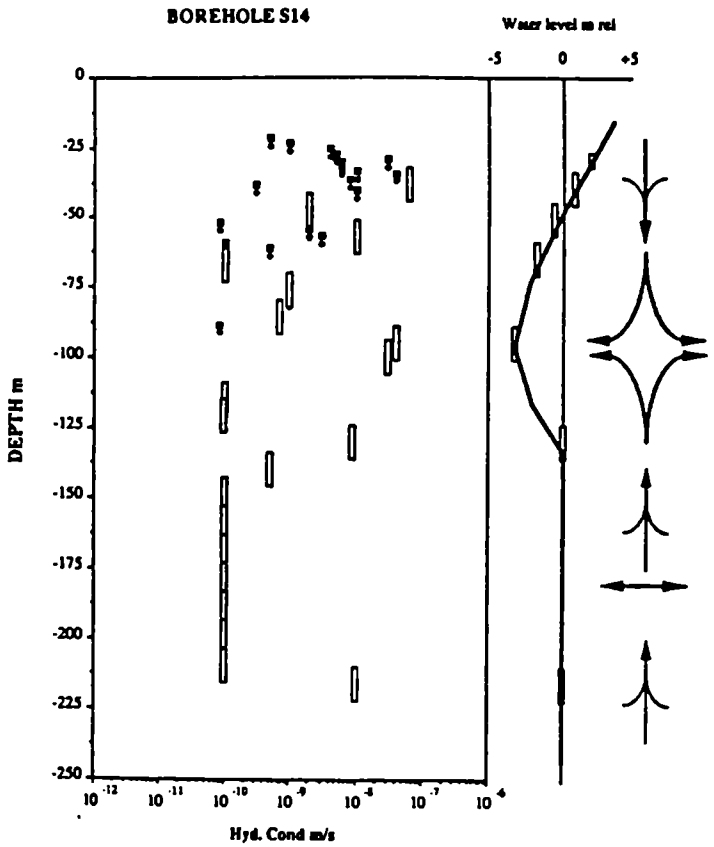
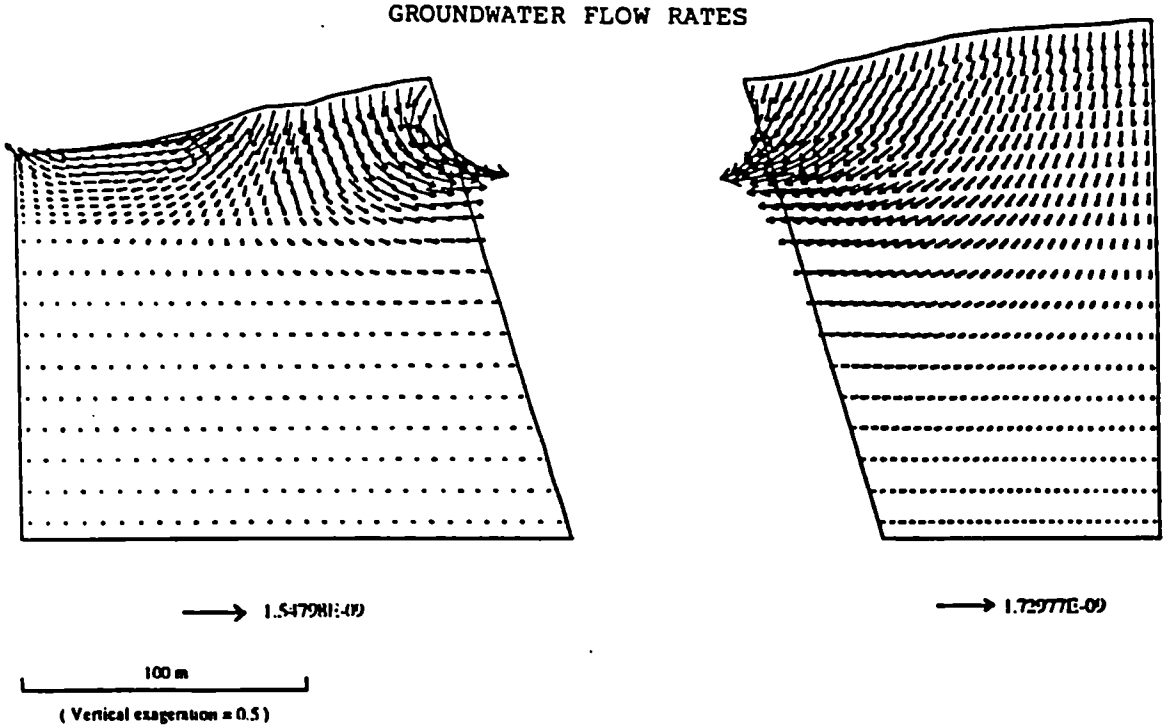


FIGURE 3

GROUNDWATER FLOW RATES



Title:	Fundamental studies on the interaction of humic substances
Contractor:	National Environmental Research Institute
Contract N°:	FI2W/0081
Duration:	from 01-06-1991 to 30-05-1994
Period covered:	01-01-1992 - 31-12-1992
Project Leader:	Lars Carlsen

A OBJECTIVES AND SCOPE

The overall objective of the project is to covalently label humic materials with a radionuclide (eg C-14, H-3, I-125) in order to use the labelled material during investigations of their interactions in

(a) complexation reactions with cations (eg Eu, Sn, Co, Ni) and cation competition reactions (eg with Na, Ca)

(b) sorption of humic and humic complexes onto solid surfaces and

(c) precipitation/dissolution behaviour of humic material.

The radionuclidic labelled humic material will provide information on the presence of the complexed radionuclide as well as information on the "free" humic material.

The project is carried out by a collaborate effort of the National Environmental Research Institute (DK) and Loughborough University of Technology (UK).

B WORK PROGRAMME

The project is subdivided into three phases:

Phase 1: Preparation of labelled humic materials:
a) Preparation of C-14-labelled humic material from C-14-labelled phenol or C-14-labelled methylamine.
b) Preparation of iodine-labelled humic materials.

Phase 2: Characterisation of the labelled humic material:
a) Determination of the acidity, functional group capacity and size distribution of the non-labelled and labelled humic materials.
b) Determination of the europium binding capacity of the non-labelled and labelled humic materials.

Phase 3: Studies on the aqueous and solid surface chemistry of the labelled humic material
a) Investigation and determination of the associating capacities of the labelled humic material with radionuclides of interest (eg Ni, Sn, Co).
b) Investigation of solid surface sorption using columns filled with sand.

C PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Humic- and fulvic acids are able to complex polyvalent metal ions, e.g. radionuclides, leading to soluble complexes of significant strength, thereby decreasing the sorption of these compounds to soils and sediments. The interaction of humic materials with radionuclides may significantly influence the availability and transport of the latter in the environment. Typically, studies along these lines have focussed almost exclusively on the radionuclides, whereas the actual role of the humic material has been elucidated only indirectly. In order directly to study the behaviour of the naturally occurring organic macromolecules in relation to the environmental fate of radionuclides, radio-labelled humic- and fulvic acids can advantageously be applied. Radio-labels such as ^{14}C and ^{125}I have successfully been covalently incorporated in humic- and fulvic acids. Labelling of humic substances as well as preliminary migration studies are discussed

Progress and results

Labelled humic materials have successfully been achieved chemically by incorporation of ^{125}I or ^{14}C. In both cases a covalently bound label has been found.

Labelling with iodine

^{125}I has been incorporated into humic acids by the action of Chloramine-T, which is widely used in protein iodination.

When reducing agent is omitted from the reaction mixture, 100% apparent incorporation of ^{125}I is achieved. However, the iodinated humic material is not stable. Reaction with reducing agents such as sodium metabisulphite leads to reduced incorporation to between 40 and 60 %, but with increased stability. In Figure 1 the separation of iodinated Aldrich humic acid from unreacted iodide is shown.

Investigation of the stability of the sodium metabisulphite treated labelled material in the absence of sand indicates that the iodine is gradually lost from the humic material with time. This could be due to an equilibrium being established between bound and free iodine. However, this loss of iodine activity from the humic material is only of the order of 5% of the total iodine activity.

The stability of the produced iodinated humic material was further elucidated by sand column migration studies using Drigg sand and groundwater. These experiments revealed similar retention of unlabelled and labelled humic materials, with 30-35 % of applied activity being recovered from the column. The speciation of the eluted activity, however, is significantly different if the labelled humic acid was produced in the presence and absence of reducing agent, respectively. In the absence of reducing agent up to 35 % of the eluted activity is in the form of free iodide, which is reduced to approximately 5% after treatment of the initial reaction mixture with reducing agent.

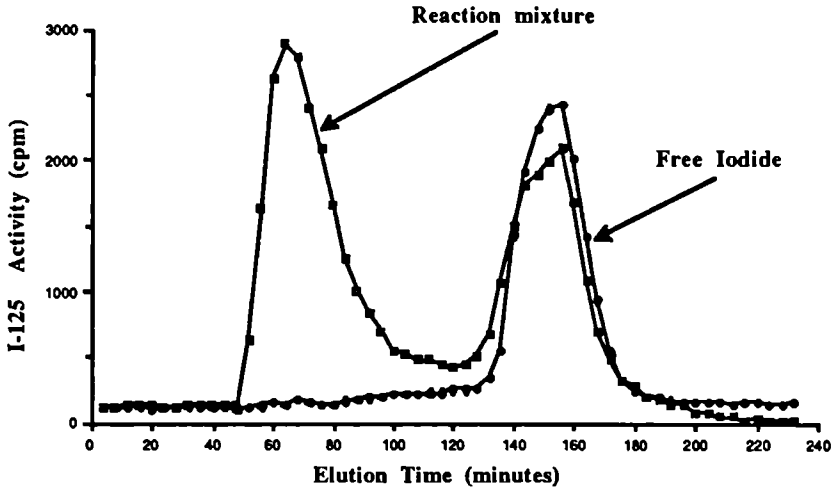


Figure 1. Separation of reaction mixture consisting of ^{125}I-labelled Aldrich humic acid and free iodide (column: Sephadex G-25, eluent: 0.05 N NaCl, 15 mL/h)

Based on the above findings it is concluded that halogen labelled humic material produced by direct labelling techniques is suitable for use in migration studies.

Labelling with carbon

Two methods of labelling humic materials with ^{14}C have been examined, using dissimilar techniques and routes for radionuclidic incorporation. ^{14}C-phenol can, applying an enzyme catalyst, be incorporated into the humic acid skeleton with a 100% yield. Alternatively part of the carboxylic acid groups present in the humic material can be converted into methylamides, applying carbodiimides, such as 1-ethyl-3-dimethylaminopropyl carbodiimide (EDC), which have been used in protein chemistry as cross-linking agents and in the determination of carboxylic acid functionality. They react with carboxylic acids to produce an O-acylisourea which, in the presence of a nucleophile such as an amine (^{14}C-methylamine), react to produce an amide, liberating a proton and a substituted urea as byproducts. When water acts as the nucleophile the carboxylic acid function is regenerated. Figure 2 shows that separation of the ^{14}C-labelled humic acid from unreacted ^{14}C-methylamine easily can be achieved.

The ^{14}C-labelled humic materials appeared perfectly stable as elucidated by sand column migration studies using Drigg sand and groundwater. Approximately 30% of the applied activity was eluted from the sand columns, the speciation of the eluted material, as determined by subsequent gel chromatography, proved the eluted label to be 100% labelled humic material, and, hence, suitable for use in migration studies.

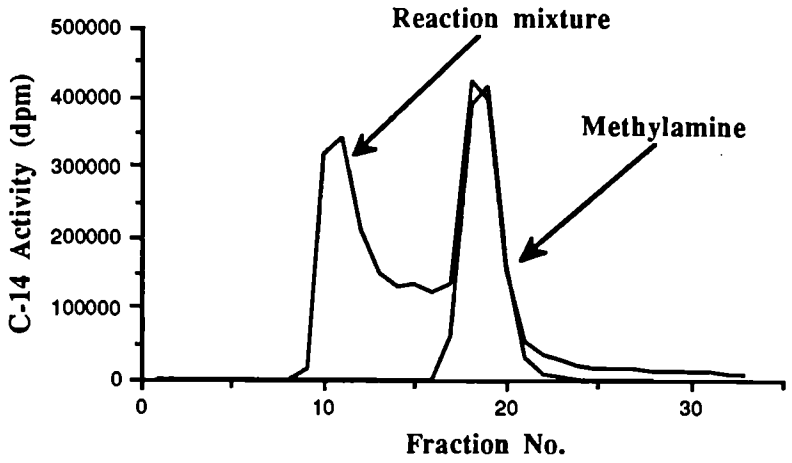


Figure 2. Separation of reaction mixture consisting of ^{14}C-labelled Aldrich humic acid and unreacted ^{14}C-methylamine
(column: Sephadex G-25, eluent0.05 M NaCl, 20 mL/h)

Migration studies

The application of double-labelled metal - humic acid complexes, i.e. both the metal and the humic acid bearing a radiolabel, offers a unique possibility for studying the migration behaviour of these complexes. Thus, for the first time it appears possible to disclose the migration behaviour of metal - humic acid complexes as such through different media.

Double-labelling with iodine and europium

A $^{125}I/^{152}Eu$ double-labelled europium - humic acid complex is easily formed by complexing a sample of ^{125}I-labelled humic acid with europium ions, the latter being spiked with ^{152}Eu. The reaction mixture was injected to a gel column, the resulting elution profiles (^{125}I and ^{152}Eu detection) being visualized in Figure 3.

The chromatographic traces display obviously two "^{125}I" peaks as well as two "^{152}Eu" peaks, respectively. Whereas the two peaks (^{125}I and ^{152}Eu) located around an elution time of 30 min. unambiguously are associated with the double-labelled complex, the "^{125}I" peak around ca. 75 min. and the "^{152}Eu" peak at ca. 140 min. correspond to free iodide and europium, respectively, the latter being eluted only following injection of and EDTA solution (at $t \approx 100$ min.). The $^{125}I/^{152}Eu$ double-labelled complex was isolated by collecting the fractions eluted between 20 and 40 min.

To study the migration behaviour of the europium - humic acid complex, the above mentioned collected sample of the $^{125}I/^{152}Eu$ double-labelled complex was applied to a column of Drigg sand, which subsequently was eluted with the

corresponding ground water. In Figure 4 the elution profiles, the ^{125}I and ^{152}Eu activities, respectively, are depicted.

Unambiguously, ^{125}I and ^{152}Eu activities are eluted simultaneously, thus, demonstrating the migration of the intact europium - humic acid complex through the sand column. It should in this connection be noted that free europium is, under the prevailing conditions, sorbed irreversibly to the column material and, thus, not eluted even following prolonged elution times.

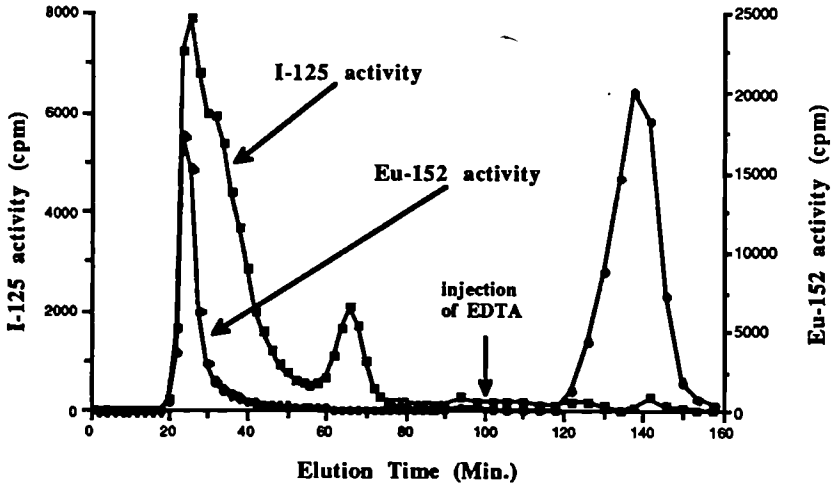


Figure 3. Elution profile on gel of double-labelled Aldrich humic acid (^{125}I and ^{152}Eu), showing respective activities

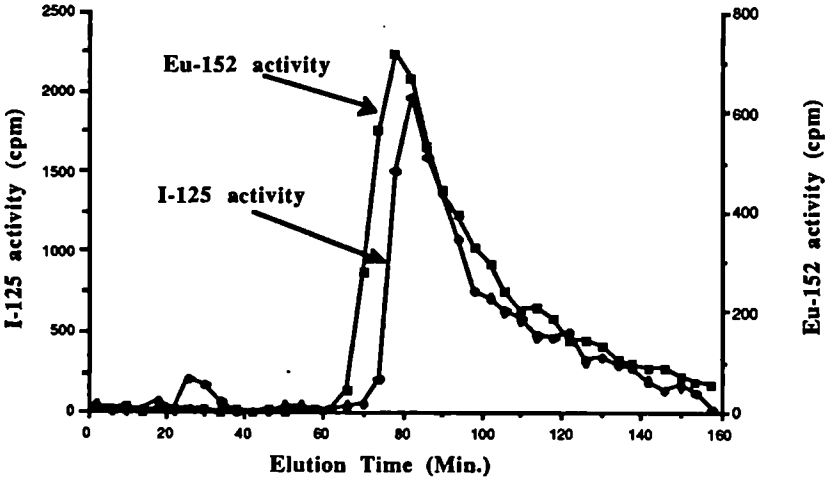


Figure 4. Elution profile through sand of double-labelled (^{125}I and ^{152}Eu) Aldrich humic acid, showing respective activities.

In order further to elucidate the actual speciation of the eluted material, the cumulative recovery eluted from the sand column of both ^{125}I and ^{152}Eu activities was recorded (Fig. 5)

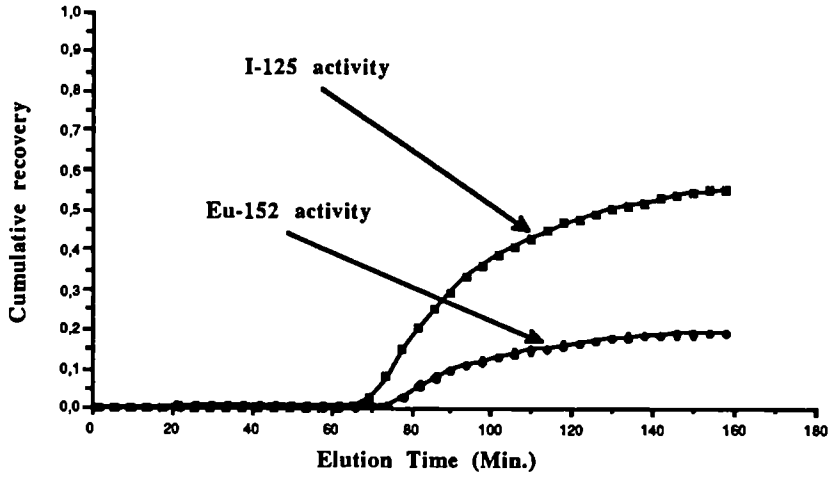


Figure 5. Cumulative recovery from sand column of both ^{125}I and ^{152}Eu from double-labelled Aldrich humic acid.

It is immediately noted that whereas approximately 60% of the ^{125}I activity is eluted during the first 160 min, only ca. 23% of the corresponding ^{152}Eu activity is eluted. Obviously, it must be concluded that, not surprisingly, part of the initially applied europium - humic acid complex apparently has dissociated on the column during the migration process. The resulting free ^{125}I-labelled humic acid is eluted simultaneous with the complex, whereas the corresponding liberated europium irreversibly was sorbed onto the sand. Hence, 23% of the initially applied europium - humic acid complex apparently was eluted as such, the remaining 77% being dissociated on the column. It is noted that only part of the free humic acid, originating from the dissociated complex, was eluted in agreement with the above reported results on the migration of ^{125}I- and ^{14}C-labelled humic acids on sand.

Double-labelling with carbon and nickel

The migration of nickel has been studied analogously applying a $^{14}C/^{63}Ni$ double-labelled nickel - humic acid complex. Figure 6 visualizes the elution profiles of ^{14}C and ^{63}Ni activity, respectively, following passage of a sample of a ^{14}C-labelled humic acid reacted with ^{63}Ni spiked nickel ions.

The peaks (^{14}C and ^{63}Ni, detection) eluted in fractions 11-18 are unambiguously associated to the $^{14}C/^{63}Ni$ double-labelled nickel - humic acid complex, whereas the "^{63}Ni" peak eluted in fractions 35-40 corresponds to free nickel, however, eluted only following injection of EDTA.

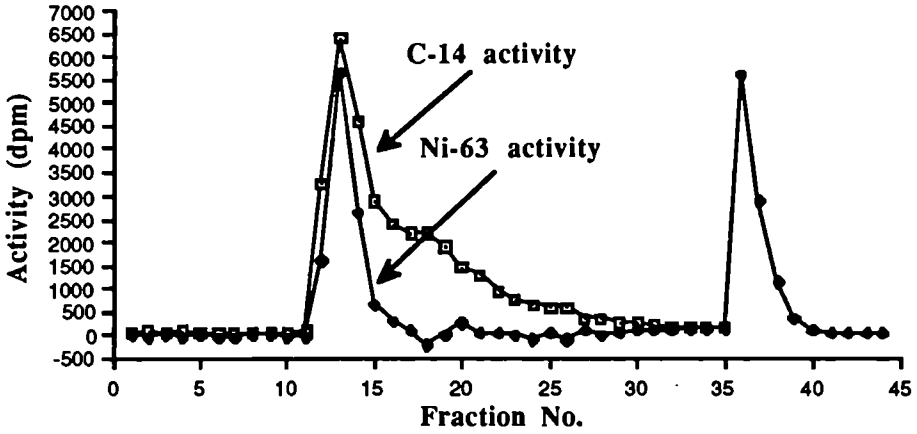


Figure 6. Elution profile of activity of Aldrich humic acid labelled with ^{14}C and ^{63}Ni.

Conclusions

The above reported studies have demonstrated that radiolabelled humic materials rather easily can be obtained through pure chemical reactions, the reaction products being stable with respect to elimination of the label.

It has unambigously been demonstrated that intact metal - humic acid complexes migrate through sand columns eluted with the corresponding ground water.

Although the above described labelling of humic acids have been carried out using the commercially available material (Aldrich), these labelling methods should be applicable to any humic material, thus, allowing the production of site-specific labelled material. The labelled materials produced by these methods may not only be of use in "fate studies" - the effect of humic materials on the migration, degradation and extractability of metallic and organic pollutants, but they may also provide a useful tool in investigations on the effect of humic-pollutant interactions on, for example, the uptake of pollutants into plants.

List of publications

1) L. Carlsen, P. Lassen, J.V. Christiansen, P. Warwick, A. Hall and A. Randall *Radiolabelling of humic and fulvic materials for use in environmental studies,* Radiochim.Acta. 58/59 (1992) 371-376

2) Lars Carlsen, Peter Warwick, Pia Lassen and Amanda Randall,*Studies on humic acid labelling,* in press (presented at the MIRAGE plenary meeting, Bruxelles, apr. 1992

3) Peter Warwick, Lars Carlsen Amanda Randall, Rui Zhao and Pia Lassen, *^{14}C and ^{125}I labelling of humic material for use in environmental studies,* Chem.Ecol. in press

4) Lars Carlsen, Pia Lassen, Peter Warwick and Amanda Randall, *Radio-labelled humic- and fulvic acids: A new approach to studies on environmental fate of pollutants,* in press (presented at the IHSS-6th conference, Bari, sept. 1992)

5) Lars Carlsen, Pia Lassen, Peter Warwick and Amanda Randall, *Radio-labelled humic materials in migration studies,* in press (presented at the MRS Fall '92 meeting: Scientific Basis of Nuclear Waste Management, Boston, dec. 1992).

ROCK MATRIX DIFFUSION AS A MECHANISM FOR RADIONUCLIDE RETARDATION: NATURAL RADIOELEMENT MIGRATION IN RELATION TO THE MICROFRACTOGRAPHY AND PETROPHYSICS OF FRACTURED CRYSTALLINE ROCK : PHASE 1.

Contractors: University of Exeter (UK), University of Oviedo (E), Commissariat à l'Energie Atomique, Fontenay-aux-Roses (F), University of Liverpool (UK), University of Franche-Comté, Besançon (F), University of Oxford (UK).

Contract No.: FI2W-CT91-0082.
Duration of contract: 01.03.91 - 28.02.93.
Period covered: 01.01.92 - 31.12.92.

Project Leaders: M. J. Heath (Exeter), M. Montoto (Oviedo).

A. OBJECTIVES AND SCOPE.

Rock matrix diffusion is an important element in radionuclide migration models: diffusion from water-conducting fractures into the rock matrix provides a potentially important mechanism for the retardation of nuclides migrating from a repository. Recent studies of crystalline rocks have shown, however, that free diffusion of nuclides from fractures into the rock matrix does not always take place and that very little of the rock adjacent to fractures may be available for diffusion.

Although mathematical models describing diffusion have been developed in the past, they have never been furnished with complete physical and chemical data from actual sites. The aims of the study are: (1) to observe evidence of past diffusion of uranium and its daughters from fractures into the rock adjacent to fractures; (2) to relate observed diffusion phenomena to the physical properties of the rock; (3) to construct physicochemical profiles across fractures and into the adjacent rock to allow complete characterisation of past diffusion and assess the potential for future diffusion; and (4) to develop a mathematical diffusion model that can be validated by reference to geological evidence and be incorporated reliably into overall radionuclide migration models.

B. WORK PROGRAMME.

(1) Determination of rock properties and examination of evidence for past diffusion in a series of rock slices at distance of up to 50 cm from hydrogeologically-active fractures;
(2) Quantitative petrophysical analysis and the determination of key physical properties (accessible porosity, dry density, void index, kinetic water behaviour, dynamic properties);
(3) Quantitative microstructural analysis using optical, fluorescence, acoustic and confocal laser microscopy, digital image processing and stereological techniques;
(4) Geochemical analysis (major elements, iron chemistry, uranium and thorium, Rare Earth Elements, selected trace elements);
(5) Uranium disequilibrium studies by alpha spectrometry;
(6) Uranium microcartography by autoradiographic, fission track and SEM/EDX techniques;
(7) The development of a mathematical diffusion model based upon real geological/geochemical data.

C. PROGRESS OF WORK AND OBTAINED RESULTS.

State of advancement.

The study is being focussed on granite cores obtained from the El Berrocal field site in Spain. Owing to early delays in obtaining samples, the work programme has been compressed. Despite these difficulties, four cores have been obtained; analysis, using a wide variety of techniques, has reached different levels of advancement for each core. The work undertaken can be described under the following headings:

1. Field sampling, sample preparation and distribution (Oviedo, Exeter);
2. Petrophysical characterisation (Oviedo, Besançon, Oxford);
3. Uranium microcartography (CEA Fontenay-aux-Roses, Exeter);
4. Uranium series investigations (Exeter, Harwell);
5. Geochemistry (Exeter, CEA Fontenay-aux-Roses);
6. Uranium series diffusion modelling (Liverpool).

Complete profiles have been determined for two of the cores studied (EB4, EB5) while data for the other two (EB6, EB7) are still being obtained.

Progress and results.

1. Field sampling, sample preparation and distribution.

Four cores from the El Berrocal study site have been provided by the Centro de Investigaciones Energéticas, Medio Ambientales y Tecnológicas (CIEMAT) in Madrid (Table I). Initial sample collection has been coordinated jointly in Oviedo and Exeter, with subsequent core cutting in Exeter following non-destructive testing on intact cores in Oviedo.

Sample number	Borehole number	Depth	Comments
EB4	S-16	37.85 - 38.24 m	Fe deposition zone; altered and iron-stained near fracture; sub-horizontal fracture.
EB5	S-14	161.07 - 161.18 m	Carbonate zone; appears unaltered; sub-horizontal fracture.
EB6	S-14	119.90 - 120.50 m	Carbonate zone; appears unaltered; sub-vertical fracture.
EB7	S-14	227.60 - 227.73 m	Carbonate zone; appears unaltered; sub-horizontal fracture.

TABLE I. List of borehole core samples, El Berrocal.

Two cores with sub-horizontal fractures (samples EB4 and EB5) have been cut longitudinally and distributed for geochemistry and uranium disequilibrium studies, petrophysical analysis and mercury porosimetry, and full data sets are now available for these samples. Preliminary data are also available for a third core, EB6, which is a sub-vertical fracture for which the cutting scheme has been modified. The geometry of core EB6 means that a shorter profile is obtained (the maximum length of which is the core diameter). Non-destructive testing has also begun on sample EB7. Additional work has continued on oriented cores obtained by drilling in the mine adit.

By agreement, responsibility for sample preparation and sample distribution has been transferred from Oviedo to Exeter.

2. Petrophysical characterisation of the El Berrocal granite.

Different studies have been carried out to characterise petrophysically the rock matrix and to determine petrophysical profiles for each core in relation to distance from the fracture.

Before cutting, each core has been subjected to non-destructive testing in Oviedo using ultrasonic techniques to determine any possible anisotropy in the rock matrix. Following core cutting, a series of petrophysical parameters have been determined on rock slices obtained at different distances from the fracture.

Porosity has been determined in Besançon using mercury porosimetry techniques which provide an accurate evaluation of the range of pore dimensions along the accessible cracks in the rock. In order to understand the water dynamics through the rock matrix, a series of elemental physical properties (open porosity, void index, water content after two days, five days and under saturation) have been determined in Oviedo. Finally, the following petrographic components and parameters of petrophysical significance have been evaluated in Oviedo: volume percentage of minerals (Vv), specific surface of grains (Sv(grains)), mineral affinity, specific surface of microcracks (Sv(cracks)) and microcrack orientation. The best results have been obtained when very different microscopy techniques have been applied to the same thin section, combining the information obtained by polarising light, fluorescence, confocal laser scanning, acoustic and scanning electron microscopy, the latter coupled with energy dispersive X-ray analysis. The petrographic components thus observed have been mapped and quantified using stereology and digital image analysis of the images obtained.

Confocal laser microscopy has been applied in Oviedo for a real three-dimensional fractographic analysis of the rock matrix, specifically the relationship between the fissures and the rock-forming minerals, and the orientation of fissures (strike and dip). A geometrical procedure has been developed in Besançon to evaluate the dip of cracks as they are observed under fluorescence microscopy.

To quantify the weathering of feldspar crystals at grain level, acoustic microscopy had been applied in Oxford; the study has also attempted to evaluate possible anisotropies in small volumes of the rock matrix.

Non-destructive testing: ultrasonics.

The velocity (Vp) and flight time of longitudinal waves have been measured in cores prior to cutting. In samples EB5 and EB7, the flight time has been measured in "virtual" slices 11 mm thick and parallel to the fracture surface, along four directions (45° from each other), normal to the core axis. The results obtained show that, in general (but mainly in sample EB5), Vp is lower in the zone close to the fracture and is fairly constant away from the fracture.

This behaviour is the same in all of the measurement directions, although in sample EB5 (Figure 1), Vp is slightly higher in one direction that in the other three directions. It appears that an unobserved internal fissure exists in the core, crossing directions E_1R_1, E_2R_2, E_3R_3 (Figure 2). Microfissuration studies using different microscopy techniques are currently being undertaken to confirm this interpretation of the observed behaviour.

Sample EB6 has a sub-vertical fracture and has been analysed differently, measurements having been made along two directions normal and parallel to the fracture at different distances (Figure 3).

Physical properties.

Tests of open porosity, void index, water content after two and five days and under saturation have been performed on samples EB5 and EB6 following ASTM and ISRM standards and recommendations. The results are presented in Figures 4 and 5, where it can be observed that values decrease with increasing distance from the fracture.

Confocal laser microscopy.

Fluorescein-impregnated "thin" sections, mainly 300 μm but some 500 μm in thickness, have been studied under confocal laser scanning microscopy using a Leica CLSM. It has been shown that, under normal instrumental conditions, microfractographic information can be obtained at a depth of 170 μm into the rock thin section. In the work undertaken, particular attention has been paid to the microcrack network in altered feldspar grains, which have a high capacity for radionuclide retention.

A procedure is being developed to map the orientations of fractures automatically. The results obtained to date prove the usefulness of CLSM in the study of microcrack networks in rocks. Efforts are currently being aimed at the development of a quantitative microcrack analysis system, and at techniques for the determination of connectivity and tortuosity, which will be applied during Phase 2 of the project.

Acoustic microscopy.

Acoustic microscopy has been used to quantify the weathering of feldspar grains at grain level. The anisotropy of surface wave velocity, V(z), (and thus the elastic properties) of feldspar grains has been assessed in two thin sections prepared from sample EB4. The results of analysis of K-feldspar with the line focus beam acoustic microscope has revealed interesting anisotropy in surface wave velocity, values varying between 3000 and 5000 m/s.

V(z) curves have also shown that there are two modes of surface acoustic wave, suggesting that perhaps the longitudinal wave velocity could be used instead of Rayleigh wave velocity to quantify rock weathering at grain level.

Quantification of petrographic components.

Digital image analysis and stereological techniques have been applied in Oviedo to images obtained under different microscopy techniques using "vertical" thin sections (relative to the fracture surface) obtained from borehole core and from an orientated core (A1) drilled in the El Berrocal mine.

These studies have provided detailed information on the relationship between the different petrographic parameters, including the specific surface of microcracks that run across feldspar grains, specific surface of grain boundaries between quartz and feldspar and orientation of microcracks. The specific surface of microcracks running between or within the different minerals present is shown in Figure 6, for example, while the results obtained for the first 24 mm slice (nearest the fracture) from core A1 are summarised in Table II.

	Mineral percentage			Mineral specific surface (mm^{-1})			Mineral affinity			Fissure specific surface (mm^{-1})		
	Q	F	M	Q	F	M	Q	F	M	Q	F	M
Q	33	59	08	3.87	8.41	0.94	2.40	0.20	0.50	1.41	0.88	0.06
F								1.80	0.80		6.36	0.15
M									7.80			0.23
CE	2.8	1.8	1.1	9.7	8.0	9.4					5.5	

TABLE II. Quantitative petrographic data obtained from thin sections prepared from the first slice of core A1. CE = coefficient of error (%); Q = quartz; F = feldspar; M = mica.

It is now intended to compare these results with those obtained using fission track analysis at CEA Fontenay-aux-Roses in order to determine which microcracks have been exploited for uranium migration.

Mercury porosimetry.

Porosity profiles of sample EB4 have been obtained using mercury porosimetry in Besançon. Small cylinders (24 mm in diameter and 14.2 mm in height) have been drilled in rock slices cut parallel to the fracture surface. An irregular variation in porosity has been observed, varying

between 0.95% and 1.21%, with a mean of 1.14% (mean square deviation = 0.11%) (Figure 7). The distribution of microcrack diameters has also been calculated; Figure 8 shows this distribution for the rock slice obtained 12 - 24 mm from the fracture. Porosimetric analysis of the other cores is in progress.

3. Uranium microcartography.

The microdistribution of uranium in the El Berrocal granite has been mapped using fission track techniques (CEA Fontenay-aux-Roses) and alpha-autoradiography (Exeter) in order to understand better the migration behaviour of the element in the rock and identify migration pathways. Uncovered thin sections, cut perpendicular to the fracture surface, have been prepared from granite cores so that variation in the microdistribution of uranium with distance from the fracture can be observed. Sections for fission track analysis have been mounted on pure silica slides, while those for alpha-autoradiography have been mounted on conventional glass slides.

Fission track analysis.

Fission track analysis of sample EB4 has been carried out at CEA Fontenay-aux-Roses, and three major modes of uranium distribution have been observed:

- point sources showing very dense clusters of tracks associated with uranium-bearing accessory minerals ('resistate uranium'); the track density is proportional to the uranium concentration which increases from apatite and zircon, through monazite and xenotime, to uraninite and autunite;

- zones with scattered sources associated with the uranium enclosed within the major primary or secondary phases of the rock; this dispersed uranium can be mobilised during alteration processes; these scattered tracks are mainly associated with certain crystals of biotite, chlorite and altered plagioclases;

- inter- and intra-granular linear zones corresponding to uranium situated in microfissures, cleavages, grain boundaries etc.; it is this fraction of the uranium which is most easily mobilised; a good correlation exists between the linear track distributions and iron oxyhydroxide microfracture fillings.

Qualitative evaluation of the track density associated with these three modes of distribution of uranium has shown that (1) there is a fairly heterogeneous distribution of the uranium-bearing accessory phases; (2) there is a fairly homogeneous distribution of the scattered tracks; and (3) there is a strong increase in the density of linear track features close to the fracture.

Alpha-autoradiography.

Alpha-autoradiographic analysis of sample EB4 has been carried out in Exeter for comparison with the results of fission track analysis. Nine thin sections have been studied, corresponding in position to each of the fission track sections, using CR39 film over an exposure period of 11 weeks. As in the fission track work, the results show alpha-particle sources to be distributed (1) as point sources, (2) dispersed within

certain major mineral phases, notably biotite, and (3) concentrated along microfissures. As in the fission track analysis, the density of microfractures containing alpha sources is greatest close to the fracture.

4. Uranium series investigations.

Uranium series investigations are being carried in Exeter and Harwell to determine key activity ratios in rock slices from each sample core.

Interlaboratory comparison, alpha spectrometry.

Granite powders from sample EB4 have been divided and analysed by alpha spectrometry at both Exeter and Harwell as an interlaboratory comparison to ensure the quality of the data being obtained. The results have shown a generally good correspondence between the two laboratories.

Uranium series profiles.

Results from sample EB4 show a uranium enrichment on the fracture surface (27 ppm), falling within a centimetre or so of the fracture to levels of 13 - 14 ppm (Figure 9). The fracture surface also shows an enrichment in radium. The rock immediately adjacent to the fracture also has a high U-234/U-238 isotopic ratio, again falling rapidly to values nearer equilibrium within 25 mm of the fracture (Figure 9). These uranium characteristics are reflected in the iron chemistry which shows an increase in the iron oxidation in the 20 mm immediately adjacent to the fracture.

Both the U-238 and Ra-226 profiles appear to have a diffusional shape, though the radium profile is a little erratic within the rock matrix. The U-234/U-238 data also support a diffusional origin for the profile.

Preliminary results from sample EB5 suggest that a uranium profile similar to that observed in EB4 may be present, but further analyses are required before this can be confirmed.

5. Geochemistry.

Major and trace element geochemistry is being determined in Exeter and CEA Fontenay-aux-Roses. These studies are paying particular attention to geochemical variation (major elements, selected trace elements, Rare Earth Elements, iron chemistry) in the rock close to fractures.

Uranium and thorium.

The uranium concentration profile for sample EB4 shows that mobilisation of this element has taken place close to the fracture (Figure 9), there being an enrichment immediately adjacent to the fracture where concentrations of 27 ppm are observed. Two other samples from about 10 cm from the fracture also show some enrichment in the data obtained by NAA. The samples from between 0.5 cm and 5 cm from the fracture have relatively low uranium conventrations. Beyond 10 cm, uranium values are again low and not significant. The uranium enrichment at around 10 cm from the fracture is not observed in the XRF data. Very small samples were used in the neutron activation analyses and the uranium values obtained may have been significantly affected by the presence of small, imperfectly crushed, accessory minerals with high uranium values; in the larger samples used in the XRF analysis, the influence of these small accessories is much smaller.

The profile obtained for thorium does not show any mobilisation of this element.

In contrast to the results from sample EB4, the geochemical uranium data for sample EB5 shows no significant uranium enrichment on the fracture surface but only a slight increase in uranium concentrations in the rock adjacent to the fracture. The isotopic data do suggest, however, that there has been some surface deposition of uranium. Further data are awaited before firm conclusions can be reached for the EB5 profile. As in EB4, the thorium data for EB5 show fairly constant values throughout the profile.

Rare Earth Elements.

The chondrite-normalised Rare Earth spectra have been obtained for sample EB4. The Rare Earths analysed (La, Ce, Sm, Tb, Yb) do not show any significant mobilisation on the scale of the whole rock. A good correlation is observed between thorium and Rare Earth concentrations. An excellent superposition is observed for the Rare Earth spectra from each of the rock slices analysed in the profile, confirming the low mobility of the REE in the environment of the fracture.

Iron chemistry.

Results from sample EB4 show an increase in the oxidation of iron in the 20 mm or so immediately adjacent to the fracture with fairly constant levels for the rest of the profile studied. There is a slight enrichment in total iron on the fracture surface. The iron oxidation profile correlates well with the uranium profile (Figure 9) suggesting that the redox conditions exercise a strong control over uranium mobility in the near-fracture environment. In sample EB5, both total iron and the level of iron oxidation fall near the fracture, reflecting the different geochemical environment at the greater depth from which this sample was obtained.

Other elements.

Hafnium, scandium, rubidium and cesium show no significant mobilisation in the EB4 profile. The results are particularly interesting for the alkali elements (Rb, Cs) which are readily mobilised in many geochemical environments. Sodium also shows no mobilisation near the fracture. In contrast, arsenic and antimony are enriched close to the fracture, and a good correlation is seen between arsenic and uranium. Zinc and manganese are also significantly enriched on the fracture surface.

6. Uranium series diffusion modelling.

The data being acquired in the various studies described above will provide the input for a mathematical diffusion model being developed in Liverpool. The intention is to model the uranium concentration and uranium isotopic activity ratios with distance from the fracture for comparison with the observed profile data in order to estimate values of the solid/solution exchange coefficient, Kd, and effective diffusivities. Modelling studies to date have used the data from published sources, data from the present study being incorporated as they become available.

A review of existing data has shown that values of 'long-term' Kd for uranium can be estimated simply by comparing the enrichment of uranium in the near-fracture rock with the concentrations commonly encountered in

fracture water. This simply assumes that fracture water and alteration minerals near the fracture are in equilibrium with respect to ion-exchange of uranium. It is the decrease in uranium concentration within a few centimetres of the fracture (as seen in the EB4 profile) that suggests that uranium has migrated by diffusion from the fracture. Thus, the uranium diffusion models can be made to fit most of the published profile data without too much trouble. It appears that, whether the uranium originates in the fracture water or the interior of the core-block, the high enrichment often seen in the data shows that 'long-term' Kd values can be as high as 10 m^3/kg. This value is at the upper end of the range estimated from laboratory estimates.

The U-234/U-238 profile values are, however, incompatible with these simple models. As far as the U-234/U-238 activity ratios are concerned, it can generally be observed from some profiles that U-234/U-238 values near the fracture are often less than or equal to unity, despite there being enrichment of uranium in the same zone. This is in contrast to the U-234/U-238 activity ratios of fracture water which are often greater than unity. As most chemical reaction rates of oxidation of iron, of U (VI) to U (IV), and absorption of uranium onto iron are likely to be much faster than the decay or growth of U-234, either there cannot be a simple state of exchange equilibrium in the near fracture zone between uranium in the alteration mineral and uranium in the water, or other processes are in operation.

One area of difficulty is associated with the complex distribution of uranium in the rock (in primary phases, accessory minerals and along microfractures). It seems very likely that the analyses presented in the profiles are characterised by U-234/U-238 ratios of < 1 in the primary grains and an intergranular uranium in which the U-234/U-238 ratios may be nearer to that of the contacting water. If this is correct, there is a need to carry out uranium series analyses of mineral separates, particularly of the intergranular uranium in the current El Berrocal samples. Unfortunately, this is probably not feasible for core profiles as there is not sufficient material to work with. The results of fission track analyses do, however, provide useful information here, as it is possible to identify the relative distributions of uranium in primary phases, accessory minerals and along microcracks, and detailed analysis of the fission track images is now in progress.

List of publications.

HEATH, M. J., MONTOTO, M., RODRIGUEZ REY, A., RUIZ DE ARGANDOÑA, V. G. and MENENDEZ, B. (1992). Rock matrix difusion as a mechanism of radionuclide retardation: a natural analogue study of El Berrocal granite, Spain. Radiochimica Acta, 58/59, 379-384.

MONTOTO, M., RODRIGUEZ REY, A., MENENDEZ, B., MARTINEZ-NISTAL, A., RUIZ DE ARGANDOÑA, V. G., SUAREZ DEL RIO, L. M. and CALLEJA, L. (1992). Microfractography of "El Berrocal" granite. Proc. 5th NAWG/ARAP Meeting, Toledo.

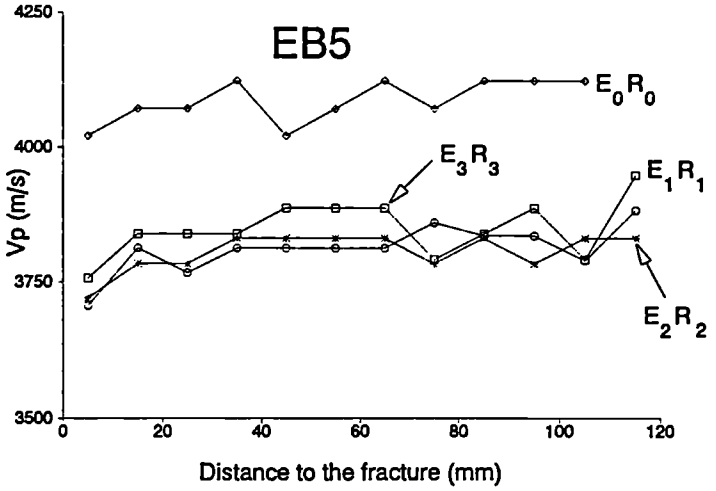


Figure 1. Longitudinal wave velocity (Vp) profiles, sample EB5, corresponding to the four directions of Figure 2, normal to the core axis.

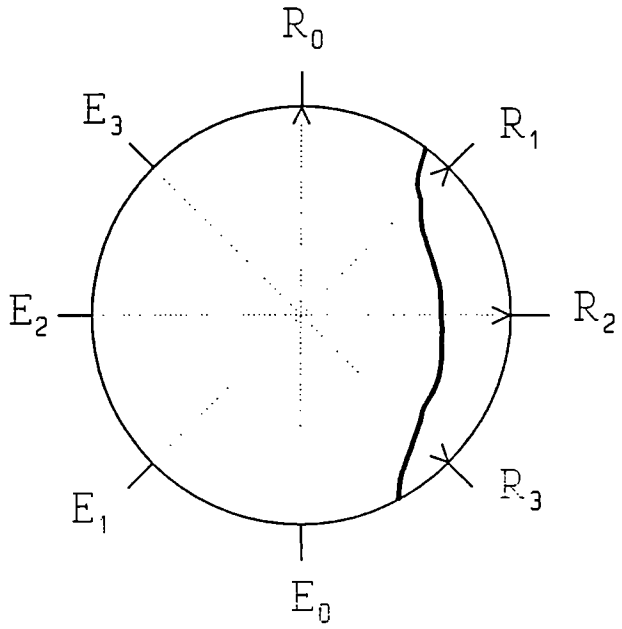


Figure 2. Sketch of the four directions along which the Vp measurements of EB5 have been made. A microcrack seems to run across three of these directions.

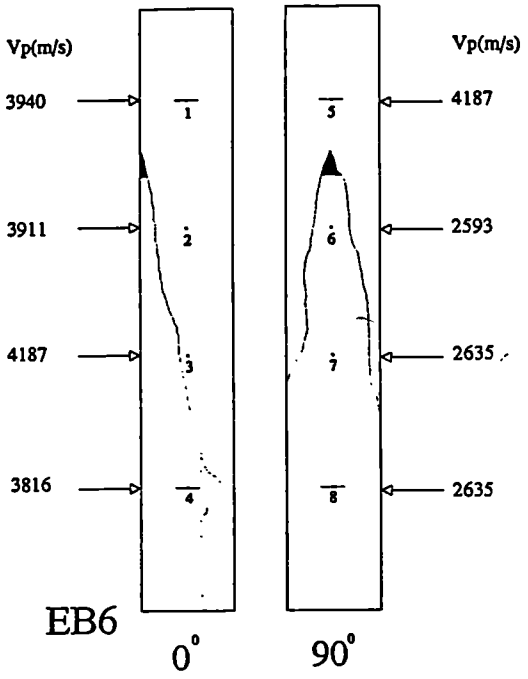


Figure 3. Sketch of core sample EB6 with the values of Vp and transducer locations (1, 2, 3...).

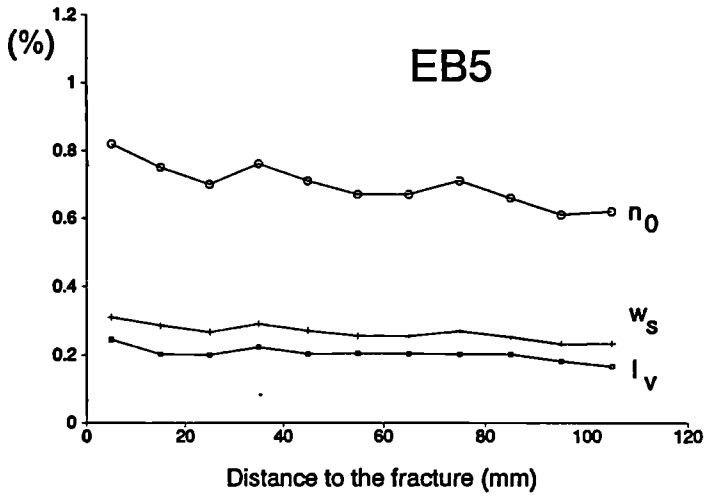


Figure 4. Physical property profiles of sample EB5. nO = open porosity; Iv = void index; Ws = saturation water content.

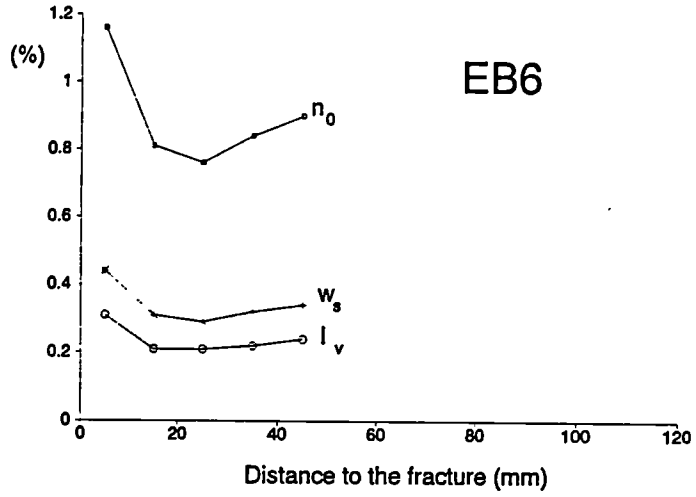


Figure 5. Physical property profiles of sample EB6.
nO = open porosity; Iv = void index; Ws = saturation water content.

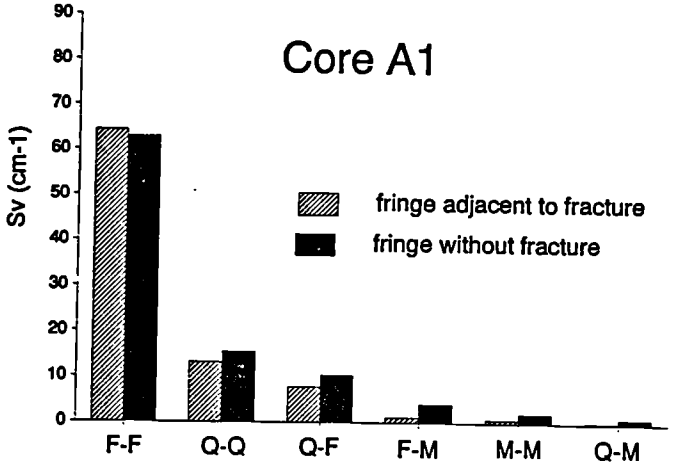


Figure 6. Mean values of the specific surface of microcracks that run between or across the different rock-forming minerals, measured in vertical sections in core A1. Each thin section is divided into two zones (fringes), one of which contains the fracture on one side, the other of which is about 12 mm from the fracture.
F = feldspar; Q = quartz; M = mica.

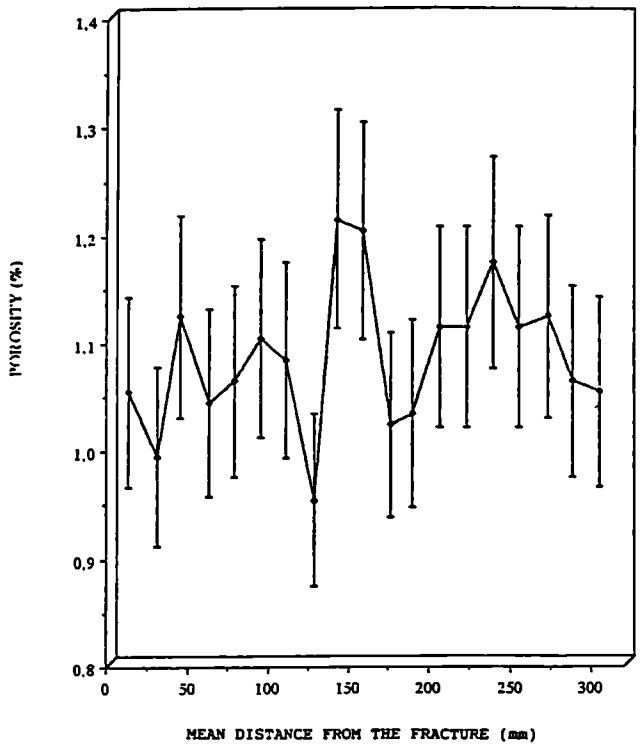


Figure 7. Mercury porosity profile of sample EB4.

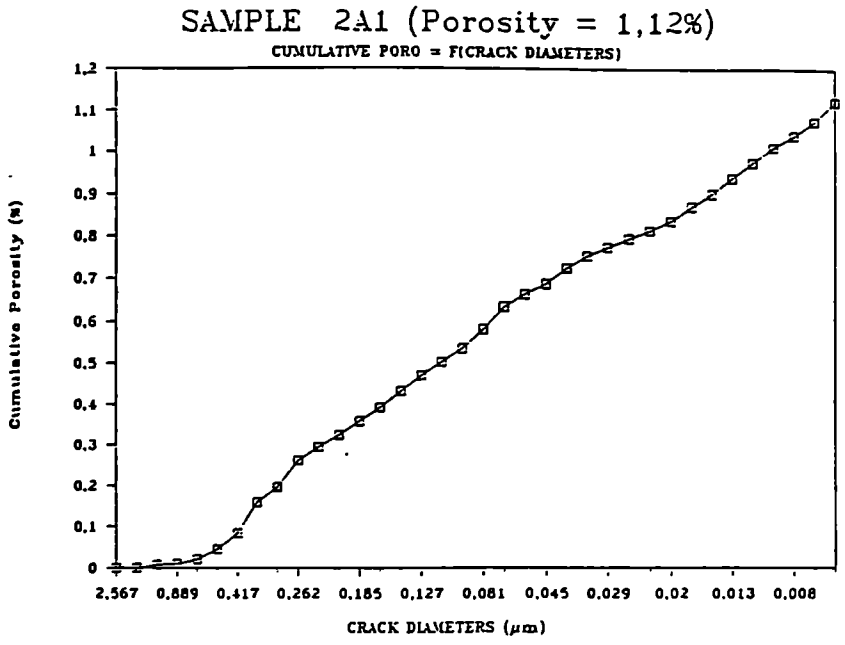


Figure 8. Distribution of microcrack diameters obtained by mercury porosimetry, sample EB4, 12 - 24 mm from the fracture.

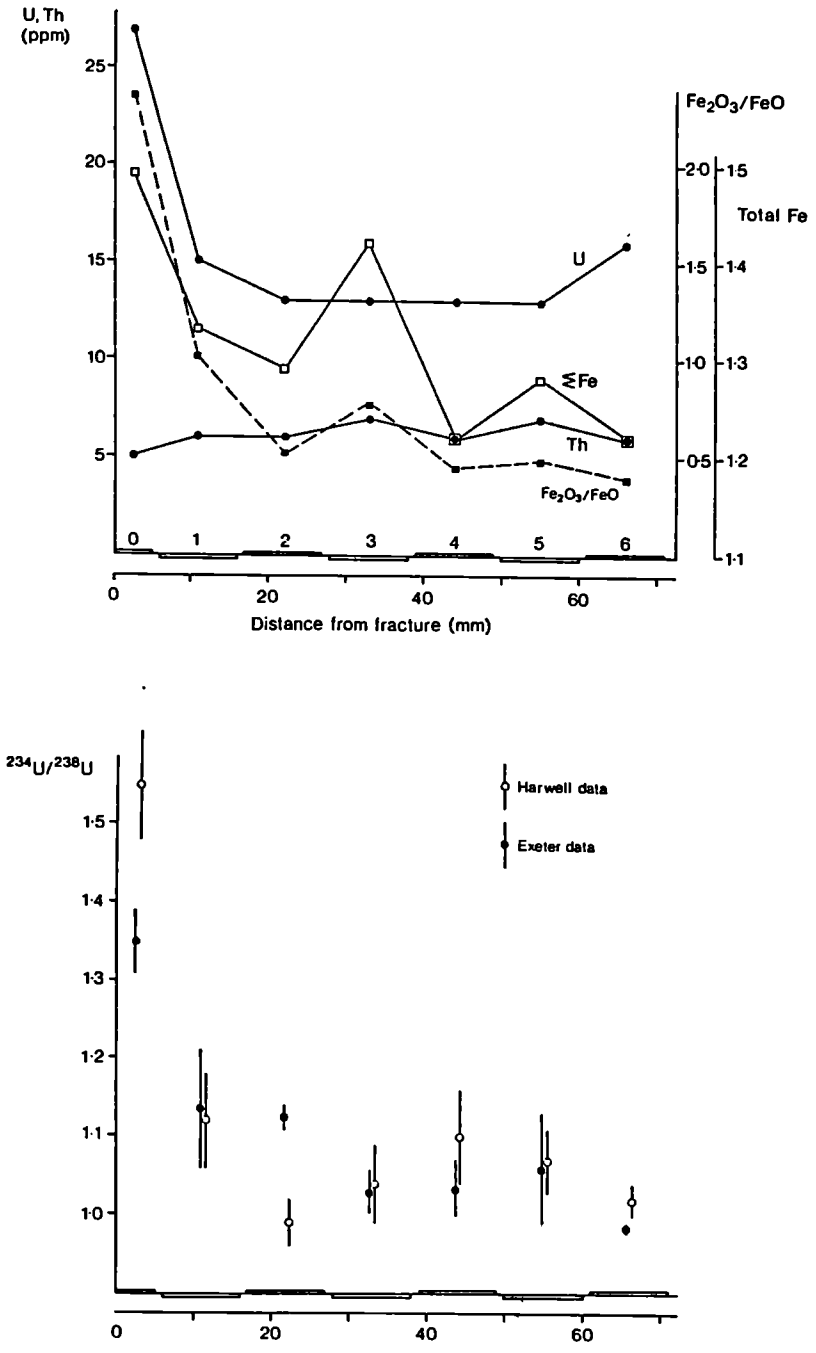


Figure 9. Geochemical profile, El Berrocal sample EB4:
Above, variation in U, Th, total Fe and Fe oxidation with distance from the fracture (using XRF data); Below, variation in U-234/U-238 activity ratios, comparing Exeter and Harwell data (error bars 1 σ).

Effects of Humic Substances on the Migration of Radionuclides: Complexation of Actinides with Humic Substances

Contractor:	Institut für Radiochemie, Technische Universität München
Contract N°:	FI 2W-CT91-0083
Duration of the contract:	July 1991 - June 1994
Period covered:	January 1992 - December 1992
Project leader:	J.I. Kim, G. Buckau

A. OBJECTIVES AND SCOPE

The aim of the present research programme is to study the complexation behaviour of actinide ions with humic substances in natural aquifer systems and hence to quantify the effect of humic substances on the actinide migration. Aquatic humic substances commonly found in all groundwaters in different concentrations have a strong tendency towards complexation with actinide ions. This is one of the major geochemical reactions but hitherto least quantified. Therefore, the effect of humic substances on the actinide migration is poorly understood. In the present research programme the complexation of actinide ions with humic substances will be described thermodynamically. This description will be based on a model being as simple as possible to allow an easy introduction of the resulting reaction constants into geochemical modelling of the actinide migration. This programme is a continuation of the activities of the COCO group in the second phase of the CEC-MIRAGE project.

The laboratories participated in the research programme are:

TUM:	Technische Universität München (coordinator: J.I. Kim, G. Buckau)
CEA-FAR:	Centre d'Energie Atomique, Fontenay-aux-Roses (V. Moulin)
UM:	Universität Mainz (N. Trautmann)
KUL:	Katolieke Universiteit Leuven (A. Maes)
JRC-Ispra:	Joint Research Centre, Ispra (G. Bidoglio)

B. WORK PROGRAMME

The programme consists of the following three main tasks:

Task 1: Complexation reactions of actinide ions with well characterized reference and site-specific humic and fulvic acids

Task 2: Competition reactions with major cations in natural groundwaters

Task 3: Validation of the complexation data in natural aquatic systems by comparison of calculation with spectroscopic experiment

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

In this report period a number of methodical developments are in progress. The effective ligand concentration is one of the important parameters for the evaluation of the metal ion complexation behaviour of bulk polyelectrolytes like humic or fulvic acids. Studies by KUL and TUM show that the effective ligand concentration of humic acid is related to the protonation of the ion exchanging groups. For a precise evaluation of the complexation reaction, however, a direct measurement of the effective ligand capacity under given experimental conditions is necessary. The humate and fulvate complexation has been studied for tri- and pentavalent actinide, and lanthanide ions, over a wide experimental range. pH is varied between 3.0 and 9.0, the ionic strength between 0.001 and 3.0 M with metal ion concentrations between 10^{-14} and 10^{-4} mol/L. Competition reactions with Ca(II) and Cr(III) are investigated by KUL, CEA, JRC-Ispra and UM. Studies over this wide experimental range is important, considering the different conditions to be found in various geological formations. For validation of the experimental results seven different experimental methods are used.

Progress and results

1 Complexation reaction of actinide ions with reference and site specific humic acids.

For the present study, humic and fulvic acids from three different sites and a commercial humic acid from Aldrich Co. are used. They are purified, protonated and characterized previously [1-4]. The commercial product is included as a reference material for the purpose of intercomparison. These products are named as follows:

Gohy-573 HA:	Humic acid from Gorleben (FRG)
Gohy-573 FA:	Fulvic acid from Gorleben (FRG)
Fanay-Augeres HA:	Humic Acid from Fanay Augeres (F)
Fanay-Augeres FA:	Fulvic Acid from Fanay Augeres (F)
Boom-Clay HA:	Humic acid from Boom Clay (B)
Boom-Clay FA:	Fulvic acid from Boom Clay (B)
Aldrich HA(I):	Humic acid from Aldrich Co. (Commercial)

The participating laboratories have agreed upon the introduction of additional batches of the reference humic acid, since the original amount purchased was not sufficient to meet with growing experimental demands. KUL and UM prepared batches of Aldrich HA: KUL (Aldrich HA(II)) and UM (Aldrich HA(III)). KUL has furthermore purified and characterized humic acid from Podzol B as an additional product for comparison.

Methods of isolation and purification of humic substances as well as the results of characterization are described elsewhere [1-4].

For interpretation of the complexation behaviour, the proton exchange capacity of each humic substance is of main importance. The proton exchange capacities of the studied humic substances determined by different groups using pH-titration are:

	Proton exchange capacity (in meq/g)			
	TUM	CEA-FAR	KUL	JRC-Ispra
Aldrich HA(I)	5.43 ± 0.16	6.0 ± 0.5	2.7/3.9[1)]	5.24
Aldrich HA(II)	4.18 ± 0.15		4.38 ± 0.07	
Aldrich HA(III)	4.61 ± 0.11			
Gohy-573 HA	5.38 ± 0.20	5.2/5.2	3.5/4.5[1)]	
Gohy-573 FA	5.70 ± 0.09			
Fanay-Augeres HA	1.85 ± 0.05	3.4 ± 0.2		
Fanay-Augeres FA	6.93 ± 0.06	5.7		
Boom-Clay HA	4.22 ± 0.02			
Boom-Clay FA		Under investigation		
Podzol-B HA			5.4	

1): pH=7/10

1.1 Experimental techniques

TUM

UV/Vis-spectroscopy, time resolved laser fluorescence spectroscopy (TRLFS) and ultrafiltration are applied for the study of the M(III)-humate complexation. UV/Vis-spectroscopy is used for the study in the µmolar concentration range of both Am(III) and humic acid. By TRLFS the Cm-humate complexation is investigated in the nmolar concentration range with a low loading of the humic acid ligand. By energy transfer from humic acid molecules to metal ions, the fluorescence yield of the Cm-complexes is enhanced. By selective excitation at different wavelength, the spectroscopic speciation of Cm^{3+} and Cm-complex is optimized. Ultrafiltration is used for the Am-humate complexation study covering the metal ion concentrations ranges of both spectroscopic methods.

CEA-FAR

TRLFS is applied for the study of the humate complexation of Cm and Dy using fixed excitation wavelength of 337 nm and 355 nm, respectively. Further development of this

technique by coupling with a dye laser to allow variation of the excitation wavelength is in progress. The competition effect of Ca on the Dy-humate complexation is also studied by this method. By UV/Vis-spectroscopy the humate complexation of Np(V) is investigated. The complexed and the free NpO_2^+ ions are quantified by the extinctions at 991 nm and 981 nm, respectively.

UM

A three step-laser-resonance-ionization mass spectroscopy system is used for the detection of actinides in the femtomol concentration range. This detection system is coupled with two different experimental methods for the separation of the NpO_2^+ ion from the complexed form. The separation techniques are electrophoretic ion focusing and ion exchange chromatography. The first experiment applying the separation methods on the humate complexation of Sm(III) is performed.

KUL

Two different experimental methods are used for the study of the Eu-humate complexation. The cation exchange technique has been used by KUL over several years [5,6]. The competition of Ca on the Eu-humate complexation is also studied by this method. The second experimental method is the dialysis technique. By both experimental techniques the influence of different competing ligands (oxalic acid, diglycolic acid, iminodiacetic acid and acetylacetone) on the Eu-humate complexation is also studied.

JRC-Ispra

TRLFS and continuous fluorescence measurements are applied for studies of the complexation of REE (rare earth elements) with humic acid as well as the competition effect of Cr(III). By TRLFS the fast fluorescence of the humic acid is separated from the fluorescence of REE. In the continuous fluorescence measurement, the quenching of the fast fluorescence from humic acid is a measure for the complexation.

1.2 Results of the complexation study

TUM

The humate complexation of trivalent actinides with Gohy-573 HA is investigated at pH between 3.0 and 6.0 and the ionic strength between 0.1 M and 3.0 M. The metal ion concentration is varied from the nmolar to the µmolar ranges in order to examine whether the degree of loading of the humic acid influences the complexation behaviour. By UV/Vis-spectroscopy the species involved are quantified by spectral peak deconvolution. By TRLFS the fluorescence titration method is used (cf. CEA). Using ultrafiltration the

free metal ion is separated from the colloidal humate complex by their size difference. No significant difference in the results is found between the three experimental methods.

The loading of the humic acid by Cm(III) or Am(III) varies from approximately one percent to a level of saturation in the pH ranges under investigation. No influence on the complexation constant with the degree of loading is observed. The complexation constant for Gohy-573 humic acid is found to be: logß(An(III)-humate) = 6.18 ± 0.15. The complexation constant for this humic acid is somewhat higher than that for the fulvic acid of the same origin (logß = 5.86 ± 0.11 [7]). Comparing the results for the Gohy humic acid with previous studies for Aldrich humic acid and Bradford humic acid [8-10], no significant differences in the reaction mechanism and the complexation constant are found.

CEA-FAR

The complexation of Cm and Dy with humic acid is investigated between pH 4.2 and 6.9 at constant ionic strength of 0.1 M. To investigate the influence of the ionic strength the Cm(III) humate complexation is also studied in 0.001 M $NaClO_4$ at pH 4.2 and 6.1. The experimental method is based on measuring the total fluorescence intensity as a function of the humic acid concentration at a constant metal ion concentration. The quantification of the humate complex and free metal ion is made by analysing the fluorescence titration curve [11].

The effective ligand concentration, expressed as a complexation capacity, is found to be dependent on pH, ionic strength and the total metal ion concentration. The complexation constants evaluated by taking the complexation capacity into account are found to be independent of pH and ionic strength. This is in agreement with the results from TUM and KUL. However, the complexation constants determined by CEA-FAR are found to vary significantly with the metal ion concentrations. Similar results have previously been found by JRC-Ispra [12,13].

Experiment on the Np(V) humate complexation shows the result similar to those found by TUM [14] and UM. Further measurement and detailed examination of the data are in progress.

UM

The complexation of Np(V) in the femtomolar concentration range with Aldrich and Gohy humic acids is investigated. The humic acid concentration is varied between 20 mg/L and 200 mg/L (appr. 0.1 to 1.0 mmol/L). In order to investigate the influence of pH and ionic strength on the complexation reaction, pH is varied from 3.0 to 9.0 and ionic strength from 0.001 M to 0.1 M.

Over the whole experimental range a 1:1 complex is found to be the main complexed species. Due to the low metal ion concentration, a saturation of the humic acid ligand by the NpO_2^+ ion is not approached. Therefore, the loading capacity cannot be evaluated and, on calculating the complexation constant, the effective ligand concentration is not taken into account. For this reason direct comparison of the "apparent" complexation constants (logß*) from this work with published data from TUM [14] is difficult. The evaluated apparent Np(V) humate complexation constant is described by the following relation:

$$\log\beta^* = (0.39 \pm 0.02) \times pH + (1.93 \pm 0.16)$$

No difference in reaction mechanism between the Aldrich and Gohy humic acids is found. However, the complexation strength of the Gohy humic acid is found somewhat higher.

KUL

The complexation of Eu(III) with Podzol humic acid and Aldrich humic acid is studied. The Eu(III) concentrations are 3×10^{-7} and 3×10^{-8} mol/L and the humic acid concentration is varied between 10^{-5} and 10^{-4} mol/L. pH is varied from 4.0 to 10.0 in 0.1 M $NaClO_4$. In the non-hydrolysing range (pH 4.0 - 6.0) no influence of pH on the complexation constant is found if the variation of the free ligand concentration is taken into account ($\log\beta = 6.88$). In the presence of competing ligands the formation of Eu humate complexes is strongly enhanced and data are interpreted by "apparent" complexation constants for the formation of mixed complexes. This interpretation is used not only for added ligands like oxalic acid but also for the hydroxyl and carbonate ions. The critical carbonate concentration for the formation of mixed humic acid/carbonate complexes is evaluated to be 10^{-6} mol/L. It is concluded that for modelling under in situ conditions the formation of mixed complexes of Eu(III) with humic acid and hydroxyl ions as well as carbonate ions should be taken into account.

2 Competition reactions with cations in natural groundwaters

CEA-FAR

The competition effect of Ca(II) on the Dy(III)-humate complexation is studied at pH 5.0 in 0.1 M $NaClO_4$. At Dy and humic acid concentrations of 2×10^{-6} mol/L and 3.3 mg/L, respectively, the Ca concentration is varied between zero and 34 mmol/L. At the maximum Ca concentration a decrease of the fluorescence signal of approximately 40% from the Dy-humate complex is observed. However, in the average Ca concentration

range of natural waters ($1x10^{-5}$ to $4x10^{-3}$ mol/L) no significant effect on the Dy-humate complexation is found.

UM

The influence of the Ca concentration on the Np(V)-humate complexation is examined by electrophoretic focusing used for species separation. Experiments are done at pH 5.0 in 0.1 M $NaClO_4$ with 10^{-13} mol/L Np(V) and a humic acid concentration of 30 mg/L. Ca is shown to have a considerable effect on the Np(V)-humate complexation. Increasing the Ca concentration from 10^{-6} mol/L to 10^{-3} mol/L, the concentration ratio of complexed Np to the free ion decreases by a factor of approximately 7.

KUL

Studies on the competition effect show that high Ca concentrations are necessary to diminish the Eu(III)-humate complexation. At a Ca concentration of 10^{-2} mol/L the Eu(III)-humate complexation is decreased by approximately 0.3 log units.

JRC-Ispra

JRC-Ispra has studied the competition effect of Cr(III) on Tb(III) and Eu(III) with humic acid (Gohy-573 HA) at pH=5.5 in 0.1 M $NaClO_4$. Kinetic studies show that the equilibration of Eu(III) and Tb(III) is fast, whereas the exchange equilibrium with Cr(III) requires approximately 24 hours. The complexation strength of Cr(III) with humic acid is of similar strength as Eu(III) and Tb(III). The complexation constant derived for Cr(III) is $\log\beta_{(Cr(III)\text{-}HA)} = 6.3$. This confirms that the magnitude of the complexation mainly depends on the oxidation state of the metal ion [12,13].

3 Validation of the results in natural aquatic systems by comparison of calculation with spectroscopic experiment

Work on this task is in progress.

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COLLOID MIGRATION IN GROUNDWATERS: GEOCHEMICAL INTERACTIONS OF RADIONUCLIDES WITH NATURAL COLLOIDS

Contractor:	Institut für Radiochemie, Technische Universität München
Contract N°:	FI2W/0084
Duration of contract:	May 1991 - April 1994
Period covered:	January 1992 - December 1992
Project Leader:	J.I. Kim, B. Delakowitz

A. OBJECTIVES AND SCOPE

The aim of the joint research programme is to determine the significance of groundwater colloids in far field radionuclide migration. The characterization, quantification and theoretical interpretation of colloid-borne transport phenomena of radionuclides in selected Gorleben aquifer systems are the main objectives of the present research programme. Gorleben aquifer systems are chosen because they are well characterized in terms of their hydrological and geological properties and because they contain substantial amounts of colloids of different chemical compositions as well as considerable quantities of chemical homologues and natural analogues of radionuclides, e.g. M(III), M(IV), M(VI), and Th and U decay series. The research tasks are investigated jointly by the four laboratories (listed below) in close coordination of experimental capacities of each laboratory.

TUM: Technische Universität München, F.R.G. (coordinator: J.I. Kim, B. Delakowitz)
AEA: AEA Technology, Harwell, U.K. (M. Ivanovich)
GSF: Gesellschaft für Strahlen- und Umweltforschung, München, F.R.G. (P. Fritz)
Atkins: W.S. Atkins Engineering Sciences, London, U.K. (D. Read)

B. WORK PROGRAMME

B.1 Sampling of groundwaters, colloids and sediments under well controlled conditions (TUM, AEA, GSF)

B.2 Characterization of colloids, groundwaters and sediments (TUM, AEA, GSF)

B.3 Generation of pseudocolloids of radionuclides ($Z \geq 3^+$): Am(Eu) for M(III), Pu(Th) for M(IV), Np for M(V), U for M(VI); (TUM)

B.4 Transport process study by scaled column experiments (TUM, GSF, AEA, Atkins)

B.5 Synthesis and theoretical interpretation (Atkins ES)

B.6 Liaison with related studies within the MIRAGE programme (e.g. calculation tool)

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The sorption of highly charged ($Z \geq 3^+$) actinide ions onto groundwater colloids can be considered in terms of the generation of actinide "pseudocolloids". The latter play an important role for the migration behaviour of actinides in the geosphere [1, 2]. Previous studies in the second phase of the CEC-MIRAGE project [3] demonstrated the importance of the generation of pseudocolloids and their migration for the quantitative description of colloid-associated radionuclide migration in given aquifer systems. For the present study, groundwater samples and sediments were collected from four boreholes that penetrate the geologically and chemically heterogeneous Gorleben aquifer systems [4]. The sampled groundwaters were submitted to parallel ultrafiltration using filters of different pore sizes to estimate the size and quantity of natural colloids present. Groundwaters, colloids and sediments have been characterized for their chemical composition and physical properties. Trace elements of higher oxidation state ($\geq 3+$) in groundwaters are found to be strongly sorbed onto humic colloids with a size range between 100 nm down to about 1 nm. The sorption onto and the desorption from the humic colloids is shown to be reversible and pH dependent. Different ^{14}C contents in the humic acid (HA) and the fulvic acid (FA) fractions allow the assumption of FA being originated from near-surface soil, whereas the HA fraction may be originated from the organic matter of older sediments (lignite). Hydraulic properties of scaled sand columns for the study of radionuclide transport are determined using ^{3}HHO and $^{82}Br^-$ radiotracers. Results indicate still differing hydraulic conditions.

Progress and results

1 Sampling of groundwaters, colloids and sediments

Groundwater and colloids were collected anaerobically (N_2 + 1% CO_2) from selected aquifer systems from the geological site foreseen for the future German nuclear waste repository at Gorleben. The sampling procedure is explained in detail in the previous report [4]. Sediments were collected from drill cores, corresponding to sampled boreholes.

2 Characterization of groundwaters, colloids and sediments

Different analytical tasks, coordinated and arranged by the participating laboratories are:
- Chemical composition of groundwater, colloids and sediments (TUM, AEA),
- Size distribution and population quantification by SEM/TEM, LPAS and ultrafiltration (TUM) and PCS and TEM techniques (AEA),
- Provenance of colloids by isotope analysis (GSF, AEA),
- U-series disequilibrium study on colloids, groundwaters and sediments (AEA).

2.1 Experimental techniques

Analytical methods and laboratory techniques employed by TUM, AEA and GSF for the characterization of groundwaters, colloids and sediments are described elsewhere [4, 5].

2.2 Chemical composition of groundwater and colloids

The physical characteristics, partly measured in the field, and the chemical compositions determined in groundwaters of boreholes Gohy 572, Gohy 611, Gohy 573 and Gohy 2227 are varying due to their different aquifer conditions [4]. The salinity, given as an electrical conductivity ($\mu S\ cm^{-1}$) generally increases with the aquifer depth and, as expected, the highest salinity among the four groundwaters is found in the one (Gohy 2227) nearest to the salt dome surface. High DOC concentrations are found in Gohy 573 and Gohy 2227. These boreholes are intersecting stratigraphic intercalations of lignite within the sampled aquifers. There is no correlation between the salinity and DOC concentration. DOC in the groundwaters, separated and characterized according to a known procedure [6] is observed as a composite of humic and fulvic acids, which are loaded with various metal ions and behave as colloids. For this reason they are named "humic colloids".

Ultrafiltration using a flat bed filter system with a variety of nominal filter pore sizes from 1000 nm down to about 1 nm was carried out for the four groundwaters under investigation. Concentrations of DOC in the filtrates show a gradual decrease with decreasing the pore size of filters. At the smallest pore size of about 1 nm, between 91.2% (Gohy 2227) and 95.7% (Gohy 573) of DOC are filtered whereas the measured values for DOC in the filtrates at 1000 nm, 450 nm and 100 nm are almost identical (Fig. 1). From these data and according to the results obtained from the earlier work [6, 7], it is apparent that the predominant amount of humic colloids is found in the size range less than 100 nm down to about 1 nm.

The filterable amount of DOC and the M^{2+}-, M^{3+}-, M^{4+}- and U-ion present in the humic rich groundwater Gohy 2227 is shown in Fig. 2. At the smallest pore size available, about 91.2% of the DOC, 16.4% of M^{2+}, 87.3% of M^{3+}, 88.7% of M^{4+} and 65% of U are filtered off, the values being an average of analytical data obtained from three different samples of groundwater Gohy 2227: Gohy 2227/1, Gohy 2227/2 and Gohy 2227/3. In Fig. 2, it is apparent that the amount of the divalent alkaline-earth metal ions Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} filtered at 1 nm is lower compared to the filterable amout of the metal ions of higher oxidation state ($\geq 3+$). This can be explained by the lower complexation strength of the divalent metal ions towards humic substances ($\log \beta = 3.8 - 4.7$ [6, 8]) compared to that of the higher valent metal ions ($\log \beta = 6 - 13$ [6, 11]). The amount of colloid bound U in the samples is somewhat lower (65%).

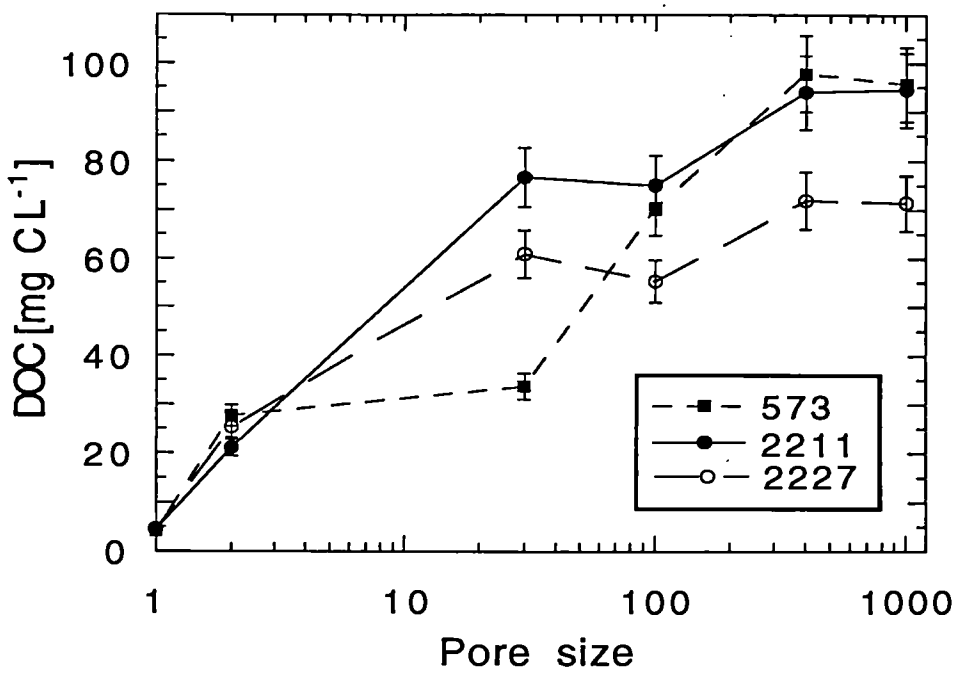

Figure 1: DOC concentration in ultrafiltrates of the groundwaters Gohy 573, Gohy 2211 and Gohy 2227 at different pore sizes

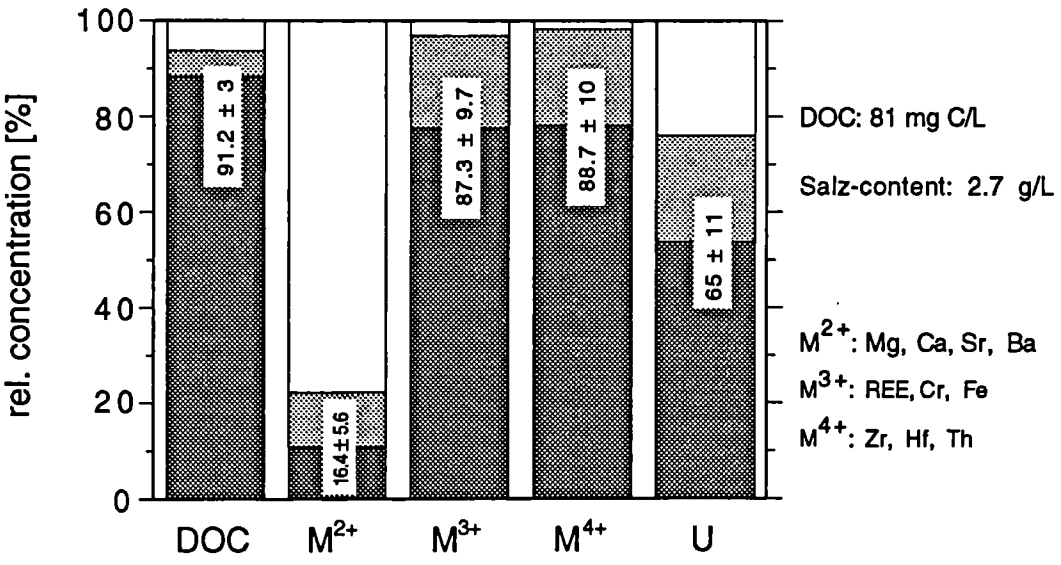

Figure 2: Groundwater Gohy 2227: Concentration of DOC and metal ions filtered at 1 nm pore size normalised to the concentration in the unfiltered groundwater

As a typical example, the metal ions loaded on humic colloids in the groundwater Gohy 573 are compared with their concentrations in this groundwater filtered at 1000 nm and 400 nm. Colloids are fractionated by ultrafiltration at different pore sizes from 400 nm

down to about 1 nm and are analysed by neutron activation analysis (NAA). The analytical values of the prefiltered groundwater and the filtercakes are given elsewhere in detail [5]. The metal ions, Ca^{2+}, Sr^{2+} and Ba^{2+}, are associated with humic colloids in a relatively large portion. In the colloid fraction filtered at 1 nm, as an average, 61.4 ± 6.5 % of the total concentration is found for each divalent ion in the groundwater. The mole fraction of the divalent ions loaded on humic colloids changes from groundwater to groundwater, depending on their total concentration and the amount of DOC [6]. The trace metal ions of higher oxidation state (≥3+) are strongly associated with humic colloids. The filtration at about 1 nm pore size shows an average 92.9 ± 11.5 % of these ions being bound on thus filtered colloids. Trace ions associated with humic colloids are the trivalent rare earth elements (REE; 94.4 ± 9.2 %), tetravalent Zr, Hf, Th (98.2 ± 14.5 %), pentavalent Ta (87.7 %) and hexavalent U (73.7 %). The trivalent Fe follows the same tendency. In Gorleben groundwaters with relatively large amount of humic substances, generally more than 80 % of metal ions of higher oxidation state (≥3+) are sorbed on colloids collected on 1 nm filters [6]. The strong association between humic colloids (given as DOC) and the trivalent rare earth elements, Lu and Yb, is shown in Fig. 3. The tetravalent Zr and Hf and the hexavalent U present in these groundwaters are also strongly bound on humic colloids [5].

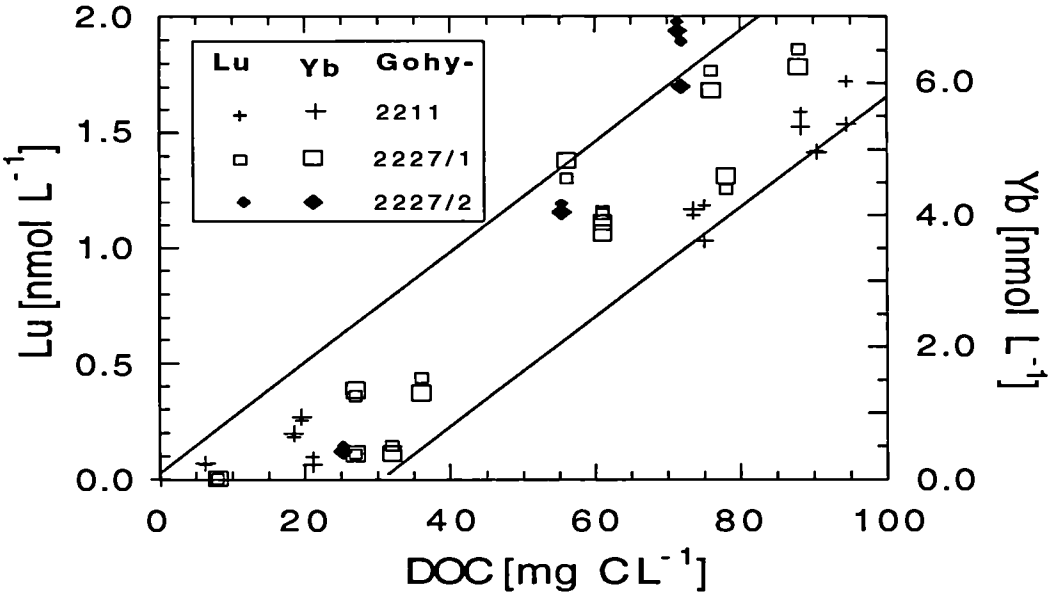

Figure 3: DOC concentration and concentrations of Lu and Yb in filtrates of groundwaters Gohy 2211, Gohy 2227/1 and Gohy 2227/2 at different pore sizes

2.3 Chemical and mineralogical composition of sediments

The chemical compositions of the sediment samples from drill cores taken from boreholes Gohy 573, Gohy 611 and Gohy 2227, given in the previous reports [4, 5], show marked differences in concentrations of SiO_2, Al_2O_3, Fe_2O_3 and K_2O, the main components of quartz, feldspar and clay minerals. This is supported by mineralogical studies. The

lowermost lignite found in borehole Gohy 573 is overlaid by relatively pure quartz-sand whereas the lignite in borehole Gohy 2227 is covered by sediments with a higher portion of clay (marl). In the case of borehole Gohy 573, concentrations of lanthanides and other metalic elements in the lignite are ten times higher than those of the quartz-sand. This is not the case for borehole Gohy 2227, where the lanthanides and other elements are equally distributed between lignite and overlying sand and marl. Differences might be accounted for the different sorption behaviour of the overlying sediments owing to varying clay content. Another reason could be different sources for the lignites found in drill cores of the two boreholes Gohy 573 and Gohy 2227. The high concentrations of humic colloids in the groundwater samples Gohy 573 and Gohy 2227 are probably related to the glacial lignite intercalations. However, it is yet not known, whether these colloids are generated in-situ or originated from lignites elsewhere. For this reason, a more detailed characterization of the lignites is in progress.

2.4 Colloid size distribution and population quantification

2.4.1 Colloid quantification by PCS and PALS

Particle counting by photocorrelation spectroscopy (PCS) at AEA for unfiltered groundwaters from boreholes Gohy 573 and Gohy 2227 indicates that particle populations are different among these samples [4, 5]. Quantification of colloidal particle concentrations in various filter fractions are now being determined by the more sensitive laser induced photoacoustic detection of light scattering (PALS) technique at TUM. This work is in progress. Results obtained so far are preliminary and will be reported later.

2.4.2 Colloid investigation by TEM and SEM-EDX

Results obtained so far by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) lead to a model of the smallest identifiable humic colloids being as large as 1 to 10 nm or 1,000 to 100,000 Dalton, respectively. After diafiltration, filters with pore sizes larger than 30 nm contain much less than 50% of the colloids present in the unfiltered groundwater. The size fraction between 30 and 100 nm contain more or less homogenious layers, obviously composed of deformed colloids attached to each other. Aggregates, which form particles with visible shape and structure, are only detected in the fractions larger 100 nm. They are usually irregulary structured or sometimes ball-shaped, as shown in Fig. 4.

More than 100 particles on each filter were investigated by X-ray analysis (EDX) and visual observation. Generally, more than 95 % of the analysed groundwater colloids have more or less the same composition: Main components are carbon and oxygen. Sometimes, very small peaks of sulphur or chlorine appear (indicating contents of less than 2% of the particle mass). Less than 5% of the analysed particles contain varying amounts of

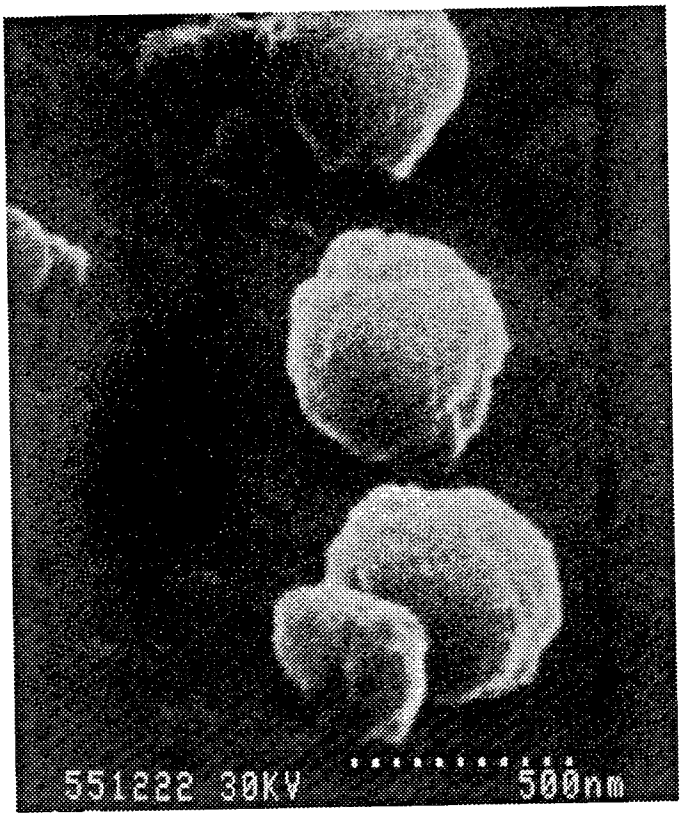

Figure 4: Groundwater Gohy 572, size fraction >30 nm: Colloidal particles found after diafiltration.

silica (0.5 to 50 weight %), iron (2 to 50 weight %), aluminium (only in connection with silica, about $^1/_3$ of the silica content), and/or magnesium, calcium, sodium and potassium (all of these elements less than 5%).

2.5 Isotope studies

Determination of the isotopes ^2H, ^3H, ^{13}C, ^{14}C and ^{18}O has been carried out at GSF in groundwater samples of the boreholes Gohy 201, 611, 612, 572, 573 and 2227. ^{14}C and ^{13}C were measured in the humic acid (HA) and fulvic acid (FA) DOC fraction. In groundwater samples of the boreholes Gohy 201, 611 and 2227, the isotopes ^{34}S and ^{18}O were also measured on dissolved SO_4. Results obtained so far have been reported in the previous six-monthly progress reports [4, 5].

The tritium model age calculated according to a piston flow model is less than 40 years for the sample of the near-surface groundwater Gohy 611 and above 50 years for all other groundwater samples. Groundwater model ages calculated on $^{14}C_{DIC}$ and $^{14}C_{DOC}$ concentrations for the deeper aquifers Gohy 572, Gohy 573 and Gohy 2227 are older

than age assumptions based on stable isotopes (^{2}H, ^{18}O). ^{14}C contents of the humic acid (HA) fraction are very low or not detectable and result in very high ^{14}C model ages (approx. > 25,000 a) [4, 5], whereas ^{14}C contents of the fulvic acid (FA) fraction are higher and give model ages which are more consistent with a younger postglacial Holocene age (not older than approx. 12,000 a). ^{14}C concentration in an isolated FA from groundwater Gohy 2227 has been confirmed within the 2σ error range by both GSF and AEA Technology [4, 5]. The different isotopic results for the HA and FA fractions indicate a different origin for the two fractions: It may be assumed that the FA has originated from near-surface material (soil), whereas the HA fraction originated from organic matter of older sediments (lignite), either local or from an enhanced input of organic rich glacial melt water approx. 12,1000 a ago.

The ^{34}S and ^{18}O contents measured in dissolved sulphate of the relatively young groundwaters Gohy 201 and Gohy 611 are characteristic of sulphate from atmospheric fallout. The high ^{34}S content of the sample Gohy 2227 is possibly the result of strong isotope enrichment due to sulphate reduction.

2.6 Study of U/Th-decay series disequilibrium

Surface characterization of some drill core samples from boreholes Gohy 573 and Gohy 2227 have indicated that solid/solution exchange processes are taking place [4, 5]. However, the U series data obtained to date are ambiguous in terms of the humic colloid provenance and the source of their natural actinide loads. Thus, for example, total sand samples $^{234}U/^{238}U$ activity ratios are all close to unity indicating little exchange with groundwaters; the lignite total sample, on the other hand, indicate U uptake. The solid phase distributions of U and Th indicate significant components of total U and Th residing in the original phase of the lignite samples in contrast to sand samples where the residual mineral phases contain most U and Th. From the U/Th isotope ratios found in the surface phases of the solids it has been inferred that active radionuclide exchange is taking place in these aquifers.

The question of colloid provenance and the origin of the colloid borne actinides in the Gorleben aquifer has been adressed through the U series disequilibrium data. Although the conclusions are somewhat ambiguous, it is possible that the humic colloids present in groundwater Gohy 573 and Gohy 2227 have different isotopic histories and possibly different sources, other than local lignite [4, 5].

3 Generation of pseudocolloids of radionuclides

Actinide ions with a variety of possible oxidation states (≥3+) are in general unstable in groundwater at neutral pH, besides a dioxoactinyl ion of pentavalent state [9], because of their strong tendency towards the hydrolysis reaction [10]. For this reason, they are easi-

ly sorbed on aquatic colloids through either complexation or ion exchange reaction [11, 12]. The generation of such colloids, termed actinide "pseudocolloids", may lead to an apparent solubility of a given actinide being much higher than its thermodynamically available solubility [13]. For this reason, the generation of actinide pseudocolloids may facilitate the migration, or eventually the retardation, of these elements in a given aquifer system [7]. Task 3 of the present research program concentrates on the mechanisms that may

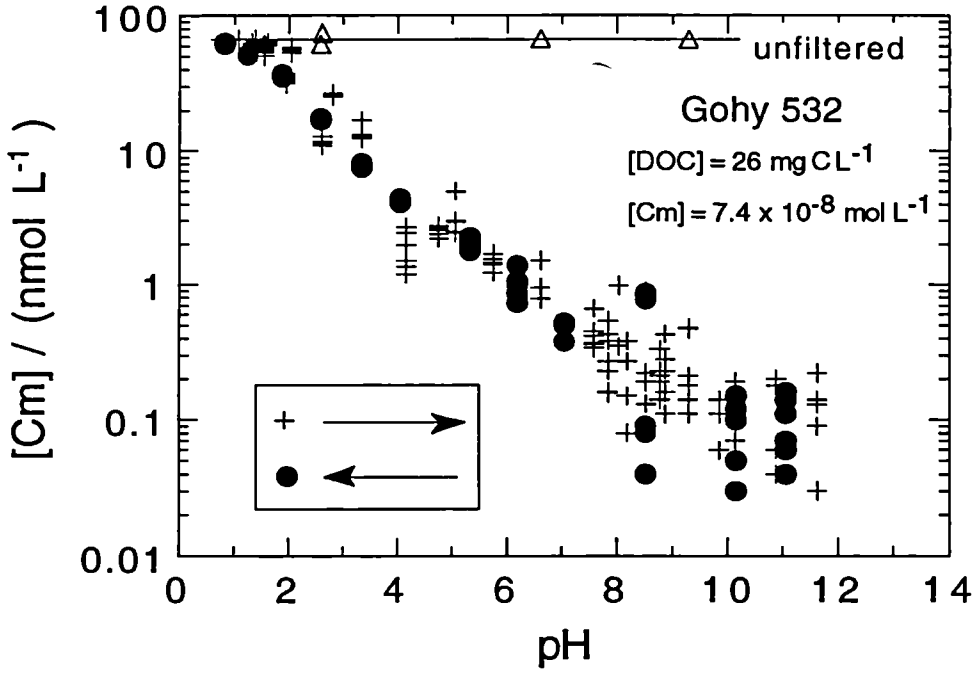

Figure 5: Cm(III) concentrations in the unfiltered groundwater Gohy - 532 and its filtrates at 1 nm pore size, both given as a function of pH. The symbol (o) signifies the forward pH titration and (+) the backward titration

lead to the generation of actinide pseudocolloids in the selected groundwaters. The main intention is to investigate how actinide pseudocolloids are generated in groundwaters rich in humic substances. The generation of actinide pseudocolloids by sorption of actinide ions on groundwater colloids is studied at TUM with actinide ions of three important oxidation states (trivalent, tetravalent and pentavalent). The study of the hexavalent ion is confined to the behaviour of the naturally occuring uranyl ion in the groundwaters. Results of sorption/desorption experiments carried out so far with the trivalent ^{241}Am and ^{244}Cm and the tetravalent $^{232/234}Th$ in humic rich groundwaters from the Gorleben aquifers are reported in detail in the present six monthly progress report [5]: The $^{241}Am^{3+}$, $^{244}Cm^{3+}$ and the $^{232/34}Th^{4+}$ ions introduced in the original groundwaters are found to be sorbed quantitatively on humic colloids (Figs. 5, 6). The sorption and desorption behaviour is depening on the pH.

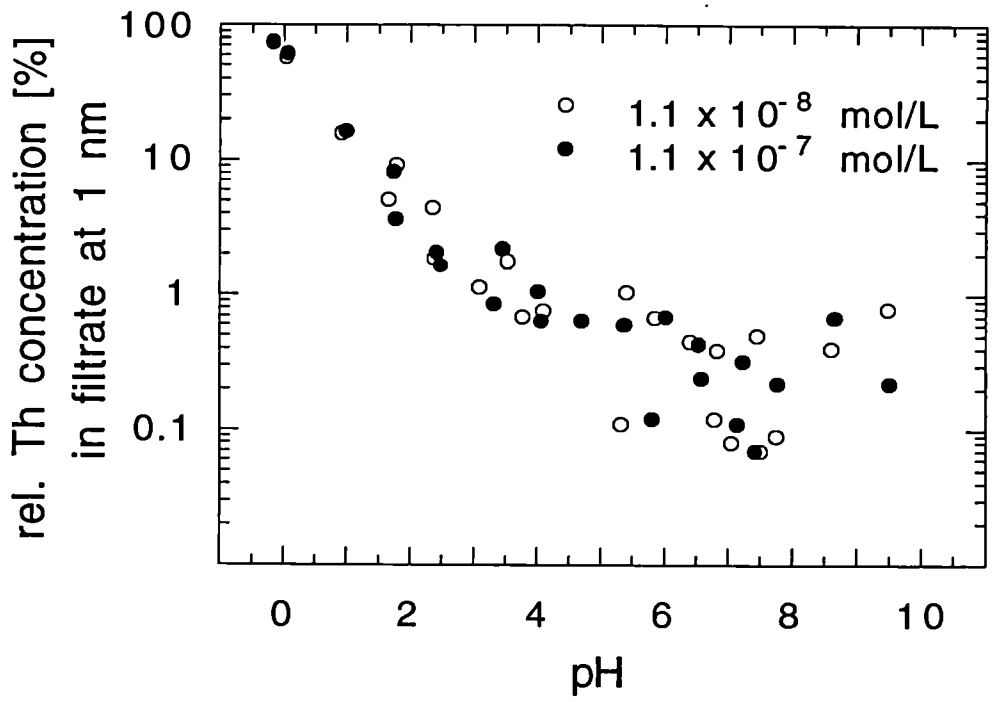

Figure 6: Groundwater Gohy 2227: Th(IV) concentrations in filtrate at 1 nm pore size given as a function of pH

4 Transport process study by scaled column experiments

Column experiments have been designed by close collaboration among all participants (TUM, AEA, GSF, Atkins ES). Groundwater from the borehole Gohy 2227 is used for the column experiments, as this has been well characterized during earlier work and because it contains substantial amounts of humic colloids. The sand used for the column experiments was sampled from the sediments overlying the Gorleben salt dome and is comparable with the Pleistocene quartz-sand of the borehole Gohy 2227. Estimation of microstructure parameters (sediment surface, pore size distribution) of the sand is carried out at GSF [4, 5]. The hydraulic properties of each groundwater-sand column have to be determined very carefully until stable conditions are achieved in order to assess the migration behaviour of radionuclides in question (Am (III), Th (IV), Np (V), U (VI)). Hydraulic properties (filtration velocity, flow velocity, effective porosity) are determined by both GSF and TUM for all groundwater-sand columns foreseen for the radionuclide migration experiments. Radiotracers used for the determination of the hydraulic properties are ^{3}HHO (at GSF) and $^{82}Br^{-}$ (at TUM). The results obtained so far by both GSF and TUM still show a slight decrease of the effective porosity within a time span of more than 12 monthes indicating a clogging of the columns which may be caused by precipitation of the humic substances. The hydraulic properties of the groundwater-sand columns will be controlled by further radiotracer experiments. Column experiments using

Am (III), Th (IV), Np (V) and U (VI) to study the migration behaviour of these radionuclides will be performed after the hydraulic properties remain constant. For this purpose actinide-spiked groundwater solutions have been prepared at TUM.

A pilot study is being developed by GSF and TUM using Eu(III) as an injected migrant in the presence and absence of $^{125/131}$I-labelled humic colloids. The humic colloids will be extracted from groundwater Gohy 2227. This will be used for the assessment of the radionuclide migration behaviour (break-through characteristics) within a scaled sand-groundwater system in the presence of natural humic colloids. The AEA group has set up an experimental rig and procedures for labelling Gorleben humic acid with man-made U and Th isotopes for the use in transmission column experiments set up at TUM. The initial experiment carried out with ^{233}U label and humic colloids from Gohy 2227 have been completed successfully [4].

5 Synthesis and theoretical interpretation

A comprehensive review of extant organic complexation models has been carried out by Atkins ES, with the objective of identifying suitable state-of-the-art codes for adoption and enhancement. Ideally such a model would have the following capabilities:

- simulation of both cation and anion binding,
- treatment of the amphoteric nature of humic substances, allowing reversibility if uptake is to be considered,
- treatment of organic-inorganic interaction in terms of whole system speciation,
- representation of colloid transport.

In addition, a centralised Gorleben database has been developed, containing both generic and site-specific data.

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Title: The role of colloids in the migration of elements.
Contractor: Risø National Laboratory, Denmark.
Contract N°: FI2W/0085.
Duration of contract: from 1/4 1991 to 1/4 1994.
Period covered: 1/1 1992 to 31/12 1992.
Project leader: B. Skytte Jensen.

A OBJECTIVES AND SCOPE

The objectives of the present investigation is to quantify the behaviour of colloids under varying chemical conditions by means of suitable laboratory experiments. The aim is to derive thermodynamic equations, which may be used for the modelling of their fate in natural systems.
If this is not possible because of the very complicated nature of the system, empirical response functions will be derived.

Numerous studies of selected aspects of colloid behaviour have been reported in literature. However, most of these studies are too specific to be of interest for the present study.
Colloids may be of almost any composition, their peculiar behaviour being a consequence of their large surface and the increased importance of their specific interface chemistry.

To narrow the field of interest, the study will focus on humic acids, whose importance in natural systems is well recognized.
Only one humic acid, purchased as sodium humate from Aldrich-Chemie, D-7924 Steinheim, Germany, will be studied. Despite the fact that humic acids isolated from different places deviate in composition and probably also in structure, it is expected that they will display a similar overall behaviour being characteristic for polyfunctional aggregates, although they no doubt will demonstrate not identical interaction constants.

B WORK PROGRAMME

1 To collect useful information on humic acid behaviour, which can support the present investigation.

2 To study and quantify flocculation processes induced by the addition of polyvalent cations in competition with other ions.

3 To follow the distribution of trace elements (R.E.) between flocculate and solution. If possible the amount of cations bound to dispersed humic acids will also be determined.

4 As a tentative model for the thermodynamic interpretation of the experimental data the humic acids will be modelled as finely dispersed ion-exchangers with a possible limited miscibility of surface phases.

5 If the suggested model is not found satisfactory, an empirical expression describing the behaviour of the selected humic acid will be derived.

C PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Literature search is progressing with the identification of several recent and important papers on humic acid structures, properties and behaviour.

A stock solution of the selected humic acid is being characterised and a qualitative reaction pattern established.

A set of elaborate matrix experiment has been performed, in which the flocculation behaviour of a fixed amount af humate in solution was exposed to systematically varied total concentrations of calcium - and sodium ions. In each experiment 30 mixtures were characterised by the measurement of the residual concentrations of sodium, calcium, humate and pH in solution after a centrifugation and also after a subsequent milipore filtration. Some preliminary conclusion have already been presented.

Progress and results

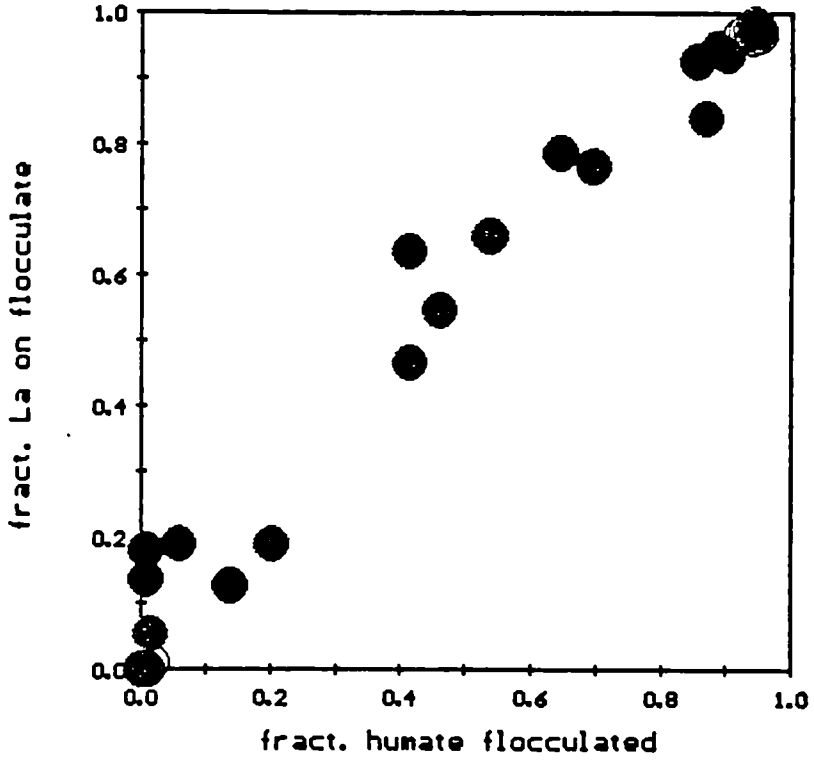
1 The at present favoured model for humic acids describes them as aggregates of smaller units bound together by groups of polyvalent ions like Fe^{3+},Al^{3+},Ca^{2+} etc. The aggregates are assumed to possess poly-electrolytic properties, but may also be ascribed ion-exchange properties.
The stock solution of the selected sodium humate has been dialysed for 14 days to remove impurities of neutral salts. During this process was observed the continuous leaching of coloured components, which could be the result of a de-polymerisation reaction in the humate solution, a reaction which therefore could be reversible.
The pH of the dialysed stock solution is measured to 6-7.

2 It has been observed that the humate solution does not form a visible precipitate with a one molar NaCl solution, but does so in a saturated solution.
Flocculation occurs with the addition of magnesium and calcium salts, in which respect the latter is more effective.
By saturation with gypsum or calcite, the former solid with a larger solubility product provokes a partial flocculation, whereas this could not be observed with calcite added.
After isolation of the calcium induced flocculate, it could be 're-dissolved' in both pure water and in a one molar NaCl solution, which demonstrates the reversibility of the flocculation process.
A complete elemental analysis of the humate solution has been made. The results show that the humate still contain appreciable amounts of different cations, which seem to be rather strongly bound, and therefore has, under natural conditions, to be accepted as unseparable parts of the humic acid.
The analytical data indicate a 'molweight' pr. functional group in the humate to about 200, which corresponds well to some substituted benzoic acids, which could have arisen from the degradation of lignin.

The matrix experiments have produced a lot of data, which clearly demonstrate the competition between protons, sodium ions and calcium ions for binding sites on the humate irrespective if it is in solution or found as a flocculate. In the latter case the flocculate must nescessarily be electroneutral and a charge balance being established.

3 The distribution of trace amounts of rare earth elements between flocculate and solution as a function of solution composition has been measured by ICP-MS. The fraction of RE removed from solution has been found to be almost directly proportional to the fraction of humate being removed by flocculation.

Figure 1.
Trace La bound onto humic acid flocculate.

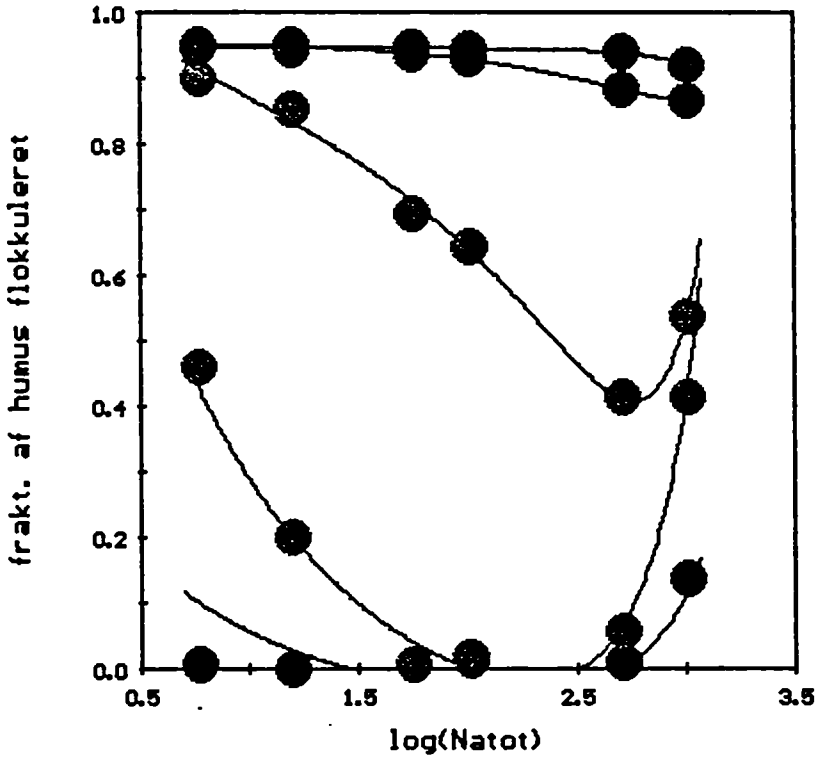


The fractions of added trace amounts of lanthanum removed from solution as a function of the fraction of humate flocculated.

4 A strict thermodynamical modelling approach seems not to be feasible based on the present data, because the concentrations of free ions in solution could not be determined with a reasonable certainty. This means that the speciation in solution could not be calculated and thermodynamic equilibrium constants not be specified.

5 However, an empirical modelling of respons-curves for flocculation of humate as a function of total calcium and total sodium present in the system is easily accomplished and may be usefull in more elaborate modelling approaches. The modelling expression is a simple matrix-equation making the best least-squares fit to the experimental data.

Figure 2.
The fraction of humate flocculated as functions of total Ca and Na concentrations.



Experimental points and modelled response-curves for humate flocculation at different total calcium concentrations as functions of total sodium concentrations in the system.

THE ROLE OF COLLOIDS IN THE TRANSPORT OF RADIONUCLIDES IN GEOLOGICAL MEDIA

Contractors: CEA, CIEMAT, CNRS, GERMETRAD, GSF, INFM, INTERA
Contract n°: FI2W/0097
Duration of contract: from October 1, 1991 to September 30, 1993
Period covered: January - December 1992
Project Leader: CEA, V. Moulin

A. OBJECTIVES AND SCOPE

The main objective of this programme is to understand how colloids could influence the migration behaviour of radionuclides in geological formations. This is being achieved firstly, by identifying the *retention mechanisms* of colloids and pseudocolloids to mineral surfaces by static and dynamic experiments, and secondly by investigating the formation of pseudocolloids. These studies will provide an insight into retention mechanisms and there upon validate retardation parameters used in *transport models,* which will be developed to predict colloid transport under conditions relevant to geological disposals. Moreover, this research is focused on *model systems* (surfaces, colloids) selected from studies carried out on the El Berrocal site (Spain).

This programme is carried out in collaboration with: CEA (Fontenay-aux-Roses; V. Moulin), CIEMAT (Madrid; P. Rivas), CNRS (Orsay; J.C. Dran), GERMETRAD (Nantes; F. Goudard), GSF (Münich; H. Lang), INFM (Padoua; G. Della Mea), INTERA (Henley-on-Thames; P. Grindrod).

B. WORK PROGRAMME

B.1. Colloid properties

B.1.1. Colloid characterization

B.1.2. Application to a site

B.2. Sorption mechanisms

B.2.1. Association of radioelements with colloids

B.2.2. Interaction of colloids and pseudocolloids on mineral surfaces

B.3. Transport mechanisms

B.3.1. Transport experiments in model systems without organic coatings

B3.2. Transport experiments in model systems with organic coatings

B.4. Modelling

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

The main emphasis of work in this period (Jan-Dec 92) has involved:

- the characterization of natural colloids from El Berrocal groundwaters (oxidized and reduced conditions), with particular interest to their stability;

- the interaction of actinides with colloidal suspensions through static experiments and radiochemical analysis;

- the interaction of ionic or colloidal solutions of heavy elements analogue to actinides with mineral surfaces through static experiments and ion beam analysis;

- the transport behaviour of radioelements within model porous media through column experiments; the influence of organic coatings has been specially investigated;

- the development of a theoretical model to account for the transport of colloids in geological media which will be validated by means of the present experimental data.

Progress and results

1. Colloid properties (CIEMAT, CEA)

Complementary studies have been performed on the characterization of the colloids from El Berrocal groundwaters. In particular, oxidized and reduced groundwaters have been studied. This has been achieved through scanning electron microscopy after concentration by ultrafiltration for the determination of composition and size distribution of colloids, and also through photon correlation spectroscopy for the colloid size distribution. The main features of these studies were:
i) the identification of mineral phases with respect to the formation processes of colloids (neoformation, dispersion): presence of carbonate phases (Ca, Cu, Zn, Fe), aluminosilicate phases and silica colloids,
ii) the enhancement of colloid generation in reduced groundwaters.

Preliminary studies on the stability of colloids (from the natural waters and the clayey materials from El Berrocal) with respect to pH have been carried out. The results obtained on the size

distribution indicate no effect in all pH range (4-9) for colloids from natural waters, whereas an increase of the size in the acid pH range has been observed for colloids from the clayey materials.

2. Sorption mechanisms (CNRS, INFM, CEA)

Formation of peudocolloids

The sorption of radioelements onto colloidal silica has been studied in order to determine the scavenging properties of silica toward trivalent cations (such as Am) and to describe these interactions in terms of surface complexation reactions. These experiments are complementary of those performed in the last work period (with U). Apparent surface complexation constants have been determined for each cation (Am, U) and surface reactions with the hydroxyl surface sites of silica have been proposed. These values constitute at the present time only preliminary results. The future prospects are: i) study of the influence of a competing cation (Ca) ii) study of the reversibility iii) complementary studies with mica particles (case of Am retention) and silica colloids (as a function of ionic strength) iv) study of the systems involved in the experiments mentioned below.

Interaction (retention) of colloids and pseudocolloids with mineral surfaces

Static experiments involving monoliths interacting with ionic or colloidal solutions of heavy elements (Nd, U, Th) have been performed in order to identify the sorption mechanisms. Rutherford Backscattering Spectrometry (RBS) has been used to measure the amount of heavy element fixed on the mineral surface. The present results concern the interaction of Nd, U, Th solutions with silica (untreated and prehydrated) and heamatite, as a function of pH, ionic strength and cation concentration. The main conclusions are:

* *influence of surface composition*: a much higher scavenging efficiency of haematite compared to silica (U) has been observed.

* *influence of surface state:* it has been noticed a small increase of U and Nd sorption on silica by prehydration; but no conclusion yet for Th.

* *Influence of solution parameters:* the main features are i) an increase of the amount sorbed with cation concentration (U), ii) a small decrease of the amount sorbed when increasing ionic strength (U, Nd; no conclusion yet for Th).

* *reversibility* (with respect to solution composition): reversibility was not observed for untreated or prehydrated silica.

The future experiments will deal with i) the interactions of cations with monoliths (mica/U, Th, Nd and haematite/Th, Nd) in the presence of competing cations (Ca) and with organic-coated surfaces ii) the interactions of colloid/pseudocolloid systems with monoliths (including silica, mica, haematite as monoliths and silica, iron oxides associated with U, Nd or ceria, thoria colloids as

colloids/pseudocolloids) in order to investigate the stoechiometry conservation, the identification of the fixation mechanisms and the role of organic coatings.

2.3. Transport mechanisms (GSF, GERMETRAD)

Transport experiments in model systems in the absence of organics (GSF)

The aim of the batch and column tests performed in this task is to get a precise characterisation of the liquid/solid systems used as much as possible which may be important for the interpretation of the planned experiments with colloids.

Stable monodisperse material, glass beads in two different grain sizes and quartz sand from Schnaittenbach/Bavaria in two fractions, which has a similar chemical composition to the El Berrocal material have been investigated.

In the batch tests, the water mainly used is a synthetic one similar to the El Berrocal water with regard to the main anionic components like CO_3^{2-} and SO_4^{2-}. In addition the influence of an anion (Cl^-) and a competing cation (Ca^{2+}) has to be clarified with respect to changes of boundary counditions. In parallel 0.01 M NaCl and $CaCl_2$, respectively, were used as the supporting electrolyte solutions (for simplifying possible reactions within the liquid/solid phases) to show the influence of different ions on the transport process.

Sorption/desorption coefficients of Zr, Sr, Eu, Ce for glass beads and quartz sand have been determined in the presence or not of competing ions (Ca, Cl). No influence of Ca has been observed on the Zr behaviour, whereas an effect on Sr sorption/desorption coefficients has been observed. The influence of KCl on the behaviour of Eu and Ce appears dependent on the KCl concentration and the nature of the sorbant (glass bead or quartz sand).

The flowthrough column tests with glass beads in different electrolyte media (NaCl, $CaCl_2$) have been performed with different radionuclides (Na, Cl, Ca, Cs, Eu) in order to identify the transport processes. The main features are: Cl appears as an ideal tracer, Na elution presents a tailing, Ca presents interactions with glass material, Cs shows a slight tailing and Eu is fixed in the upper part of the column.

Transport experiments in model systems in the presence of organic coatings (GERMETRAD)

This work period was mainly devoted to the study of the pH effect on the elution of americium on the humic acid column as well as the effect of the flow-rate on the elution curves. The main results are the following:

* at acidic pH (4.5 to 5.5) in acetate buffer, the retention of Am on the humic acid column increases when decreasing the pH as it could be expected from the variation of the loading capacity of the humic substances as a function of pH,

* at pH 8, in carbonate buffer, Am is not fixed on the humic acid column and is eluted faster than in phosphate buffer (at the same pH), and the profile shapes are different.
* in phosphate buffer (0.05 M, pH 8), the elution curves exhibit a strong dependance with the flow rate: as the flow rate decreases, the elution rate of americium decreases.
In parallel to these transport experiments, a new procedure has been developed to fix humic acids on solid surfaces via the C in phenolic groups.
The future experiments will be devoted to: i) the effect of flow-rate in acetate and carbonate buffers ii) the transport behaviour of pseudocolloids in humic acid columns.

4. Modelling (INTERA)

A theoretical approach to the dispersion and elution of colloids and tracers within saturated heterogeneous porous and fracturated media has been developed. As a result of this approach, calculations for model flow geometries have yielded two quantitative predictions for the transport of free colloids with reference to a non-sorbing tracer within the same medium: i) the average migration velocity of the free colloids is higher than that of the tracer, ii) the ratio of the equivalent hydrodynamic dispersion rates of colloids and tracer is dependent only upon colloid properties.
This method has been used for the calculation of free colloid elution and dispersion rates from experimental breakthrough curves. Results have been obtained which support the modelling predictions made previously on the basis of theoretically upscaling microscopic conditions.

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V. Moulin, N. Labonne, M. Theyssier, JP. Vilarem, MC. Magonthier, MT. Ménager, J.C. Dran, M.C. Milcent, JP. Durand, F. Goudard, A. Bioret, J. Piéri, G. Della Mea, C. Wolfrum, P. Gomez, M.J. Turrero, P. Rivas, L. Perez del Villar, P. Grindrod, M. Edwards (1992) The role of colloids in the transport of radionuclides in geological media. RT DSD/92.74 (2nd progress report CCE 0097)

P. Grindrod,, R.C. Brown And N.D. Gealy, Colloid migration and dispersion within saturated media: a modelling perspective, Draft, Intera Technical Report I2421-1, 1992.

Title: Analysis of the geoenvironmental conditions as morphological evolution factors of the sand-clay series of the Tiber valley and Dunarobba forest preservation.
Contractor: Dipartimento di Scienze della Terra - Università di Roma "La Sapienza".
Contract N°: FI2W/0121
Duation of contract: from August 1992 to January 1995.
Period covered: August 1992 to January 1993
Project leader: G. Valentini.

A. OBJECTIVES AND SCOPES

Based on the large presence of fossil trunks in the fluvio-lacustrine deposits of the Tiber basin outcropping near Todi, Umbertide and Dunarobba (Umbria region, Central Italy), the proponents of this research believed extremely interesting to study such geological environment that may be considered as a "natural analogue". Indeed, it could constitute a large and rare data source and natural laboratory, in order to achieve further informations about geological formations as nuclear waste repositories. It has been considered worth of interest to study the boundary conditions of fluvio-lacustrine deposits and the factors which have made possible the preservation of vegetable substances because of the maintenance of a reducent environment. Other important factors to be investigated appear to be those ones capable to induce modifications and alterations of the original conditions. Based on such analyses, the following topics have been considered of basic importance:

1) the acquisition of the geological, tectonic and hydrogeological boundary conditions;

2) the definitions, in the area of Dunarobba forest, of the whole stratigraphic sequence

along with the structural, hydrogeological and geochemical conditions, the mineralogical and petrographical features, the permeability as regards to endogenetic gases, density and water natural content of rock bodies and finally the tensional and consolidation conditions;

3) the reconstruction of the past geomorphological conditions underwent by the continental deposits and the present geomorphological framework.

In order to achieve an exhaustive definition of most of factors which have been acting in preserving the described environment, it has been realized a partnership network which include Rome University (I) , Perugia University (I) and Exeter E.R.C.(U.K.).

B. WORK PROGRAMME

The present research has been subdivided into 8 tasks:

Task 1- Geological, structural and morpho-structural surveys on the outcropping rock formations and drawing of geological cartography.
Task 2- Geophisical prospectings (gravimetric and geoelectrical surveys).
Task 3- Geochemical investigations (chemical and isotopic features of groundwater and endogenetic gases).
Task 4- Assessment of rock bodies permeability (water and gas permeability tests, consolidation state analyses, geotechnical property indexes).
Task 5- Petrographical and mineralogical analyses (diffractometry, microscope, microprobe)
Task 6- Paleontological, palinological and organic matter analyses of the clays surrounding the fossil truncks.
Task 7- Evaluation of interaction between organic (wood) and inorganic (clay) matter (uranium/thorium disequilibrium patterns analysis by alpha-spectrometry)
Task 8- Geomorphological investigation aimed at modelling the evolution of the area (morphological evolution rate, alteration of geotechnical properties of the rocks, secondary permeability development, hydrogeochemical evolution).

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advacement

In the first six months tasks 1, 2 and 4 started. Stratigraphic and sedimentological analyses (task1) have been performed in order to define the several lithostratigraphic units. A preliminary photogeologic analysis (scale 1:70.000), aimed at roughly define structural lineaments of the area, has been completed.
A gravimetric prospecting (task 2) along two profiles crossing the basin has been conducted. They provide first significant data on the sandy-clay sequence thickness.
Preliminary laboratory investigations have been carried out to evaluate the geotechnical properties of outcropping fluvio-lacustrine deposits.

Progress and results

ROME AND PERUGIA UNIVERSITIES

Stratigraphic and sedimentological study (P.L.Ambrosetti, G.Basilici, D.Esu, O.Girotti)
The aim of the stratigraphic and sedimentological study in the Tiber basin is the reconstruction of the sedimentary bodies (lithostratigraphic units, lithosome, etc.) and of the depositional environments where the fossil forest was formed. Conti and Girotti (1977) [1] performed the most important study about Tiber Basin. The authors described 4 stratigraphic units ("lower grey clays", "clayey-sandy complex", "upper detritic complex", "travertines") characterized by coarser deposits upward (clay, sandy-clay, sand, gravel) and heteropic contact between travertines and sands and gravels. The first part of the present study recognized a different stratigraphic organization of the Tiber basin and proposed the first paleo-environmental interpretations of these deposits. The lithostratigrahic units in the studied area have been introduced after stratigraphic (lithological) and sedimentological (genetic features) analyses. Sedimentological approach, even if not orthodox for a lithostratigraphic definition have been an obligate stage since preliminary investigations suggest that lithological study alone was not able to distinguish the several units. An example is given by the similarity in size and shape of grains between FBU and SMCU (see below): only the recognizing of their genesis (depositional features) allowed to distinguish them. Such a criterion has also been justified by other authors [2]. On these premises, four lithostratigraphic units have been recognized. The names used (geographic) refer to the better site of outcropping, where all the main features of each unit can be observed. From the bottom to the top the units are:
- Fosso Bianco Unit (FBU)
- Ponte Naja Unit (PNU)
- Santa Maria di Ciciliano Unit (SMCU)
- Acquasparta Unit (AU).

In fig. 1 vertical and lateral contacts among the units, both in the northern and southern sectors of the basin are shown. The FBU was deposited in a deep meromictid lake, showing at the margin Gilbert-type fan-deltas and characterized by prodelta turbidites and mud flows (sensu Lowe, 1982 [2] and references therein). The PNU consists of deposits formed by alluvial fan in humid environment, with very interesting cyclic sequences of pedogenesis-sedimentation. The stage of the FBU and PNU is respectively lower Pliocene (Zanclean) and upper Pliocene (Piacentian). The fossil Forest is contained within SMCU, that represents an alluvial plane, with meandering rivers and recurrent floods. With the AU the sedimentation in the Tiber basin ends.
The last unit is formed by lacustrine and paludal limestones and travertines. SMCU and AU are early Pleistocene in age. Until now a geological map (scale 1:50000) covering 40 square kilometres around Dunarobba forest, was produced. Nevertheless it is necessary to extend the geological survey to the southern and northern sectors of the basin, and to introduce biostratigraphic analyses (e.g. pollens, ostracods, molluscs, and vertebrates analysis) in order to have an invaluable tool for correlations among stratigraphic sections.

ROME UNIVERSITY

Studies on the relation between endogenetic gases behaviour and geological setting (S. Lombardi, G. Etiope)

A key-point for the studies of the clayey sequences of the Medium Tiber Valley lies in the investigation of their permeability in respect to underground fluids. In order to study the permeability as regard to endogenetic gases, investigation will be performed by means of soil gas analyses, gas migration studies and analyses of gas in groundwater integrated by other geologic investigative techniques such as photointerpretation and mesostructural analysis. Therefore the planned research line consists of the comparison among geochemical, morphological and structural investigations on a statistical basis.

-Soil gas surveys have been planned for tracing fault and fracture systems; they will be performed using a method which has long been experimented throughout the world and especially in the United Kingdom and in Italy, where soil gas studies have already been applied in researches for the European Community [4],[5]. Helium, radon, carbon dioxide, nitrogen, argon and light hydrocarbons will be analyzed. Regular grids with sampling densities from 1 (regional scale) to 100 (detailed scale) samples per square kilometer will be adopted. Regional sampling will be performed troughout the basin meanwhile detailed sampling will cover Dunarobba forest and other areas with particular structural features.
-Gas migration studies consist of in sito gas injection tests using vertical and/or inclined boreholes about 30 meters depth. After gas (different mixtures of helium) is injected, a soil gas collection will be made to realize the time of gas migration covering fixed distance. The knowledge of the local petrophysical parameters (obtained by geotechnical investigations) will permit the elaboration of the migration equation, and therefore a simple migration model, which best fits the experimental data.
-An attempt will be made, using the above mentioned gases, to trace the movement of groundwater. Their content in groundwater will be measured in a number of water samples collected throughout the basin. The extraction of gas from water will be made using an extraction line (pyrex glass made) which has been suitably planned for our purpose. It is actually under construction. These analyses should give rise to an important contribution to the knowledge of groundwater circulation, gas migration mechanisms and of the mixing processes between gas and groundwater (gas-water interaction) and between groundwater of different origin (meteoric-deep water interaction).
-Studies on the relationship between gas leakage and structural setting of the area will be performed by means of fracture field analyses and photogeologic studies. Their comparison with soil gas data will permit to confirm the presence of fault and/or fracture systems.

In the covered period, in addition to the setting up of the gas extraction line, the main effort regarded preliminary researches and, among these, a photogeologic study has been completed. It was performed using 1:70000 scale aerial photos in order to detect morphologic elements and photo-lineaments genetically associated with tectonic discontinuities. It was based on the analysis of shapes (landscape morphology) and drainage (hydrographic patterns). The results (Fig. 2) show the presence of five main lineaments trends:
N10W (Eastern ridge)
N40W (Northern sector, Todi)
N60W (Central sector, Dunarobba)
N20W (Western ridge)
W50E (Southern sector)
Anomalous patterns have been found NE of Montecastrilli (radial drainage) and south of Avigliano (Trellis drainage). No clear trends occur at Dunarobba but some lineaments are visible around it. A NW-SE trend from Montecastrilli to Dunarobba and SW-NE trend

north-west of Dunarobba occur. The lineaments at the boundary of the basin coincide with the known tectonic features of the area (faults in the western and eastern ridges).
The main trends suggest the presence of large tectonic discontinuities from Todi to Montecastrilli (NW-SE) cut (and pheraps shifted) by a SW-NE lineament from the south-western corner of the basin toward Acquasparta (crossing Avigliano and Dunarobba). The radial drainage near Montecastrilli suggests an uplift of that sector. However detailed photo-interpretations will be made in future using 1:33000 scale photos.

Gravity prospecting in the Dunarobba area (B.Toro, M. Di Filippo)

In order to obtain further informations about the geological setting at the bottom of the plio-pleistocenic formations and their thickness, a gravimetric survey in the studied area was carried out.
The data collection was made along two profiles having W-E direction. The first profile is constituted of 38 gravimetric stations, from Toscolano to Tartana where the carbonatic ceno-mesozoic formations are outcropping.
The second and northernmost profile, from Montenero to Acquasparta, through Dunarobba area, is constituted of 16 stations. After the data collection a Bouguer anomalies map was drawn (fig. 3): Bouguer anomalies were computed for a density value of 24 KN/m^3 and the topographic correction was computed for a distance of 29 km. The Bouguer anomalies have all positive values: they reach a maximum peak of +44 mgal and a minimum value of +18 mgal.
On the basis of the gravimetric map two preliminary bi-dimensional models were built. These models, corresponding to the profiles, were drawn along the W-E direction, which is normal to isoanomalous contours; this makes the model meaningful.
The first best fit model (profile 1) shows that the sandy-clayey formation has its maximum thickness (800 m) in correspondence of the central part of the investigated area.
Moreover, this model suggests a thickness of the clayey sequence of about 400 m in the Dunarobba area. The second best fit model (profile 2) shows a greater thickness of the clayey formations, which reaches a maximum depht of 1300 m.

Geomechanical characterization of the sandy-clayey sequences (G.Valentini, F. Bozzano, G. Scarascia Mugnozza)

The geotechnical investigations are aimed at defining the following topics:

a) permeability characters of the rock masses in which are included the fossil trunks of the Dunarobba Forest , also in relation to the presence of discontinuity surfaces ;

b) analysis of the "particles-interstitial water" system as function of past and present boundary stress conditions;

c) long term mechanical behaviour of clay bodies.

Based on these objectives and according to the stratigraphic and geological reconstructions that have been so far carried out, first results about the geotechnical index properties of the outcropping deposits (FBU, SMCU and PNU) have been attained. The performed analyses allowed to define the particle size distribution, the specific unit weight and the plasticity of 16 remoulded samples . As shown in Fig. 4 and 5, the analized samples are mainly constituted by silty-clay of medium to high plasticity, with a specific unit weight ranging from 25.5 to 27.0 kN/m^3 .
In order to assess the permeability coefficients (along the horizontal and vertical directions) and the consolidation states of the clay deposits, oedometer tests - whose data elaboration is still in progress - have been carried out on indisturbed samples having different orientations as regards to the stratification beds.

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Figures

FIG. 1 - Lithostratigraphic sketch of Tiber basin between Todi and Sangemini

FIG. 2 - Map of photolineaments (1:70000). Linear shapes and anomalous drainage patterns are plotted.

FIG. 3 - Map of Bouguer anomalies.

FIG. 4 - Triangular granulometric diagram.

FIG. 5 - Plasticity chart of samples belonging to the FBU, PNU and SMCU.

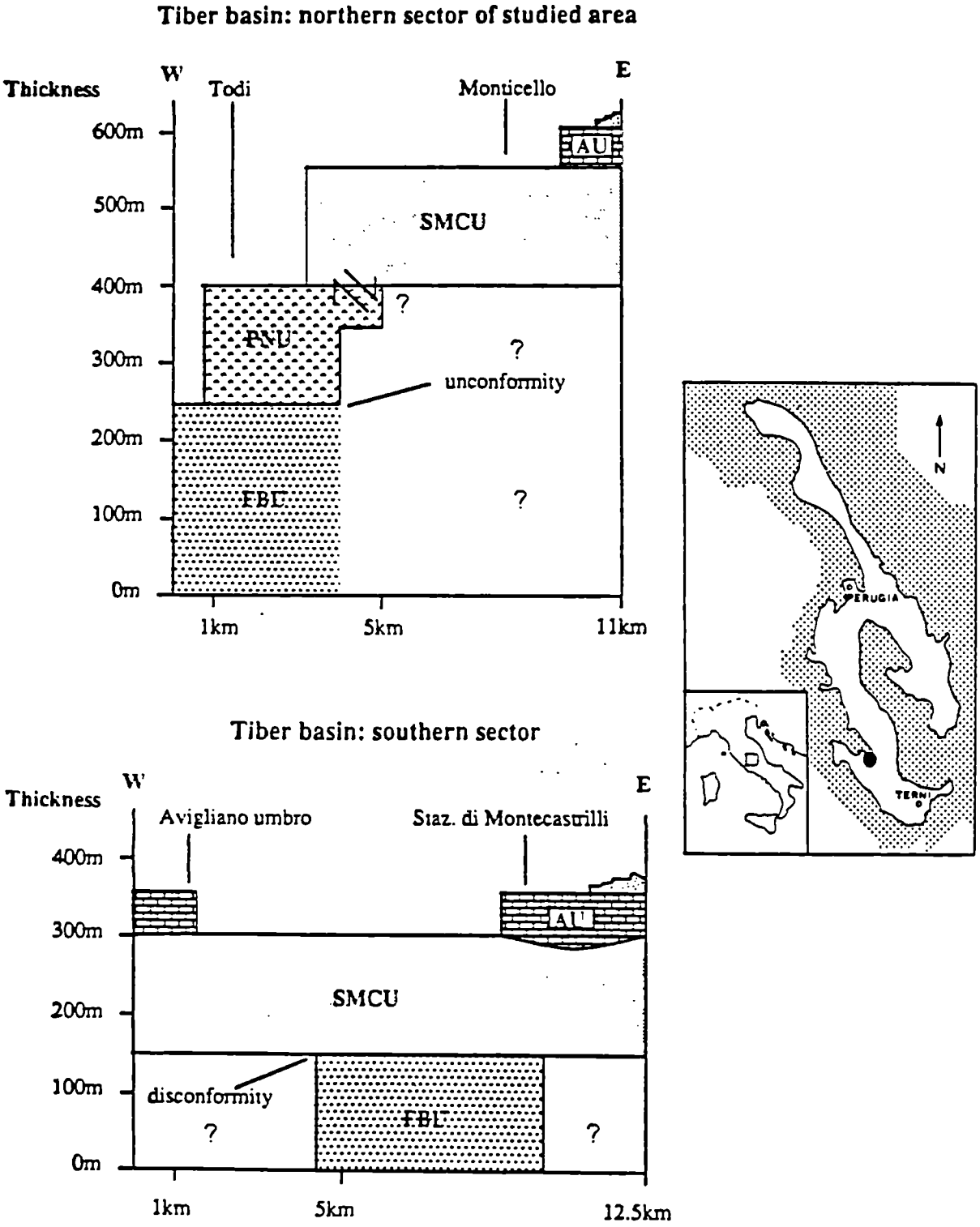

Tiber basin: northern sector of studied area
Thickness
W
E
Todi
Monticello
600m
500m
400m
300m
200m
100m
0m
AU
SMCU
PLU
FBL
?
unconformity
1km
5km
11km
N
PERUGIA
TERNI
Tiber basin: southern sector
Thickness
W
E
Avigliano umbro
Staz. di Montecastrilli
400m
300m
200m
100m
0m
AU
SMCU
disconformity
FBL
?
1km
5km
12.5km

Fig. 1

MAP OF PHOTOLINEAMENTS (1:70000) IN THE MEDIUM TIBER VALLEY

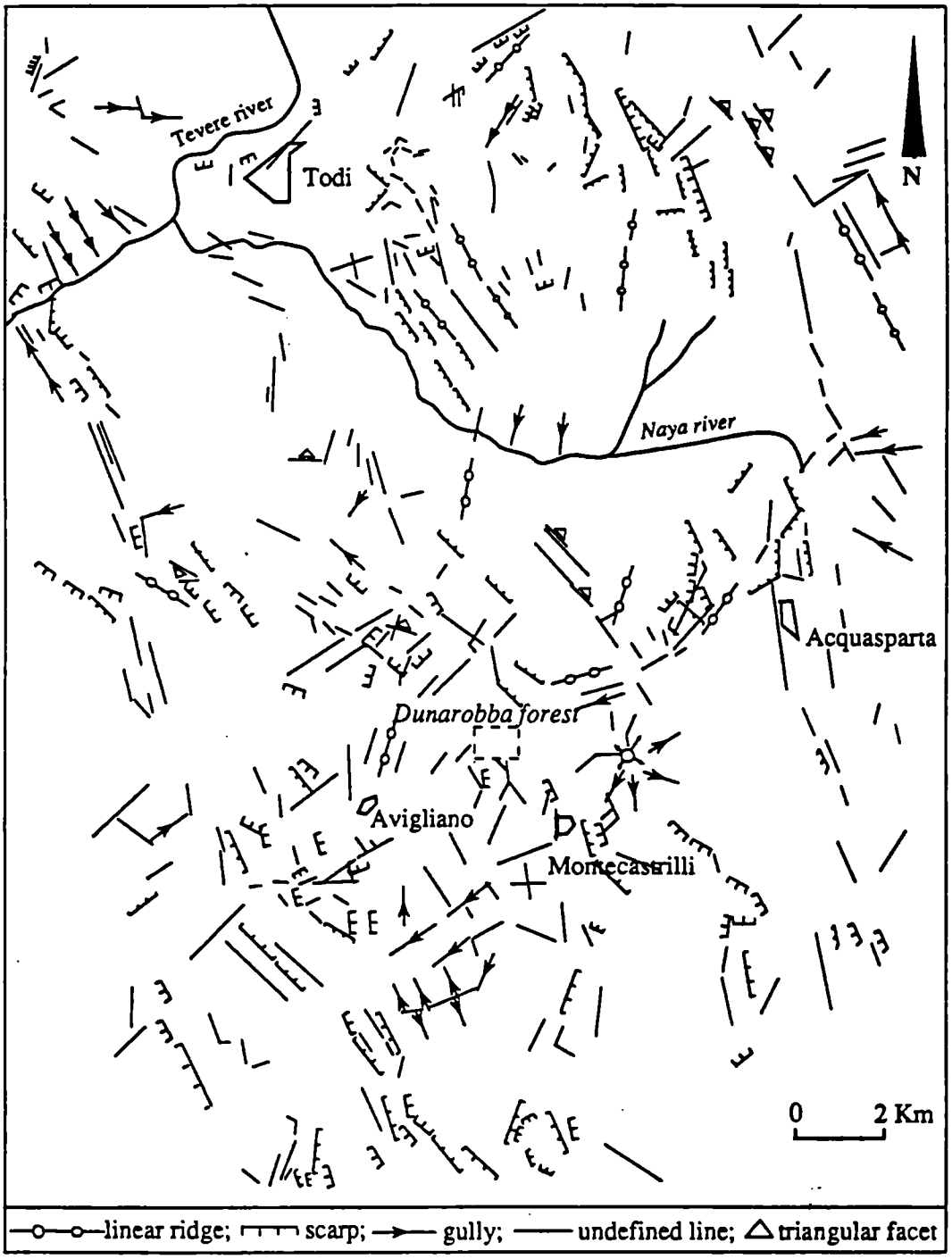
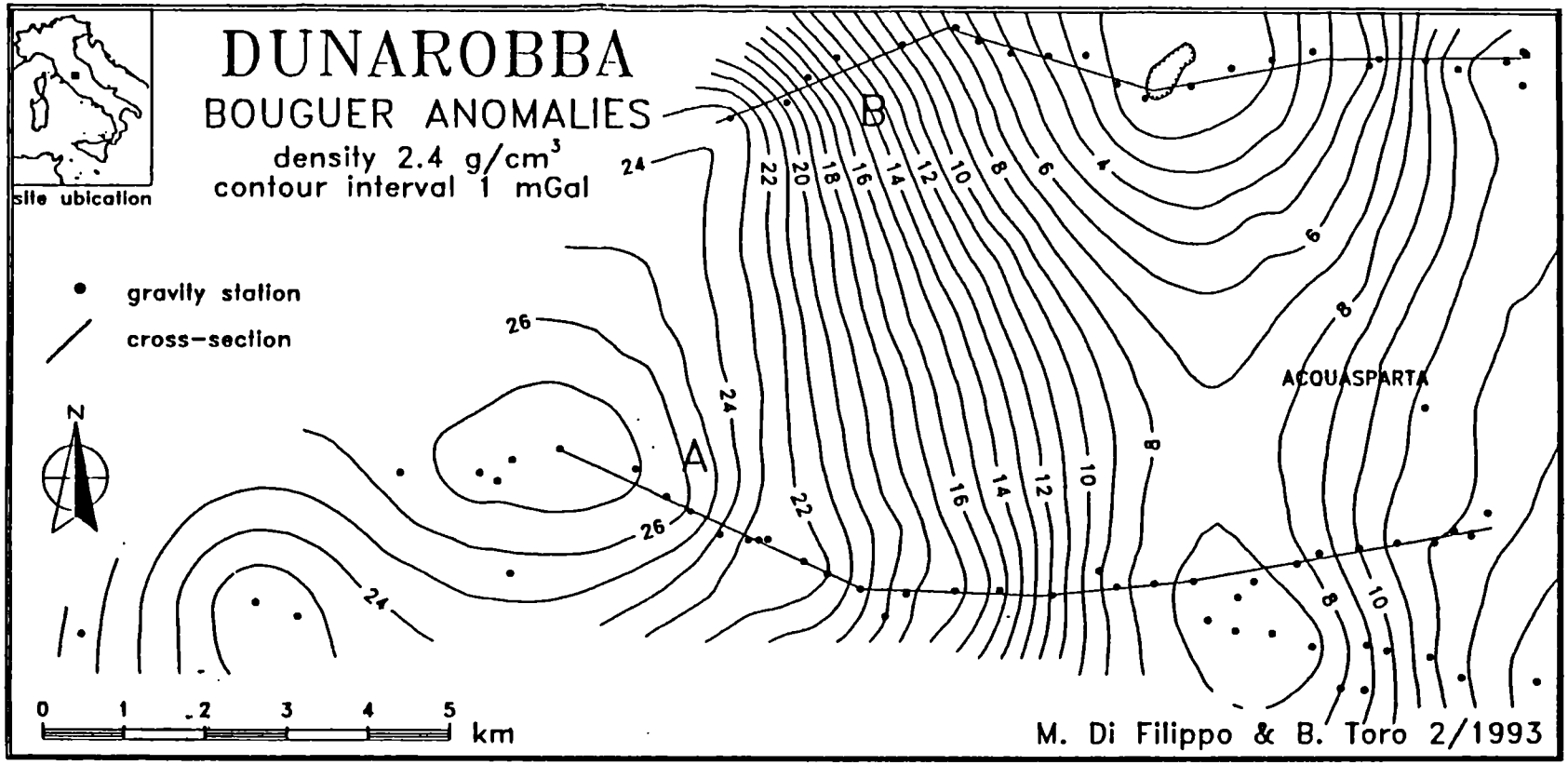


Fig. 2


DUNAROBBA
BOUGUER ANOMALIES
density 2.4 g/cm3
contour interval 1 mGal
site ubication
gravity station
cross-section
N
A
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ACQUASPARTA
0 1 2 3 4 5
km
M. Di Filippo & B. Toro 2/1993

Fig. 3

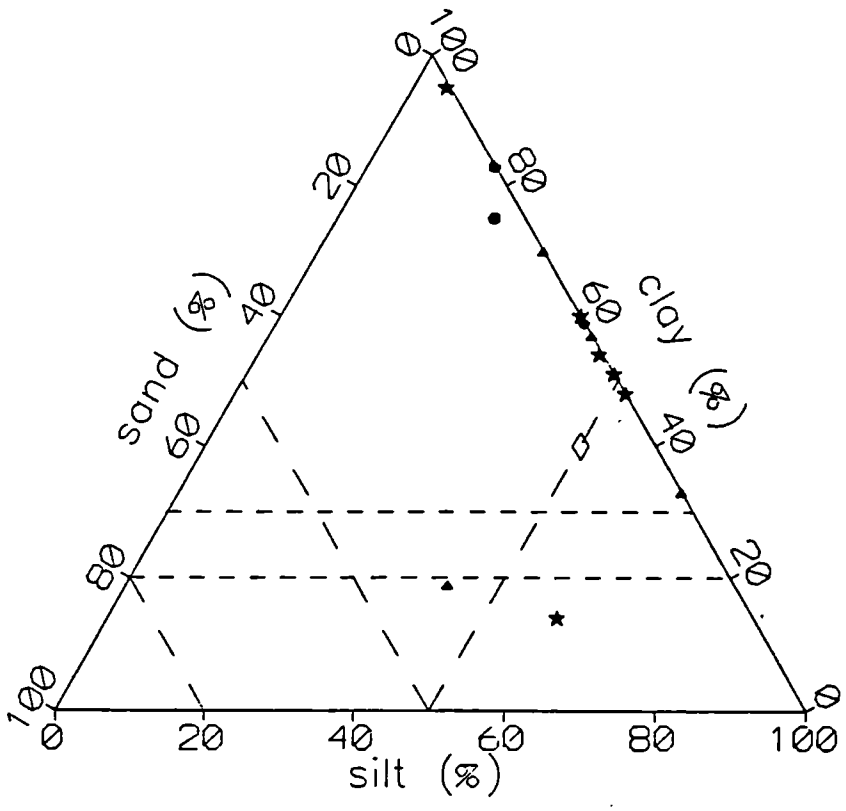


Fig. 4

★★★★★ S.M. di Ciciliano Unit
▲▲▲▲▲ S.M. di Ciciliano Unit-Dunarobba site
●●●●● Fosso Bianco Unit
◇◇◇◇◇ Ponte Naja Unit

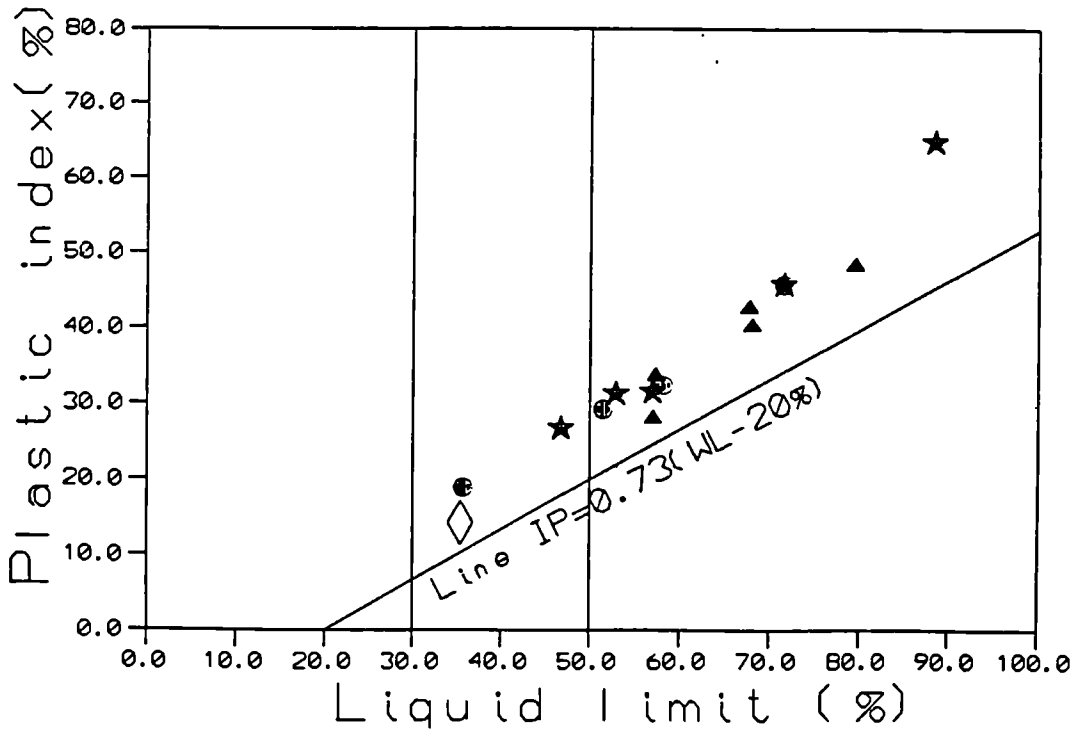


Fig. 5

Title:	CHEMVAL2 THERMODYNAMIC DATABASE
Contractor:	WS Atkins Science & Technology
Contract No.:	FI2W/0122
Duration of Contract:	09/92 to 12/94
Period covered:	09/92 to 12/92
Project Leader:	Dr. W.E. Falck

A. OBJECTIVES AND SCOPE

The principal objective of the CHEMVAL2 database project is the production of an extended, reviewed thermodynamic data compilation applicable to geochemical modelling studies in the EC member states. The database will be fully referenced to source and emphasises radio–elements and other chemical components of relevance to radioactive waste disposal.

The CHEMVAL thermodynamic database has been compiled as a result of collaborative work during the 1985–1989 CEC MIRAGE Project. Production of a standardised database has proved invaluable for comparison of simulations performed in different laboratories and has helped to increase the confidence in models now being used in national radiological safety assessments.

The continued need for a centralised database facility is clear and encompasses:

- data review for elements not currently included in the database
- coordination and compilation of data arising from the CHEMVAL2 activities and parallel research work coordinated within the CEC CoCo (Colloids and Complexes) activities.
- data management, primarily the collation and dissemination of frozen data sets.

B. WORK PROGRAMME

The work programme comprises three separate stages reflecting the various phases of the CHEMVAL2 project.

Stage 1 –agree scope of data reviews; establishment of format for database and its mode of distribution

Stage 2 –collation and review of thermodynamic data; annual issue of frozen data sets; coordination and management of less quantitative information arising from CHEMVAL2 and related projects

Stage 3 –final reporting

Database work will continue throughout the contractual period up to the completion of CHEMVAL2 in December 1994.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Stage 1 of the project has largely been completed:

- the scope and priority of the data reviews has been agreed upon
- a Quality Control Plan has been set up as a basis for review work and subsequent data dissemination and to deal with comments/recommendations from users

Progress and Results

1. Scope and priority of data reviews

Following list of elements not previously reviewed and sequence of data reviews has been agreed upon:

- errors/gaps already identified
- redox–equilibria of elements already contained in database
- Co, Ni, Se, As and V
- Cr, Lanthanides, REE
- entropy data on all species as made available by the CHEMVAL2 topic group'Temperature Correction'

2. Quality Control Plan

The value of the CHEMVAL2 database depends on the consistent handling of data reviews and the avoidance of information of unknown quality. A Quality Control Plan has been set up and is available as draft report. The QC plan sets out the procedures for amending, changing and adding entries into the CHEMVAL database. The aim is to make all changes transparent and traceable at any time.

The CHEMVAL thermodynamic database will be issued to the public in frozen versions, i.e. extracts from working versions, at certain intervals, will be released annually. Only frozen version should be used for scientific or technical work and can be referenced. Immediately after issuing a frozen version, the working version on which it was based will also be frozen and a new working version will be created. In addition, code–compatible versions, initially for PHREEQE only, will be produced. A flow diagram illustrating the interrelation between different versions is given in Fig. 1.

List of Publications

An overview over the CHEMVAL Thermodynamic Database has been presented at a number of conferences:

FALCK, W.E. and READ, D. (1992): Entwicklung eines kritisch geprüften Satzes thermo–dynamischer Daten für geochemische und hydrochemische Modellrechnungen.– Poster given at Tagung der Fachsektion Hydrogeologie der Deutschen Geologischen Gesellschaft (FH–DGG), 26–28 May 1992, Münster, Germany.

FALCK, W.E., READ, D. and THOMAS, J. (1992): The Development of an Internally Consistent and Critically Reviewed Database for Geochemical Modelling.– Budapest '92 – International Symposium on Environmental Contamination in Central and Eastern Europe, 12–16 October 1992, Budapest, Hungary.

FALCK, W.E., READ, D. and THOMAS, J. (in prep.): An Internally Consistent and Critically Reviewed Database for Geochemical Modelling.– Poster accepted for the 4th International KfK/TNO Conference on Contaminated Soil, 3–7 May 1993, Berlin, Germany.

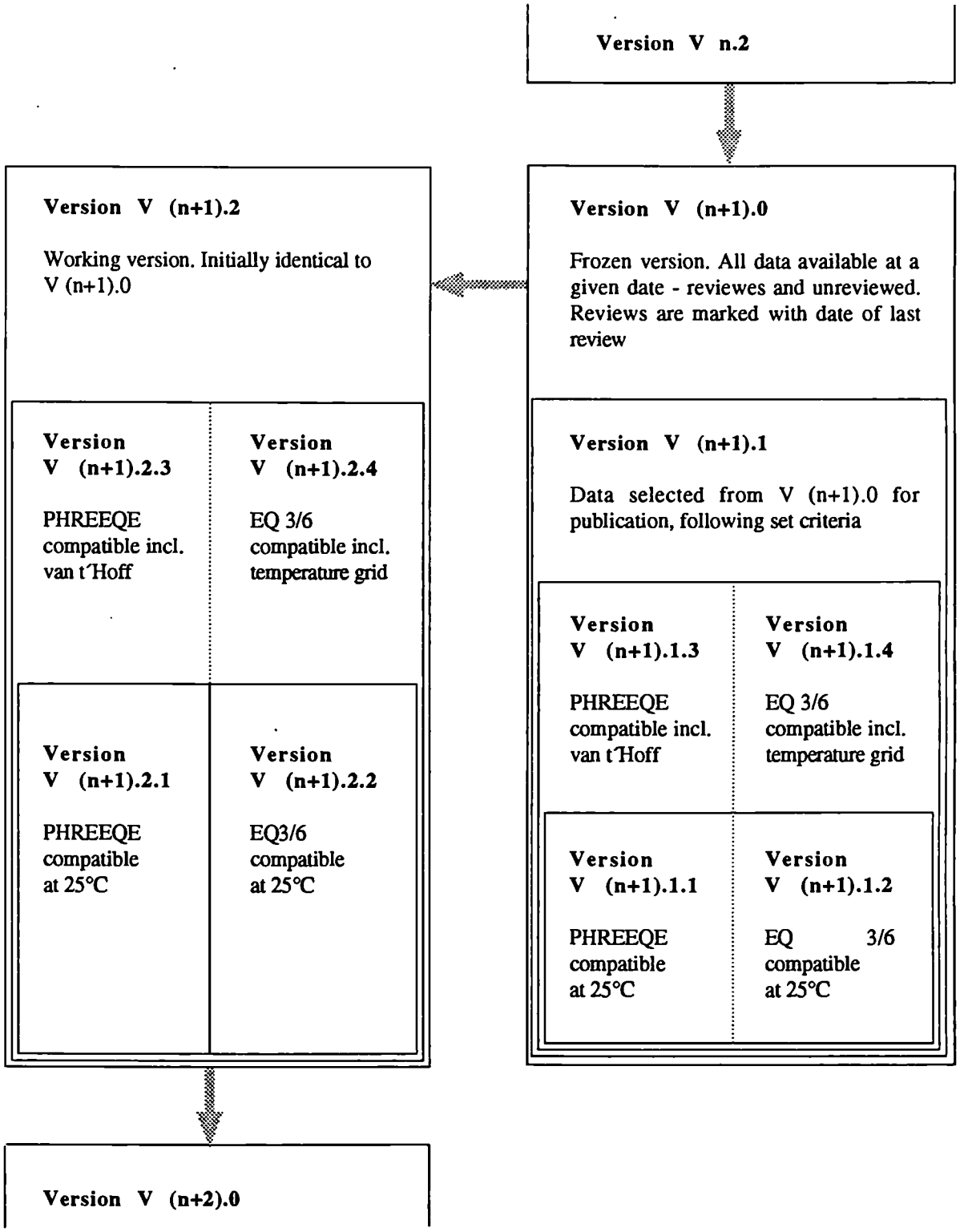


Fig. 1: Flow-Diagram for data review and distribution

Title:	Study of coupling between "fractured medium" and "porous medium" flow models
Contractors:	CEA/IPSN*
Contract n°:	FI2W/ CT 91/0086 (SMA)
Duration:	01/08/91 - 31/07/92
Period covered:	from 01/01/92 to 31/07/92
Project leader:	M. GOMIT (CEA/IPSN) - MM. GOBLET, de LOPE (CIG/ENSMP)**

A- OBJECTIVES AND SCOPE

The objective of the present study is to investigate the use of the coupled model from a methodological point of view. Modelling of fractured medium in the framework of the safety analysis of a deep geological disposal for radioactive waste generally relies on two families of models:
- the Equivalent Porous Medium model relies on the assumption that properties of the fractured medium (hydraulic conductivities, porosity, ...) can be averaged in a meaningful manner on rock volumes which can be regarded as small on the regional scale of interest;
- the Discrete Fracture Model seeks to represent each fracture of the medium, or at least a statistically equivalent set of fractures, and to describe more accurately the flow in the fractures.

In the framework of contracts with the CEA/IPSN, the CIG/ENSMP, has developed and applied two numerical tools:
- the FRACAS model /1/ is a Discrete Fracture Network (DFN) model describing flow, mass transport, heat transfer and hydromechanical interrelations in a network of disk-shaped fractures (Beacher model);
- the TRISEC code is an Equivalent Porous Medium (EPM) model which solves in three space dimensions the equations for flow and heat transfer on a variety of finite elements.

B- WORK PROGRAMME

A numerical tool based on the connexion of the FRACAS and TRISEC models has been developed by CIG/ENSMP for CEA/IPSN. Our approach is to apply this coupled model at the scale of a real site with data as close as possible to "real life". The aim of these evaluations is to see whether a distance exists from which the DFN perturbation is no more visible, and how this distance depends on the "coupling radius".

* Commissariat à l'Energie Atomique - Institut de Protection et de Sûreté Nucléaire
** Centre d'Informatique Géologique - Ecole Nationale Supérieure des Mines de Paris

C- PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The coupled Discrete Fracture Network (DFN)-Equivalent Porous Medium (EPM) model was first tested on a simple geometry with a fracture network of limited density. Piezometric head distributions as well as flow rates were in good agreement with expected values.
A more realistic model of an hypothetical site was then built, based on data from the French sites of Fanay-Augères (for the fracture geometry) and Auriat (for the large scale hydraulic conductivity). It was necessary to modify these data to some extent to make the case more characteristic of deep rock mass conditions.
The effect of the coupling radius was investigated by comparing the results of the mixt model to those of a porous medium, and intercomparing results for various values of the coupling radius.
The proposed work has been terminated during year 1992 and reported in reference /2/.

Progress and results

. Preliminary test

The aim of this test was to check the numerical behaviour of the developed code. A global domain of dimensions 11,3 x 11,3 km is modelled. Centered in it is a network of 200 fractures, contained in a domain of 1,3 x 1,3 x 1 km.
On this structure steady state flow is computed. A first set of boundary conditions describes a uniform regional flow. A second one creates a flow between a recharge and a discharge zone.
This preliminary test showed that the model behaviour is satisfying qualitatively (piezometric head maps) as well as quantitatively (flow balance on the global and local scales).

. Simulation of a typical site

The mixt model has been also used in conditions as close as possible to a real situation.
One of the main problems when using the mixt model on a real site is the extension of the zone to be modelled by a Discrete Fracture Network Model. The use of a mixt approach is dictated by a conceptual view of the site (smooth behaviour on a large scale, irregular behaviour at the local scale), but this general concept gives no way to estimate *a priori* where the transition between the two approaches must be placed. For practical reasons (the Equivalent Porous Medium part of the model being generally more economical than the Discrete Fracture Network part), it is likely that the transition will often be placed below the scale at which a REV concept makes sense. The exercise proposed here aimed at demonstrating the influence of this choice.
The dimensions of the regional domain are 4000 x 4000m (horizontal) and 3000 m (vertical). The Discrete Fracture Network zone is situated at a depth of about 1000m, and is contained in a cube. The size of this inner domain is varied between 100 and 300m to study how this influences the global as well as the local flow. On the top surface, a piezometric head is imposed to create a flow between a recharge zone and 2 discharge zones. The DFN is situated in the descending part of this flow (see figure 1). All other limits are no-flux boundaries.

The French site of Auriat shows a vertically zoned hydraulic conductivity distribution: from 6 10^{-9}m/s near the surface to values around the measuring limit (10^{-12}m/s) at a depth of 1000m. This profile of slowly decreasing conductivity is characteristic of a very low permeability rock mass. It has been for instance used in generic studies such as the PAGIS exercise.
In the present study however, a unique value of hydraulic conductivity has been used, because the generation of a layered field introduced a significant amount of data preparation without modifying the results, as had been shown by preliminary tests. The value used is equal to k_{reg} = 10^{-12}m/s. It can be considered as characteristic of a very tight rock mass.

The fracturation observations on the Fanay-Augères site showed that the fractures can be grouped into five families. The orientations inside each family can be represented by a Fisher distribution, the radii (approximated by the trace length distribution on the drift walls) as well as the fracture conductivities by a log-normal distribution.
The fracture network used in the site simulation has to comply with three constraints:
- the volume covered has to be of the order of several hundred meters, to be at least roughly comparable in scale with a repository,
- the average conductivity of the zone must be close to 10^{-12}m/s.
- the network must be well connected to demonstrate the properties of the mixt model.
The parameters of the Fanay-Augères fracture network do not obey some of these requirements, and had to be adapted. Only the parameters characterizing the fracture orientation and the dispersion of radii have been retained. The mean of the radii distribution as well as the fracture density have been arbitrarily modified to obtain a well connected network with the desired average conductivity. The latter depends also of the aperture distribution, which has been choosen as lognormal, and identical for all fracture sets. The modified fracture network has 1723 fractures for the largest extension of the fracture network zone.

The regional flow field is shown to be analogous to the field obtained from a porous medium model (figure 1). This is confirmed by a comparison of the flow rates crossing the two models: both models yield the same global flow rate.
The piezometric head maps showed that the fracture network acts as a drain for the local flow. This effect is reduced when the size of the Discrete Fracture Network zone grows. The flow rate crossing the faces of the Discrete Fracture Network zone is computed, and compared to the values obtained for an homogeneous porous medium model. The general pattern of flow is similar to the porous medium case, but a non-negligible fraction of flow enters or exits through limits which should normally see no flow (figure 2). The flow field is indeed fully 3-dimensional. The distribution of flow gets closer to the Porous Medium case when the size of the Discrete Fracture Network zone increases.
To illustrate the transition from the irregular behaviour of the Discrete Fracture Network to the smooth behaviour of the porous medium, piezometric head maps on successive cross-sections at an increasing distance from the fracture network zone were drawn. These cross-sections are either horizontal, above the fracture network, or vertical and parallel to the main direction of flow.
As a first conclusion, it can be said that the regional scale model is insensitive to the presence to the Discrete Fracture Network. The same global flux is obtained when the size of the Discrete Fracture Network region is varied. The flux through the outlets is in accordance with the results of an homogeneous porous medium calculation.

The perturbation of the regional flow by the DFN appears in maps of piezometric head as one gets closer to the DFN zone.
These observations lead us to define a volume for which the chaotic behaviour of the fracture network smoothes out. For the structure considered here, this volume can be characterized by a dimension of about 200m. This may be considered as a fair estimate of the Representative Elementary Volume for the considered fracture network.

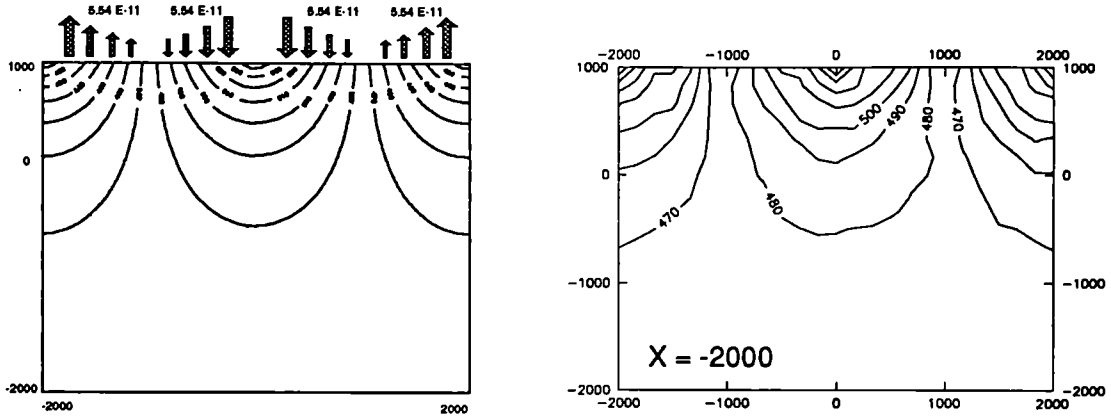
. Conclusions

This study has shown the feasibility of a mixt approach for the modelling of a large fractured rock mass.
The coupling between a Discrete Fracture Network and a Porous Medium has an artificial character because it does not rely on a physical description. However, it must obey certain rules in order to maintain the characteristics of each sub-model: the fracture network must behave as if it emerges from a large scale fracture network. On the other hand, the Porous Medium Model should behave as if it was alone, which means that the chaotic behaviour of the Discrete Fracture Network should vanish at its border. This leads to the idea of a "coupling radius" defined in order to respect these constraints. Ideally, this coupling radius should cover the scale of emergence of an Equivalent Porous Medium, if such a scale exists.
We have tried to base our demonstration study on relevant data: the fracture statistics are issued from the Fanay-Augères site. However, they had to be modified to yield a lower conductivity value and a larger scale connectivity. The retained parameters are therefore somewhat arbitrary. This does not, in our opinion, reduce the methodological value of the exercise. At the global scale, only an homogeneous value of hydraulic conductivity has been retained. This value is characteristic of a very tight rock mass such as was observed on the French site of Auriat.
Our simulation showed that the smooth behaviour of the Discrete Fracture Network appears for a coupling radius of 200 to 300 meters. This conclusion is of course highly dependent of the choosen fracture network structure. Our study must be viewed as an approach to determine this parameter in a specific situation. From this viewpoint, the fully automatic creation of the coupled structure is an advantage, as it allows to perform variations with a minimal effort. The global model has some limitations related to the structure of the Finite Element mesh. However, it can be adapted using any technique for Finite Element input preparation, to describe more realistic structures (for instance, the presence of large scale fractures which must be described explicitely in the Porous Medium part as well as in the Fracture Network part of the model).
Use of the coupled model approach implies the existence of a dominant scale of fracturation controlling the flow. Nested structures, which are the general rule in fractured rock masses, are possible only in so far as an upper bound exists. If the scale of these structures grows up to the scale of the regional flow, then the REV concept, and the coupled model, are irrelevant.
Finally, one must keep in mind that the choice of data was biased by the available computer resources. This type of model, although probably more economical than a full Discrete Fracture Network, is still much too demanding to allow the description of a densely fractured structure. Along the same line, this study has been restricted to the flow aspects, whose knowledge is a prerequisite before attempting to describe solute transport. Models taking into account mass transport would entail a further level of complexity (due in particular, but not only, to the transient aspect).

D- REFERENCES

/1/ CACAS, M-C, Développement d'un modèle tridimentionnel stochastique discret pour la simulation de l'écoulement et des transferts de masse et de chaleur en milieu fracturé (Thèse 1989)

/2/ GOBLET, P., de LOPE, L. Study of coupling between "Fractured Medium" and "Porous Medium" Flow Models - Final Report (1992)



Homogeneous porous medium model

Mixt model

Figure 1 : Piezometric head computed with an homogeneous porous medium and with the mixt model

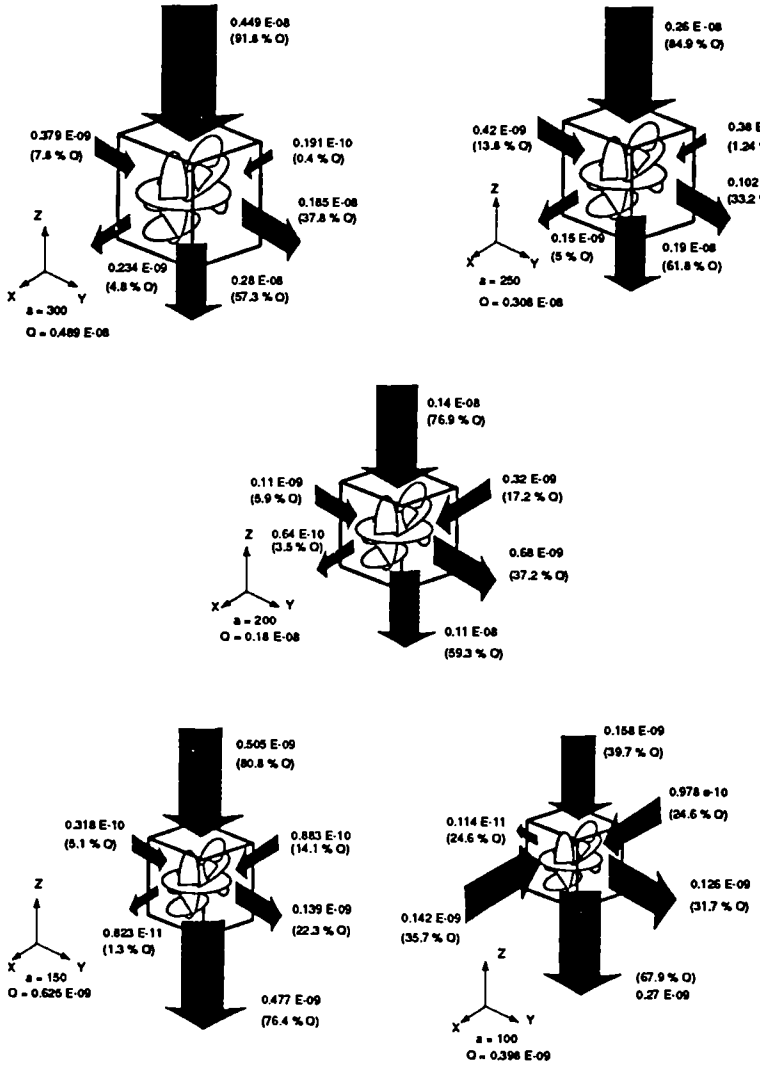


Figure 2 : Flux distribution on the coupling shell

Title:	Methods of Handling Non-Homogeneities at Different Scales in Radionuclide Transport
Contractor:	Elektrowatt Engineering Services (UK) Ltd.
Contract No.:	FI2W/CT91/0087
Duration of Contract:	1 September 1991 - 31 August 1992
Period covered:	1 January 1992 - 31 August 1992
Project leader:	Prof. M.M.R. Williams

A. OBJECTIVES

To develop a working set of equations to describe the transport of radionuclides in media with randomly varying material properties. To apply these equations to some well-defined geometrical situations and to highlight the deficiencies in current practice, much of which uses the classical advective-dispersion equation. To review the past work in the field. It is expected that the new equations will be applicable to practical situations in assessing the containment efficiency of waste repositories.

B. WORK PROGRAMME

The stated goals of this work were threefolded:

1. A review of the relevant past work done in the field of spatially stochastic radionuclide transport

2. The development of a set of equations to describe radionuclide transport in spatially random media

3. The provision of numerical results for simple geometries to compare the new equations with the results from classical methods.

These tasks have been carried out successfully and the results and conclusions have been presented to the Commission in the following reports:

* "A review of selection of papers describing the theory of transport in anisotropic media", published as EUR report 14163

* "A new model for describing the transport of radionuclides through fractured rock:
  Part 1: General theory
  Part 2: Numerical results and extension to overlapping fracture sets"

* A final report of the research project "Methods of handling non-homogeneities at different scales in radionuclide transport", summarizing the findings of the above report and to make some recommendations to future work using the new set of equations developed. This report will be published as EUR 14696.

C. SUMMARY OF THE OBTAINED RESULTS AND CONCLUSIONS

A review of the past work in the field of transport of water borne contaminant in spatially random porous media has been carried out. The review covers the period from 1921, in which G.I. Taylor developed some basic ideas of the subject, up to 1988, thereby embracing the modern advances of Dagan, Gelhar and co-workers who considered the transport equation as a stochastic differential equation and were thereby able to give a reasonable explanation of the scale-dependence phenomenon.

A new approach to radionuclide transport in fractured rock has been developed which avoids the difficulties encountered by the classical advective-dispersion model. The new equation is also much simpler in concept and application than stochastic methods currently favoured for explaining scale-dependent phenomena.
In this new theory, an angular distribution function is introduced which takes into account the random lengths and orientation of fractures (rock microstructure). Such fracture lengths are considered to be analogous to mean free paths and the random direction of motion of a marked particle when it meets an intersection of two fractures is analogous to a scattering event. By means of this analogy we can use a Boltzmann-like equation similar to that employed for neutron transport. Numerical and analytical solutions of this equation have been obtained and the results highlight the inadequacies of the classical advection-dispersion theory and also explain in a clear manner the scale-dependence of the dispersion length noted by the experimentalists.

Future work must be directed at more detailed models for the number of intersections per fracture and the associated fracture distribution function. In addition, it will be necessary to make the necessary modifications to time-dependent neutron transport codes in order to carry out detailed multi-fracture calculations in realistic situations.

D. REFERENCES

M.M.R. Williams, (1991) "A review of a selection of papers describing the theory of transport in anisotropic porous media" Report to the CEC as Task 1 of Contract FI2W/CT91/0087, published as EUR report 14163 (1993).

M.M.R. Williams, (1992) "A new model for describing the transport of radionuclides through fractured rock: Part I, General Theory" Report to the CEC on Task 2 of Contract FI2W/CT91/0087.

M.M.R. Williams, (1992) "A new model for describing the transport of radionuclides through fractured rock: Part II, Numerical results and extension to overlapping fracture sets" Report to the CEC on Task 3 of Contract FI2W/CT91/0087.

M.M.R. Williams (in press) "Methods of handling non-homogeneities at different scales in radionuclide transport" Final report of CEC Contract FI2W/CT91/0087 to be published as EUR 14696.

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THE TREATMENT OF UNCERTAINTY IN GROUNDWATER FLOW AND TRANSPORT MODELLING

Contractor:	AEA Decommissioning & Radwaste, Windscale, UK.
Contract No:	FI2W / 0088
Duration of Contract:	1 April 1991 to 31 March 1995
Period Covered:	1 January 1992 to 31 December 1992
Project Leader:	Dr J D Porter

A. OBJECTIVES AND SCOPE

Analysis and understanding of the groundwater flow in the neighbourhood of a radioactive waste repository play important roles in a performance assessment. Such analyses rely on numerical modelling in order to study the flow and transport over the very long times that must be considered. Two vital issues which must then be considered are the way in which the available data are used in constructing the mathematical model of the site and the uncertainty that is implied in the results of the model by uncertainties in the model parameters and in the model itself. The two tasks in this project address these issues. The first task is concerned with the investigation of novel approaches to the construction of mathematical models of a site. The second task is concerned with the investigation of methods for the estimation of uncertainty in groundwater flow and transport calculations.

B. WORK PROGRAMME

Task 1 Site Characterisation

1.1 Site Models: Mathematical models that can be used to represent a site will be reviewed. A computer package based on a selected method will then be written.

1.2 Inverse Problem Techniques: Methods for the inverse problem will be investigated and a selected approach will be applied in conjunction with the site models developed in Task 1.1.

1.3 Effective Properties: Methods for relating measured data to model parameters will be investigated using numerical calculations, based on the site models developed in Task 1.1.

Task 2 Treatment of Uncertainty

2.1 Methods for the Treatment of Uncertainty: Methods for the estimation of uncertainty in the results of groundwater flow and transport models will be investigated.

2.2 Parameter Sensitivity: Methods for the estimation of sensitivity coefficients will be investigated. The coefficients will be used to study the topic of data worth.

2.3 Model Uncertainty: The study of this topic will build on experience of "what-if" studies and will pay particular attention to long-timescale changes in hydrogeology.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Task 1.1: As explained in the previous report in this series, Indicator geostatistical methods [1,2] have been selected for investigation in this project. The approach is being applied to borehole data from the Gorleben site. Indicator Kriging calculations have been carried out, initially for a small region between two boreholes, and then for a cross-section spanning the Gorleben erosion channel. The results appear to be broadly consistent with the suggested geological interpretation supplied with the data, but show some interesting differences. The sensitivity of the Kriged fields to the choice of Kriging neighbourhood and to reasonable choices of the variogram parameters has also been investigated, as has the distribution of the Kriging variance.

Tasks 2.1 and 2.2: An uncertainty estimation method based on the adjoint sensitivity technique [3] has now been implemented in the AEA Technology groundwater flow code NAMMU. The method of implementation ensures that the computational cost of using the facility is only marginally greater than that of a single groundwater flow calculation. The adjoint method has been applied to the groundwater flow model used in the CEC PACOMA study [4]. It was found that the sensitivities of the model results of interest to small changes in the input parameters were well predicted by the adjoint analysis. The method was also applied to a more realistic two-dimensional multi-layer groundwater flow model. The results obtained in this case were consistent with those given by a more computationally expensive method involving multiple simulations and indicated the potential usefulness of the adjoint approach.

Progress and Results

Task 1 - Site Characterisation (subtask 1.1)

As noted in the previous report in this series, Indicator geostatistical methods [1,2] have been selected for investigation in this project. Indicator Kriging has therefore been applied to borehole data from the Gorleben site. In the analysis of the Gorleben borehole logs an indicator value of 0 was assigned to locations where clay is present and an indicator value of 1 to locations where clay is absent. The 0.5 contour of the indicator function was considered to be the boundary between the "clay" and "not clay" regions. This contour should therefore be broadly in agreement with the location of the boundary of the clay regions shown in a normal geological interpretation. The method was initially tested on a small region between two boreholes, with encouraging results. Indicator

Kriging was then applied to a cross-section spanning the whole Gorleben erosion channel. Figure 1 shows a comparison between the locus of the 0.5 contour of the Kriged indicator function and the location of clay layers in the geological interpretation supplied with the Gorleben data. It can be seen that there are similarities between the two, but also some differences. In general the Indicator results show less horizontal connectivity than the interpretation. Of course the interpretation may be making use of additional information such as seismics. Further study of these results is underway.

The sensitivity of the Kriged field to the choice of Kriging neighbourhood and to reasonable changes in the variogram parameters was also investigated. The Kriging variance was also plotted and, as expected, was found to be smallest near the boreholes. It can be used to provide a confidence interval for the Kriged value.

This work was presented at the meeting of the INTRAVAL salt working group in June 1992 and at the full INTRAVAL meeting in November 1992. In both cases the work was well received and generated some interest.

Task 2: Treatment of Uncertainty (subtasks 2.1 and 2.2)

An uncertainty estimation method based on an adjoint sensitivity technique [3] has now been implemented in the AEA Technology groundwater flow code NAMMU. In the present implementation, adjoint states may be computed for several model results of interest, for example, Darcy speed at a point and groundwater travel time from a point. Such quantities were selected because they are often of interest in assessment calculations. Physically, the adjoint state at a point corresponds to the response of the result of interest to a unit injection of water at that point. The coefficients quantifying the sensitivities of the model results to the input parameters and the boundary conditions can then be calculated from the adjoint state. The adjoint sensitivity calculation uses the same factorisation of the discrete coefficient matrix for both the groundwater flow equation and the equation for the adjoint state. Hence the computational cost of performing the adjoint analysis is only marginally greater than that of performing a single groundwater flow calculation.

The adjoint method has been applied to two cases: the two dimensional, three layer groundwater flow model used in the CEC PACOMA study [4] and a more realistic two-dimensional multi-layer groundwater flow model. In both cases the results for the sensitivities obtained from the adjoint analysis were compared with those obtained by

systematically perturbing each model parameter in turn. In the PACOMA model, the model result considered was the Darcy speed at a hypothetical repository location. As can be seen from Table 1 the results obtained from the adjoint analysis were in very good agreement with the results obtained from a series of runs in which each permeability in turn was increased by 10%. The adjoint method was then applied to the multi-layer model. The model results considered were the square of each of the components of the Darcy velocity at a hypothetical repository location. In general, good agreement was found between the sensitivities predicted by the adjoint analysis and the results obtained when each model parameter in turn was varied. However, the adjoint sensitivity method only required the computational effort equivalent to a single groundwater flow calculation to produce these results whereas the alternative method required about 20 such calculations. This suggests that the adjoint approach could play a useful role in assessment calculations, screening the model for the most important sensitivities. The effects of the corresponding parameters could then be studied in more detail.

In the next phase of the work the implementation of the method for the travel time performance measure will be tested.

Acknowledgement: This project is cofunded by the Nirex Safety Assessment Research Programme (NSARP) of UK Nirex Ltd.

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4. Winters K H, Clarke C M and Jackson C P "The UK Contribution to the CEC PACOMA Project: Far-Field Modelling of Radioactive Waste Disposal in Clay" NSARP Report NSS/R185 (1990).

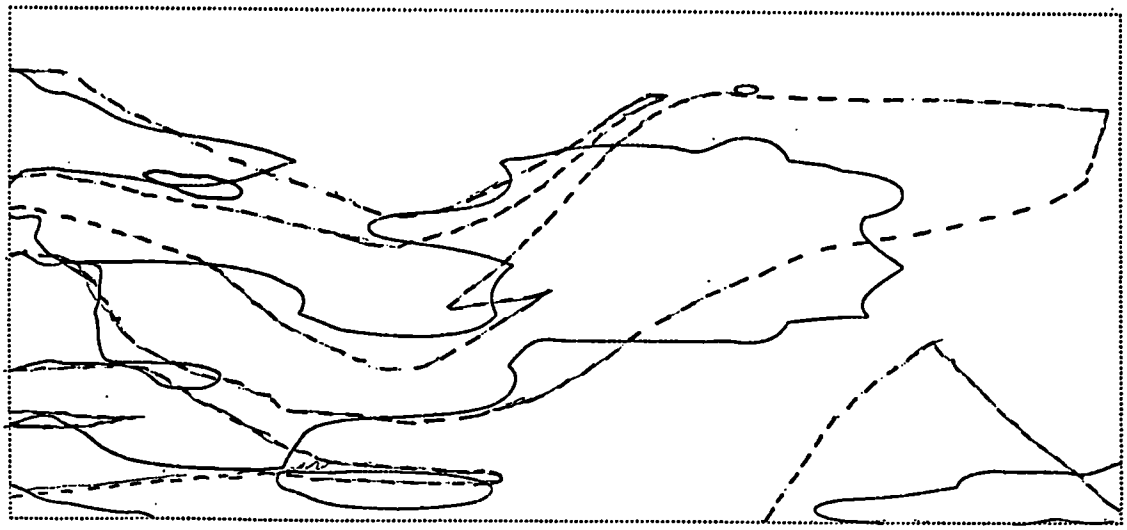


Figure 1: Comparison of locus of 0.5 contour of Kriged Indicator function (-) with boundary of clay region in geological interpretation (- -) for a cross-section perpendicular to the Gorleben erosion channel.

Rock Type	Permeability Component	% change from direct calculation	% change from Adjoint method
Chalk	Horizontal	$8.76\ 10^{-04}$	$8.56\ 10^{-04}$
	Vertical	$-7.67\ 10^{-04}$	$-8.44\ 10^{-04}$
Clay	Horizontal	0.622	0.594
	Vertical	9.29	9.28
Corallian	Horizontal	0.119	0.130
	Vertical	$3.02\ 10^{-05}$	$2.63\ 10^{-05}$

Table 1: A comparison of the actual percentage change in the Darcy speed at a point with that predicted by the Adjoint approach for a 10% increase in each of the permeability parameters.

Title: Uncertainties in the modelling of migration.
Contractor: Risø National Laboratory, Denmark.
Contract N°: FI2W/0089.
Duration of contract: from 1/9 1991 to 1/9 1994.
Period covered: 1/1 1992 to 31/12 1992.
Project leader: B. Skytte Jensen.

A. OBJECTIVES AND SCOPE

The objectives of the present investigation is to estimate the uncertainties to be ascribed to the results of modelling calculations of diffusion and convection calculations. Especially the uncertainties which are the consequences of the possible presence of unidentified heterogeneities in a given formation will be considered. Numerous other sources add up to the final uncertainty, like poorly understood and characterised geochemistry, but contrary to the first type of uncertainties, such problems may in principle be solved by intensive and well planned laboratory experiments.

Several related attempts aiming at decribing the dispersion to be expected, when migration proceed through a complex of fissures, have been reported, although measures of the expected uncertainties have not been explicitly stated.

Only recently has attention been paid to the uncertainties to be ascribed to migration modelling, wherefore the relevant tools have not been firmly established yet. Several approaches are possible mostly related to experimental work in the field or the lab. In the present investigation, computer-experiments alone will be used as the tool.

B. WORK PROGRAMME

1 To develop an algorithm which will be used for creating two- and three dimensional 'synthetic' geological formations with inhomogeneities whose positions are selected at random.

2 To develop a mass-conserving algorithm which can handle diffusion in heterogeneous media in both two- and three dimensions.

3 To develop methods for analysing for the variability in migration lengths and effective diffusion coefficients etc.

4 The effect of inhomogeneities on dispersion in two-dimensional plugged flows will be illustrated by means of conformal mapping and the implications for three-dimensional flow estimated.

5 Networks, in which the permeabilities of paths are randomly generated, will similarly serve as a model for three-dimensional migration in fissures, and a program will be developed which can handle network flows, solve for potentials, fluxes, particle migration lengths and plugged flow dispersion.

6 The calculated results will be compared with experiences from field and lab work.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

No-flow systems.

The main efforts made during the reference year have been the application of the previously developed programs for the modelling of diffusion in 'formations' with randomly positioned inhomogeneities in two- and three dimensions.

Flow-systems.

Methods for visualising plugged-flow dispersions in two-dimensional systems with inhomogeneities have been developed and used for diverse configurations of obstacles in the flowpath. Whereas the longitudinal dispersion persist after long time-spans, the transversal dispersions have only a transient local existence in two-dimensional systems and disappear after entrance of the flow into a homogeneous system.

The reason is that the streamlines are not allowed to cross in the two dimensions considered.

A network model in which permeabilities of path sections are randomly generated is being developed for estimating uncertainties and dispersion effects due to convection in fissured formations. Preliminary calculations have indicated the usefulness

of the model.
In its final version the single paths in a network will have to be ascribed not alone a resistance to flow, but also its own dispersive effect.

1 Progress and results

The algorithm for positioning inhomogeneities in two- and three-dimensional arrays was easily accomplished. By scanning the resulting arrays the effective porosity could be determined. As expected would several positions coincide with increasing numbers of obstacles, and random clustering would also occur generating variations in sizes of inhomogeneities, as would be expected in real systems.
Real systems will in most cases not be random, but display different more or less ordered structures generated by geological processes. To study these effects diffusion experiments have been done in a few ordered arrangements of the inhomogeneities.

2 A simple mass-conserving explicit finite difference algorithm for calculating diffusion in inhomogeneous media has been developed. After several hundred iterations the total amount of the diffusing species is within a few percent equal to the added amount, depending somewhat on the size of the iteration steps.

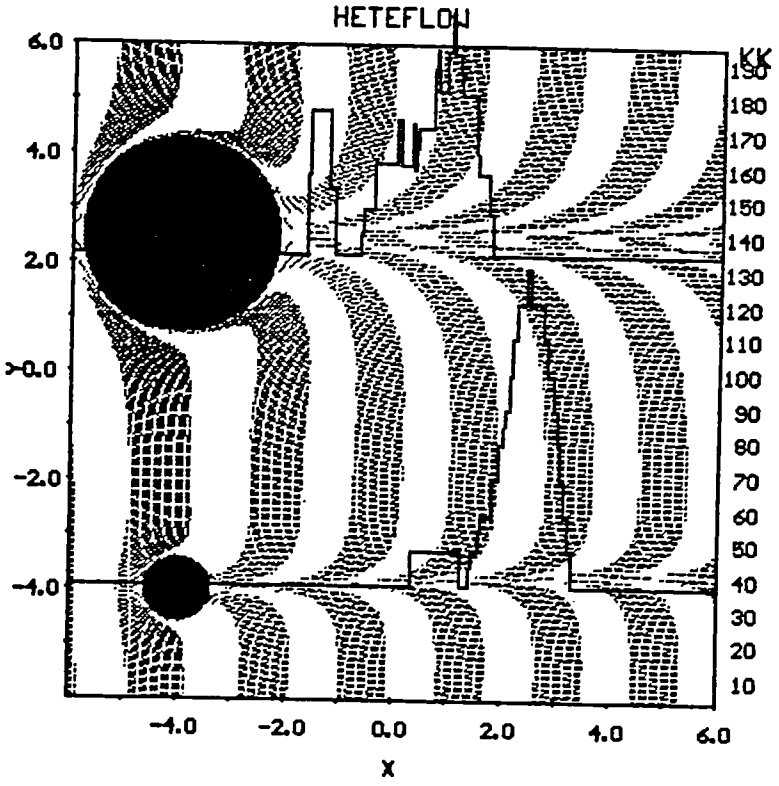
3 In the calculations performed is demonstrated a linear relationship between the effective three-dimensional diffusion coefficient and the effective porosity of the medium. The uncertainties to be ascribed to the mean effective diffusion coefficients are at maximum for porosities around 0.5, increasing rapidly with decreasing porosities.
In the evaluation the 'sampling technique' is similar to an often used slicing method used with laboratory columns.
With other 'sampling techniques' simulating elution, pumping, scanning etc., the results may be, that the mean effective diffusion coefficients do not deviate drastically from the data obtained with the slicing method, but the uncertainties might well be appreciably larger.

In the case of two-dimensional diffusion the mean effective diffusion coefficient show a larger decrease with a decrease in the effective porosity, approaching zero at porosities around 0.3.

In the one-dimensional case it is obvious, that a single non permeable inhomogeneity will completely block for any diffusion beyond its position.

4 By means of conformal mapping it is possible to illustrate two-dimensional flow around corners, obstacles etc. as well as the associated convective dispersion phenomena.

Fig.1



In the figure is demonstrated the modelled two-dimensional flow of a concentration front through a homogeneous medium with two circular obstacles with radii of 0.6 and 1.8 units. The index KK in the figure is the numbering of the streamlines.
The two 'integrated' concentration curves for branch 6 for KK ranging from 35 to 45 and from 135 to 145 reveal the increase in longitudinal dispersion with increase in size of the heterogeneity.

Whereas the streamlines are seen locally to be highly distorted when the obstacles are passed, they become equidistant again after a certain distance has been passed. This means, that in two-dimensions a pure convective flow will not give rise to any transversal dispersion. This is however a very artificial assumption which can only be realised under special laboratory conditions, and even in this case will diffusion give rise to transversal migration.
The figure indicates furthermore, that the longitudinal dispersion arising is more or less proportional with the effective radius of the inhomogeneities.

It can be shown, that in the two-dimensional case only strictly linear streamlines will not show any evidence of longitudinal dispersion, and that even the passage over a surface irregularity will result in some longitudinal dispersion in the nearest streamlines.
This means, that in practice will flow through any channel give rise to dispersion phenomena.
Whereas relatively simple mathematics is available for the handling of two-dimensional flows in systems with inhomogeneities, this is not the case for three-dimensional flows.
It is expected, although not proven, that the relation between path-length and velocity in the three dimensional case will result in a longitudinal dispersion, D_x, like in the two-dimensional case.
Due to the added dimension, the streamlines have the added freedom to intermingle and mix, even if they are not allowed to cut each other. Experimentally this will be observed as a dispersion in three dimensions with both finite longitudinal - and transversal dispersion coefficients, D_x, D_y and D_z.
It is obvious, that all these dispersion coefficients must be interdependent in some complicated way and also depend on the structure of the medium and the flow-velocity.

Networks, in which the permeabilities of local paths are randomly generated, will serve as a model for a three-dimensional migration in fissured structures. Based on its analogy with electrical circuits, a program will be developed, which can handle network flows, solve for potentials, fluxes, particle migration lengths and velocities

ultimately allowing for an estimate of convective flow dispersions.
However, to cope with the predicted dispersion effects in 'fissures', attempts to ascribe velocity distributions to each passage of these will be elaborated.

6 Finally the implications of the calculations in relation to lab and field investigations will be discussed. Both the diffusion and flow studies have indicated that difficulties may exist in obtaining comparable experimental data.

UNBIASED GUESS AS A CONCEPT TO COPE WITH FUZZY AND RANDOM PARAMETERS IN GEOCHEMICAL MODELLING

Title :	Unbiased Guess as a Concept to Cope with Fuzzy and Random Parameters in Geochemical Modelling
Contractor :	BRENK SYSTEMPLANUNG
Contract N° :	FI2W-CT91-0090
Duration of contract :	from 01.06.1991 to 30.09.1994
Period covered :	from 01.01.1992 to 31.12.1992
Project Leader :	Dr.-Ing. H.D. Brenk

A. OBJECTIVES AND SCOPE

Any risk analysis dealing with the transport of radionuclides from a radioactive waste repository on the basis of deterministic equations suffers from two severe problems. Firstly, all processes in reality are random in nature and, secondly, the data basis and the knowledge about the relevant processes will never be complete. The aim of the study is to investigate the applicability of fuzzy set theory in decision making and the potential of information theory in this context. Since ambiguity in the valuation of models and model parameters represents the main obstacle for a consent about the results, it seems very promising to apply a kind of maximum entropy method, the "method of unbiased guess", in order to deal with incomplete knowledge. While the incorporation of randomness into this approach is straightforward adequate methods have to be developed in order to deal with incomplete knowledge or subjective quantities (i.e. expert judgement). The main aim of the study is to propose a theoretically well-founded formalism serving this purpose. The capability of this formalism will be demonstrated on a non-trivial migration problem.

B. WORK PROGRAM

1. Compilation of the relevant aspects of information theory. Special emphasis is put onto the method of unbiased guess and its theoretical foundation.
2. Discussion of the problems of geochemical modelling in risk assessments with respect to uncertainty using probability density functions and the theory of fuzzy sets.
3. Development of a formalism for a consistent and unambiguous incorporation of incomplete knowledge employing the method of unbiased guess.
4. Demonstration of the applicability of the formalism using a simulated migration problem as a test case.
5. Documention
6. Project coordination

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

After having outlined the main properties of probability theory and different approaches to fuzzy theory, a number of functional expressions, similar to the entropy, have been discussed as possible candidates for a variation procedure in the sense of unbiased guess. The most recent advance is concerned with a combined treatment of random and fuzzy parameters, which takes into account measured data sets as well as expert knowledge.

Progress and results

A method was developed to handle functions of variables, which have different uncertainty characteristics. If the information about a parameter is given by a large data set of measurement results the variable is called a random variable and can be treated by the laws of probability theory. If, on the other hand, the information reduces to some subjective expert assertions, then we speak of a fuzzy variable. These fuzzy variables are treated by the laws of possibility theory. Both concepts, probability and possibility, can be generalized to so called fuzzy events, characterized by membership functions of fuzzy sets. The connection of probability and possibility is established by investigating functions, which depend on both, random and fuzzy variables. The idea for the first step is to treat the random variables as fixed parameters and perform all possibilistic inferences. Since the resulting possibility takes on values between 0 and 1 it can be interpreted as the membership function of a fuzzy set with a random argument, that is a random fuzzy event. In the second step, the expectation value of the random fuzzy event with respect to all random variables leads to a generalized probability. Applied to geochemical transport problems of radioactive waste, this kind of probability might be used to define a decision criterion for the acceptability of dose rates.

Review and development for modelling with uncertainty and variability

Contractor: Intera Information Technologies, Environmental Division;
University of Bristol, Information Technology Research Centre;
Université Libre de Bruxelles, IRIDIA.
Contract Number: FI2W/0091
Duration of contract: from 1 May 1991 to 31 October 1993
Period covered: 1 January 1992 to 31 December 1992
Project Leader: Dr. P. C. Robinson

A. Objectives and Scope

Any assessment of the safety of an underground repository for radioactive waste must consider various types of uncertainty. These uncertainties arise in each step of the assessment process: information gathering; experimentation; modelling; interpretation of results; and decision making.

These uncertainties are of many types, and are addressed with a variety of tools and techniques. For example, scenario analysis is widely used to tackle uncertainties in the future evolution of a site, and probabilistic calculations are often used for treating uncertain data.

The objective of this project is to review and investigate the types of uncertainties and techniques for handling them. In particular, an aim is to demonstrate techniques which are currently not widely used within the radioactive waste disposal community.

A particular area in which some potentially useful techniques are applied is that of Artificial Intelligence. The use of fuzzy logic is also a potentially useful area. Given this, a collaboration has been set up between those familiar with current practice (Intera), those with in-depth knowledge of artificial intelligence (IRIDIA) and a team with research experience in artificial intelligence, particularly in the application of fuzzy logic and related methods (ITRC).

B. Work Programme

B.1 Review

This phase consists of an in-depth review of:

- types of uncertainty encountered in safety assessments internationally;
- tools and techniques for handling uncertainty, including those currently used in radioactive waste disposal and in other fields;
- available data sources and their uses, including experiment, expert judgement, detailed simulation;
- presentational methods for displaying uncertainty in inputs and outputs of assessments.

B.2 Definition and investigation of important test cases

In this phase, test cases will be defined to cover the types of uncertainty and techniques identified as being most important in the first phase of the project. The aim is to demonstrate the practicalities of implementing various methodologies.

B.3 Investigation of further cases and lessons for general methodology

In this third phase, the focus is on recommendations for novel methodologies which could be used to address important issues. These will be based on the experience gained in the trial applications of the previous phase.

C. Progress of Work

C.1 General

During the year the collaborative groups within the project have been developing various approaches identified from the review phase. These approaches have been tested by application to particular problems in the radioactive waste disposal field.

In the review phase it became clear that uncertainties in radioactive waste disposal safety assessments are of many diverse kinds and occur at all levels. The uncertainties in data which have traditionally been the focus of attention are only one part of the overall picture.

Essentially the management of uncertainty cannot be separated from the overall management of the information within a project - since all of this information is potentially uncertain. Thus the handling of uncertainty must start with looking at the way this information is handled and the way decisions are made. Every decision that is made in defining the safety calculations that are to be made will effect the final predictions to some extent; it is the fact that there is a choice to be made at each decision point that leads to uncertainty in the final result.

With this in mind, and considering the expertise within the project on Artificial Intelligence techniques, the topic of how to manage information was chosen as an important area for study. This has been tackled at two levels - one looking at the high-level structure and one looking at detailed justification of decisions. These approaches have been pursued by ITRC and IRIDIA respectively.

Another area identified for study is that of quantification of uncertainties. The traditional approach to this has been through the use of probabilistic techniques. However, other approaches, e.g. fuzzy sets, have been suggested. Intera have tackled the tasks of producing a practical tool for using the fuzzy set approach and of providing an explanation of how such approach can be beneficial.

Another important area that has been considered is that of decision support - in particular how to take decisions in the absence of complete information. ITRC has used evidential support logic for a case-based reasoning method. IRIDIA has been applying a method based on belief functions.

The objective of this project is to demonstrate the feasibility of novel approaches to the management of uncertainty. With this in mind it is important to apply them to realistic situations. For the knowledge management systems we have chosen to use the SKI Project-90 summary report as the source of information. This choice was dictated by the suitability of the document (it is presented as an already structured set of implications and decisions) and the availability of people involved with the Project-90 at Intera.

For the quantification exercise it is appropriate to compare against existing probabilistic work, and an intercomparison exercise within the NEA PSAG group has been chosen. For the other test cases realistic examples have been invented based on our experience in radioactive waste disposal performance assessment work.

At the end of the year most of the development work had been completed and a number of the test cases had been undertaken. The remaining test cases will be completed in the final phase of the project.

C.2 Progress at Intera (P.C.Robinson)

The work undertaken at Intera has focused on how uncertainties can be propagated through an assessment to produce quantitative statements on the uncertainties in the assessment calculations. The work is described in two sections: the first on the origin and characterisation of uncertainty and the second on development of the QUEST simulator for uncertainty analysis.

Origin and Characterisation of Uncertainty

Uncertainties arise in all aspects of an assessment; the more detail is investigated in any area, the more uncertainty is revealed. If a particular (quantitative) calculation is analysed then it becomes apparent that a large number of decisions of various sorts were made. Each decision point gives an opportunity to choose from many different possible answers. It is the availability of these choices that gives rise to uncertainty.

Intera suggests that for each decision point it is practical to characterise the choices according to how supportable they are. This applies to decisions leading to a single real number and to decisions leading to other classes (such as choosing a conceptual model). It is not intended to imply that a range of alternatives have been considered (or are even available), but simply to represent the support available for the decision taken.

The central point that motivates the use of this type of categorisation is that the ultimate means of distinguishing between choices is subjective expert judgement. This must be based on experimental experience, but such experience cannot directly lead to a characterisation of uncertainty. In considering this it is important to distinguish between variability (which is a property of the system) and uncertainty (which is a property of the observer).

If we accept this view of how uncertainty can be characterised then we are naturally pushed towards consideration of fuzzy sets and possibility theory. This is because we wish to express the support for decisions, methods, parameter values, without necessarily asserting a-priori their independence, their possible impact upon the system, or their completeness (in the sense that all possible choices have been considered).

However, in presenting these ideas to a wider audience it is better to go directly to an explanation of how to handle the uncertainties themselves. To do this we visualise the categorisation of choices for each decision as a collection of nested sets. Two types of combination needed are needed to manipulate these nested sets: *and* and *or*. In the context of an assessment these arise in attaching a degree of support to a series of decisions and in attaching a degree of support to a result that can be arrived at in various separate ways.

The natural rules for these operations are *min* and *max*. Thus the degree of support for the combination (*A and B*) is the minimum of the individual component degrees of support, while the degree of support for (*A or B*) is the maximum of the individual components.

Developing a safety case using the nested set approach requires the identification of sets of decisions that would lead to an unsatisfactory consequence prediction. The safety case will be made by demonstrating that there are no such sets with sufficient degree of support.

The nested set approach has the advantage that a refinement, or division, of the input decisions enables more identification to be made of the 'critical' sets, whereas in a Probabilistic Safety Assessment this would result in smearing the weight of belief over alternatives. This approach is applicable to all types of uncertainty - not just parameter uncertainty. In order to demonstrate that such an approach can be used in a calculational tool, Intera have developed the QUEST code.

QUEST Development

In the initial review phase, approaches to handling uncertainty based on fuzzy methods were identified as being potentially useful in the analysis of all types of uncertainty (except purely stochastic). However, it was noted that such approaches had not received the attention given to probabilistic methods. In order to demonstrate and test the fuzzy approach (and other approaches) on the same examples as a conventional probabilistic approach, Intera is developing QUEST (Quantitative Uncertainty ESTimation).

QUEST is an interactive application operating in a window environment (under Microsoft Windows, Macintosh or Motif). The user develops a library of models and formulae (collectively called processes) which operate on a set of parameters. By declaring some parameters as uncertain, and characterising the uncertainty appropriately for the paradigm (fuzzy, probabilistic, etc), the uncertainty in other parameters can be derived and displayed.

This framework can handle both simple test cases or demonstrations (e.g. a = b * c) and complicated models, as used in radioactive waste disposal performance assessments. Probabilistic and fuzzy approaches can be used within the same code.

Within a QUEST run, the user can manipulate one or more libraries; these can be created from a scratch or loaded from disk, having been saved on an earlier occasion. When a new QUEST library is opened, processes to generate time points and samples are included. The user is offered a selection from the built-in models. The first version of QUEST has a single built-in model - MORTAL (Model of Radionuclide Transport After Leaching). MORTAL includes a leaching source term, an advection-diffusion geosphere and an equilibrium biosphere. It is the type of model that has been used for verification purposes within the NEA PSAG Level E Intercomparison Exercise.

The user can add new formulae using normal expresions, unary functions (such as exp, log etc.), multi-argument functions (min, max). Also two special functions, max-over-time and time-of-max, are also available.

Constant parameters and uncertain scalar parameters can be set values and distributions. According to the paradigm, a membership function (for a fuzzy parameter) or a cumulative distribution function (for a probabilistic parameter) will be required. QUEST operates by running its processes in a sampling loop whenever uncertainty is present. Samples for input parameters which have given memberships or probability distributions will be generated automatically as required. Samples from a membership function are uniformly generated within the extreme ranges. For each model or formula, the output membership is taken as the minimum of the input memberships for this sample.

QUEST can produce various outputs according to the paradigm in use. Output is specified through the output processes which are run like any process but produce a window as their result. The outputs currently produced by QUEST include: membership function; membership level *vs* time and scatter plots.

A first verion of QUEST is complete. It has been used to tackle a range of simple test cases, including algebraic and complex models. A demonstration and verification report will be written together with a code description report.

C.3 Progress at ITRC, Bristol (J.F.Baldwin, T.P.Martin and Y.Zhou)

SAFETIME

A system for storing, retrieving and manipulating information within a performance assessment has been developed, based on the Fril AI (Artificial Intelegence) programming language. SAFETIME (Safety Assessment in a Fril Environment for Technical Information Management and Encapsulation) is capable of representing and reasoning about the various uncertainties inherent in the performance assessment process. For demonstration purposes it has been applied to the knowledge within the far-field section of the SKI Project-90 report.

The Fril package provides an ideal basis for SAFETIME as it incorporates a consistent method for handling uncertainty, based on support logic, mass assignments and evidential reasoning. Mass assignments provide a consistent means of manipulating fuzzy and probabilistic uncertainties, enabling different forms of uncertainty to be integrated within a single framework. Evidential reasoning has been developed within this project as a means of proving a support logic in the cases of fuzzy scenarios. Fuzzy matching is used to assess the degree of similarity between features in different cases, and the inference process allows different combinations of features to contribute to the overall conclusion.

Fril uses a logic programming style, and allows uncertain data and inferences to be modelled naturally. In addition, the procedural and meta-programming aspects of the language make creation of a knowledge-based system straightforward.

SAFETIME follows the knowledge-based systems design of being split into (i) a knowledge base, incorporating specific information about the domain of interest and (ii) an inference shell, which can make deductions from the knowledge base, request additional information and interact with the user. The knowledge representation scheme used in SAFETIME draws on the theory developed by Sowa. Knowledge is expressed in terms of *concepts* and *relations* between concepts.

Each concept has a *type*, which restricts ways in which other concepts can be linked to it via relations. A number of key types and relations have been extracted from the SKI Project-90 report, and used to define *knowledge templates*, which define the permissible combinations of concept types and relations. For example, the type *physicalEffect* is used to represent any measurable processes or events that need to be included in the system (including mechanical, thermal and chemical processes).

Use of knowledge templates make it straighforward to ensure that only meaningful information is added to the system. It is, of course, rather more complex to validate the knowledge templates themselves but this task can be automated without too much difficulty. The knowledge templates in the SAFETIME system force the information to take an English-like form, with added words such as *is*, *on*. Thus the fact that the advection-dispersion model is a conceptual model of the groundwater transport process is recorded as:

((conceptual-model-of groundwater-transport is advection-dispersion-model)).

This is close to natural language, and simplifies the explanation of derived information.

In addition to defining allowed relations that each concept type may participate in, the knowledge templates record the nature of the relations including: whether the relation is unconditional (i.e. a table of facts), conditional (a set of rules) or a mixture; whether the relation can have uncertainty associated with it; whether the user should be queried in the event of missing information. In this last case, information can be added as a *Working Hypothesis* of *User*, yielding a mechanism whereby the user can add

information and test the consequences.

When information involving a *Reference* is found as a solution to a query, the system initially presents the name of the document, section and page number. A further request can be made to display the approprite text by launching the application that handles the document. This mechansm can also be used to provide an interface to "number-crunching" packages whose input data can be stored within the knowledge base. Thus the sytem can act as an intelligent front-end to existing applications.

A problem with interfacing to technical documentation is that sophisticated natural-language processing is required if the user can enter free-form text. In the SAFETIME system, the knowledge templates define permitted questions, giving queries the appearance of natural language while constraining them to be of a form required by the knowledge base. At any stage the system focuses on a particular example of one of the types and valid questions regarding this are offered. The user can navigate through the system, investigating a series of topics and sub-topics. This is more than a simple hypertext package could offer, as the sytem is using facts and rules (involving uncertainty) to reason its way to an answer.

The reasoning leading to an answer can be investigated by means of an explanation facility. This invloves the system tracing back through the rules and facts used to derive a conclusion and displaying the information, using the English-like statements in the knowledge base. The explanation also shows the propagation of support for the conclusion.

The work has demonstrated the feasibility of automating a technical reference document such as the SKI Project-90 report. The SAFETIME system encapsulates the knowledge in the document and forms an intelligent indexing and reference system, with interfaces to other software packages using input from the knowledge base. Further work is underway to deepen aspects of the knowledge base, and to show how different forms of uncertainty in the system map naturally onto the structures provided by Fril.

Fuzzy Cellular Automata

Work has also been undertaken to investigate three methods of incorporating fuzzy values into the cellular automaton model, concentrating on a system that models the diffusion equation. The first method was to interpret each cell of the automaton as corresponding to a small element of the physical system being modelled, with 0 or 1 corresponding to the presence or absence of diffusing material in that cell and then using intermediate values to show degrees of membership in the set of full cells.

An alternative approach is to use liguistic categories (eg 'about half occupied') corresponding to possibility distributions on [0,1], and to use these fuzzy numbers in place of cell occupations. The third method investigated was to retain the crisp automaton, but to fuzzify the correspondence between the automaton and the physical system, for instance by defining the distance between two cells to be a fuzzy distance. This results in there not being a unqiue definition of which cell corresponds to a given location. This apporach can be applied to the lattice-gas model which can simulate fluid flow.

C.4 Progress at IRIDIA, Bruxelles (V.Poznanski and P.Smets)

Following the earlier investigations, two potential utilities have been developed during the year. The first involves logic-based AI techniques to manipulate and present specialised knowledge used to provide parameters for a particular conceptual model of nuclear waste disposal. The second is a decision support system which enables its users to input beliefs and costs similar to those of classical decision trees and subsequently to provide an optimal set of actions to perform in order to minimize costs. This system is to be applied to the problem of conceptual model selection.

A Knowledge-based System

The knowledge-based system (KBS) being developed at IRIDIA, known as SALUT (Safety Assessment using Logical Uncertainty Treatment) grew from the earlier experiments with the MacEvidence system. The enhancements made include: the representation of quantified formulae as well as propositional statements; the capability to perform logical manipulation; the ability to add nodes to the system; and the ability to handle possibilities, defaults and error detection and correction.

Thus SALUT includes a suitable combination operator to combine expert opinion and to insert results into the main knowledge database. It also includes a deductive inference engine, which is responsible for requesting information from the main knowledge base and performing inferences. It is controlled by the user interface and/or spontaneously as data is input. It can highlight any inconsistencies in the supplied data. The user interface provides the user with access to the information stored explicitly or implicitly in the system. New information is added to the system incrementally, with the new consequences of this information being propagated by the belief support system.

The expert knowledge used in these studies is part of the SKI Project-90 documentation. For such a large project a KBS would be useful for maintaining project information, checking its consistency and providing reasoning behind the facts. The same tool could also be used for 'what if' scenarios, where it could be shown what would happen if information was added or removed from the current database.

To extract knowledge from the Project 90 report, complex statements within the report are replaced by simpler sentences. Next, logical transcriptions of these sentences are made, with extra information being added where necessary to make sense of these forms. The logical expressions themselves can be broadly categorised into three classes: (a) translations of phrases or auxillary definitions, such as "rock_around_repository"; (b) definitions of english words, such as "between"; (c) extra information to augment the original report.

These logical forms are then checked by experts, in this case Intera, who correct any errors. Finally the information is added to SALUT which checks the system for consistancey. The final system will provide a graphical network explaining how the major decisions were made in the report, where there are inconsistencies and what the major consequences are.

This final version of SALUT is only a prototype demonstrating the utility of this approach.

A Decision Support System

The Transferable Belief Model (TBM) has been developed to represent someone's degree of beliefs. The model is based on the use of belief functions and is closely related to the model of Shafer. It is based on a two-level structure, with beliefs being entered into the credal level while decisions are made from these beliefs on the pignistic level. On the credal level, belief is quantified by belief functions, whereas on the

pignistic level, beliefs are quantified by probability functions. When a decision is to be made, beliefs at the credal level are transformed into beliefs at the pignistic level.

Decision making requires that we derive a probability function that can be used to compute expected utilities of each potential decision. It means that uncertainty at the pignistic level must be quantified by a probability function. But it does not mean that beliefs at the credal level must also be quantified by a probability function. All that is required is that there exists some transformation between the representation at the credal level and the probability function that must exist at the pignistic level.

This problem in the context of the TBM can be solved through the concept of the Pignistic Transformation. Hence, when decisions must be taken, the TBM is endowed with the needed procedure to transform someones beliefs entertained at the credal level into a so-called pignistic probability that can be used at the pignistic level. The justification of the pignisitic transformation is based on rational and normative requirements.

The belief function based decision support system developed at IRIDIA takes as inputs the user's 'gut feelings' (presented as belief functions) about situations, using a user-friendly interface. The belief functions are propagated through the system by TresBel, a tool developed at IRIDIA to handle credal-level structures. Following the pignistic transformation, the pignistic probabilities are analysed by VBS-Decision which suggests the optimal decision through the user interface. The whole proceedure is controlled by 'Overall Control' system.

The Transferable Belief Model developed at IRIDIA has been applied to an example in which it is assumed that some contaminant is leaking from one of a group of sites located near to a river system. Expert belief on the effect of the location of the leakage on the location of river contamination is given. For a given set of costs of tests and remedial costs, the TBM calculates the optimal measurement stratergy for locating the leak.

A further example involving the determination of an optimal site-investigation strategy to distinguish between a number of different conceptual models is being developed.

Task 5

"Method of Evaluating the Safety of Disposal Systems"

Topic 1 **Complements to the previous evaluations**

FI2W/0008 Global dispersion models for I-129 and C-14

FI2W/0016 Performance assessment of the geological disposal of spent fuel in a clay layer

FI2W/0123 Consideration of environmental changes in long-term radioactive waste disposal system evaluations

Topic 2 **Sensitivity studies**

FI2W/0017 EVEREST : EValuation of Elements Responsible for the Equivalent doses associated with the final STorage of radioactive waste

Task 5 - METHOD OF EVALUATING THE SAFETY OF DISPOSAL SYSTEMS

A. Objectives

The methods developed hitherto shall be up-dated and the relative importance of the various radionuclide release and transport mechanisms assessed. Moreover the analysis should be extended to new types of waste so that a comprehensive safety assessment of disposal systems can be made.

B. Research performed under the 1985-1989 Programme

The projects PAGIS (Performance Assessment of Geological Isolation System for vitrified HLW) and PACOMA (Performance Assessment of Confinement of Medium-level and Alpha waste) have been completed. In addition support studies have been carried out on :

- the assessment of human intrusion into underground repository considered in PAGIS and PACOMA
- modelling the long-term evolution of geological disposal systems
- software quality assurance procedures for risk assessment codes

C. Present programme (1990-1994)

The research work to be developed covers two fields :

- Topic 1 "Complements to the previous evaluations"

  - Improved global dispersion models for Iodine-129 and Carbon-14 by NRPB-Chilton. The new models should appropriately represent possible future climatic states, which may influence the long term radiological impact from the two radionuclides.
  - Evaluation of radiological consequences from geological disposal systems in clay of UO_2 and MOx spent fuels (by CEN/SCK Mol). This study will allow to extend PAGIS evaluations to the disposal of unreprocessed spent fuel (UO_2) and recycled fuel at the end of its irradiation cycles.

- Topic 2 "Sensitivity studies"

  - EVEREST (Evaluation of the Elements Responsible of dose Equivalent associated to the final STorage of radioactive waste). This is a multi-partner project (CEA-IPSN; ANDRA; CEN/SCK; GRS and ECN) for studying the sensitivity of evaluated radiological consequences towards the elements of performance assessments (scenarios, phenomena, parameters) for deep waste repositories in granite, salt and clay at different sites.

Global Dispersion Models for I-129 and C-14

Contractor:	National Radiological Protection Board, Chilton, UK
Contract No:	FI2W/CT90/0008
Duration of contract:	from 1 January 1991 to 31 December 1992
Period covered:	1 January 1992 to 31 December 1992
Project Leader:	Dr J R Cooper

A. OBJECTIVES AND SCOPE

The objective of this project is to provide up-to-date models for assessing the radiological impact arising from the global circulation of carbon-14 and iodine-129. These radionuclides are long-lived and mobile in the environment. This gives them the potential to deliver significant collective doses to the world's population over long timescales, if released either directly to the environment or from a geologic repository for solid radioactive waste.

In this project the National Radiological Protection Board (NRPB) is collecting information on existing models and parameter values for the global circulation of carbon-14 and iodine-129, in order to develop up-to-date models. The influence of environmental changes over long timescales, for example, climatic changes, is also being considered. The final report will contain a description of the proposed models, their parameter values and example results.

B. WORK PROGRAMME

B.1 Consultation and literature search to identify available models, their implementation on the NRPB computer and comparison of their results.

B.2 Consultation and literature search for information on important processes in the global circulation of carbon and iodine and for parameter values for use in models identified in task B.1.

B.3 Review of models obtained in task B.1 in the light of information on important processes and parameters obtained in task B.2 and construction of 'state of the art' models.

B.4 Calculation of collective doses using 'state of the art' models (task B.3) considering possible future climatic scenarios and quantification of possible ranges of results.

B.5 Preparation of final report.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Tasks B.1, B.2 and B.3 have been completed during the year. In the case of carbon-14 task B.4 has also been completed and a draft section of the final report, for task B.5, has been written. The latter will form a major part of the final report for this contract because it describes the significant number of different models for carbon-14 global circulation which have been considered, the development of a new model and the results of that model. There are fewer distinct models available for the global circulation of iodine-129 and work during the year has concentrated on identifying uncertain parameter values and revising the values in current use where necessary. A revised iodine-129 model has been constructed with these new values and work is underway to run this model and finish the corresponding section of the draft final report.

Progress and results

B.1 Identification and implementation of available models

Searches of bibliographic computer data bases and consultation with individuals and organisations have been used to identify existing models for the global circulation of carbon-14 and iodine-129. In the case of carbon-14 this revealed eleven models for predicting the global circulation of stable carbon and/or of carbon-14. Four models have been implemented on the NRPB computer system and their results compared.

In the case of iodine-129 the identified models are derived from the model developed by Kocher at the Oak Ridge National Laboratory (ORNL)/1/. Smith and White at NRPB created a revised version of Kocher's model in 1983/2/. Kocher's original model and the NRPB revised version have been implemented on the NRPB computer system and their results compared.

This task is now completed.

B.2 Review of data on important processes and parameter values

The data on important processes and parameter values have been obtained principally at the same time as information on the available global circulation models. In the case of carbon, additional information has been obtained from the literature and from organisations, for example the UK Meteorological Office, dealing with the global circulation of carbon dioxide, its build-up in the atmosphere and possible effects on the future global climate. In the case of iodine-129, although some changes to model structure can be envisaged, the principal effort was directed toward gathering more information about the parameter values in use in the current NRPB model. Hence the inventories of stable iodine in ocean sediments, sedimentary rocks, soil, ground water, rainwater and the terrestrial biomass have been reviewed.

This task is now completed.

B.3 Construction of 'state of the art' models

A new compartmental model for the global circulation of carbon-14 has been constructed and is shown in Figure 1. The ocean compartments of this model were obtained by simplifying the compartment structure of the MINIBOX model/3/. The terrestrial compartments were taken from the model of Emanuel et al./4/ with the addition of extra transfers from land to sea to take account of transport of carbon in rivers/5/. A fossil fuel compartment has also been introduced into the model/6/ to allow for the assessment of the influence of fossil fuel burning on collective doses from carbon-14 releases. The model has been validated by comparison of model results

obtained using natural carbon-14 production rates and nuclear bomb test fallout with measurements of carbon-14 to carbon-12 ratios in the oceans.

A revised compartmental model for the global circulation of iodine-129 has been constructed and is shown in Figure 2. This is based upon the model developed by Kocher/1/ with the revisions recommended by Smith and White/2/. In addition the transfer of iodine-129 from sedimentary rock to the subsurface regions has been included, based upon the work of Fabryka-Martin/7/. The transfers between some of the compartments and the stable iodine inventories within them have also been updated, following the review undertaken in task B.2.

B.4 Calculation of collective doses

The new model for the global circulation of carbon-14 has been run with unit source term (1 TBq). A number of runs were performed with the source in different compartments. In each case the collective doses to the EC and world populations were calculated, integrated to a number of different times. World collective dose commitments ranged from 92 man Sv to 110 man Sv, depending upon the source compartment. Runs have also been performed with the addition of fossil fuel burning, which tends to alter the build-up of the collective dose over time but does not significantly change the final collective dose commitment. The effects of future climate change on the transport of stable carbon, and hence of carbon-14, around the biosphere are not well understood at present. Therefore, to assess the possible influence of climate change on the collective doses from carbon-14 releases, the model sensitivity to changes in transport across the atmosphere-oceans interface has been investigated. It appears that the collective dose commitments predicted by the model are not particularly sensitive to changes in these transport parameters.

B.5 Preparation of final report

A draft section of the final report dealing with the work performed on carbon-14 modelling has been prepared.

List of publications

Work performed under this contract was presented at a Technical Committee meeting on 'Methods and models for estimating the global circulation of selected environmental emissions from energy generation', organised by the IAEA and held in Vienna, 11-15 May 1992.

References

/1/ KOCHER D C, Oak Ridge National Laboratory Report, ORNL/NUREG-59 (1979).
/2/ SMITH G M and WHITE I F, NRPB Chilton Report, NRPB-M81 (1983).
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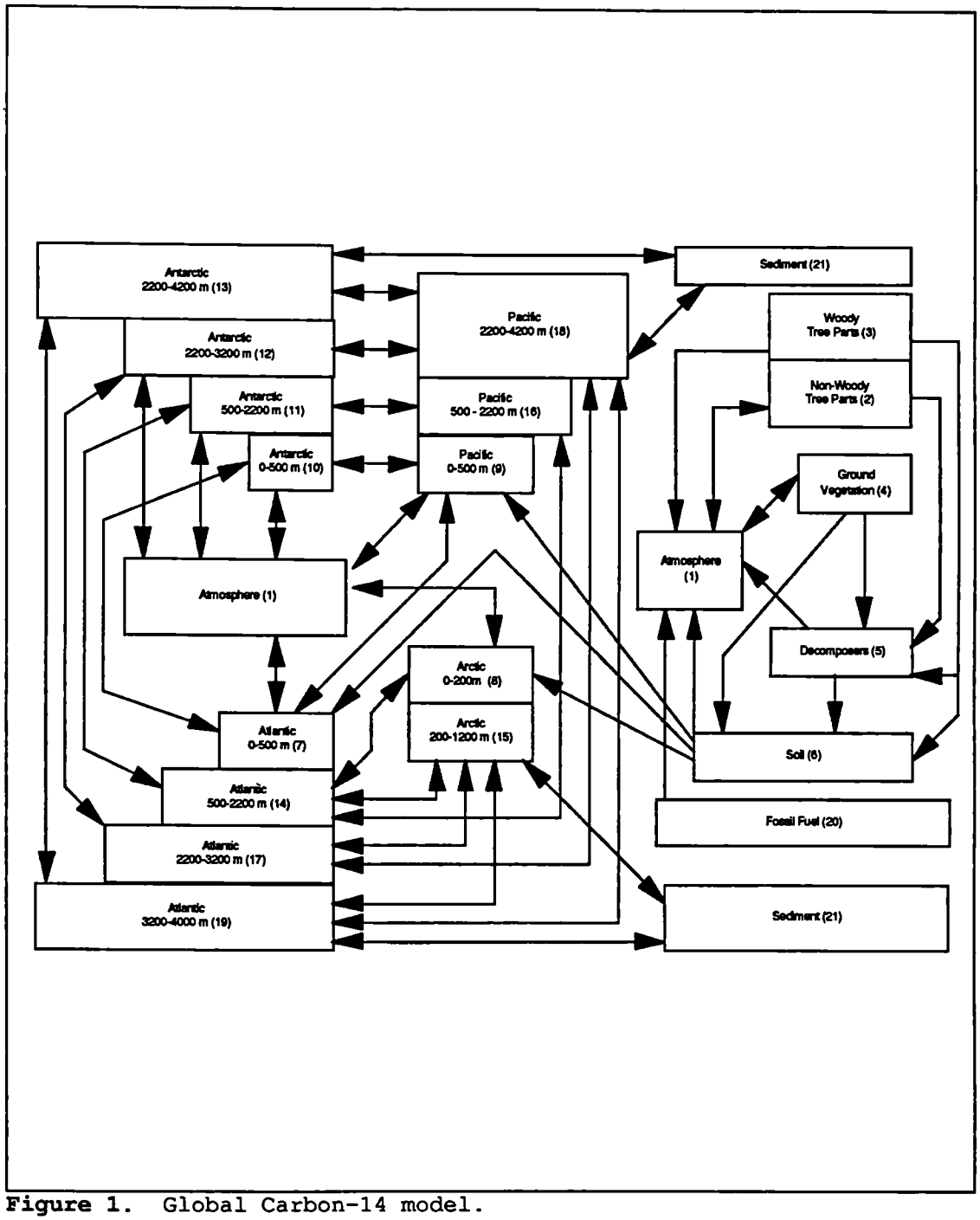

Figure 1. Global Carbon-14 model.

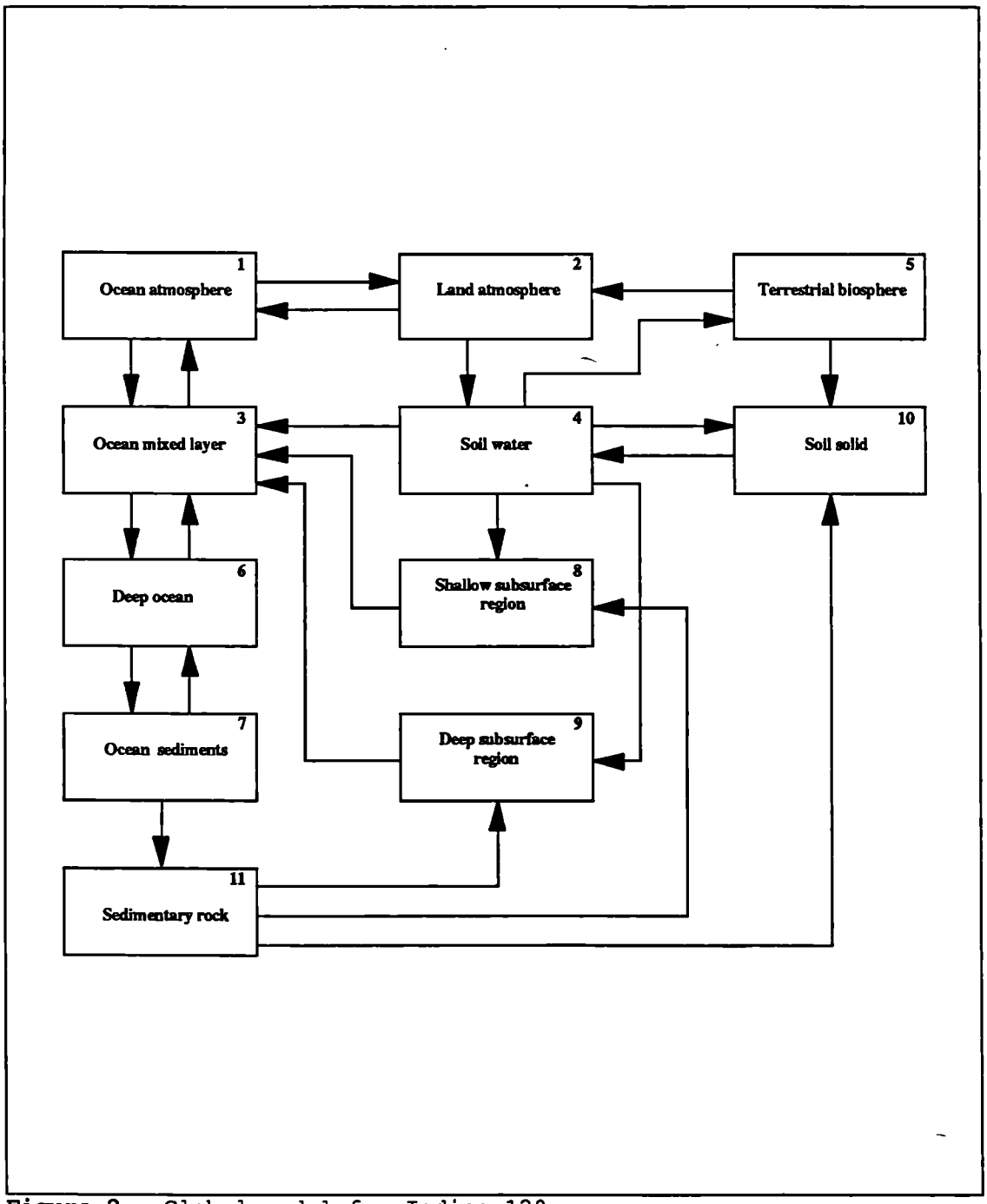

Figure 2. Global model for Iodine-129

PERFORMANCE ASSESSMENT OF THE GEOLOGICAL DISPOSAL OF SPENT FUEL IN A CLAY LAYER

Title:	Performance assessment of the geological disposal of spent fuel in a clay layer
Contractor:	Centre d'Etude de l'Energie Nucléaire - Studiecentrum voor Kernenergie CEN/SCK
Contract N°:	FI2W/CT90/0016
Duration of contract:	from 1 March 1991 to 28 February 1994
Period covered:	from 1 January 1992 to 31 December 1992
Project leader:	J. Marivoet

A. OBJECTIVES AND SCOPE

Hitherto the performance assessments, which have been carried out within the C.E.C.'s R&D programme on radioactive waste management like PAGIS /1/ and PACOMA /2/, considered mainly waste types which result from the reprocessing of spent fuel. However for technical reasons the recycling cannot be repeated more than three cycles and the economical justification of the reprocessing becomes debatable because of the relatively low cost of fresh uranium. It is therefore reasonable to consider the direct disposal of uranium oxide and/or mixed oxide spent fuels as a realistic option.

The main objective of the study is the evaluation of the radiological consequences of the geological disposal of spent fuel in a hypothetical repository located in the Boom clay layer at the Mol site.

B. WORK PROGRAMME

1. Data collection
   - 1.1 Spent fuel inventories: the radionuclide inventories of UO_2 and MOX spent fuels resulting from an irradiation in a PWR reactor up to a burn ups of 33 and 45 MWd/kg are calculated.
   - 1.2 Repository concept: the existing repository concepts are adapted to allow for the disposal of spent fuel assemblies.
   - 1.3 Near field processes and characteristics: the near field model should take into account the typical processes describing the release of radionuclides from the spent fuel.
   - 1.4 Far field and biosphere data: the data collected for PAGIS and PACOMA will be updated.
2. Adaptation of the methodology
   The methodology developed within the EVEREST project has to be adapted to the case of spent fuel disposal.
3. Models and computer codes
   A new near field model is needed.
4. Deterministic calculations
   Individual dose rates and collective doses will be calculated.
5. Stochastic calculations
   The stochastic calculation will include sensitivity and uncertainty analyses.
6. Conclusions

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

The activities carried out in 1992 have been largely devoted to the completion of the data collection. The literature on the near field behaviour of spent fuel in disposal conditions has been reviewed and the most relevant processes have been identified. An adapted near field model is being developed.

The data bases with the model parameter values that have been used for the PAGIS and PACOMA calculations have been updated.

The methodology that has been developed for the Mol site within the EVEREST project has been reexamined and adapted where necessary to make it applicable to the case of spent fuel disposal.

Progress and results

In the literature various reports and papers on the behaviour of conditioned spent fuel in repository conditions have been found. It has to be noticed that most of the publications on spent fuel consider the case of disposal in hard rocks; publications on spent fuel disposal in a clay formation have not been found.

Natural and enriched uranium fuels have been studied in the literature. For MOX fuel however no results from experimental studies are available.

On the basis of the results of the literature review it is concluded that a new near field model has to be developed. This near field model should take into account three or four different release mechanisms :

- release of gases present in the gap between the fuel pellets and the hulls;
- leaching of radionuclides from the zircalloy hulls;
- leaching of radionuclides from the grain boundaries of the pellets;
- leaching of radionuclides from the uranium oxide matrix.

It is however doubtful if sufficient data can be found in the literature which allow to make a distinction in the modelling between the third and the fourth release mechanisms.

The data which has been used in the earlier performance assessment studies PAGIS /1/ and PACOMA /2/ has been reexamined; this has led to an updating of the data bases by considering results which have been obtained recently from the Belgian R&D programme on radioactive waste disposal in the Boom clay. For the geosphere models, i.e. the host clay layer and the aquifers, the same data will be used for the spent fuel assessment as for the EVEREST calculations.

In principle the methodology /3/ that has been developed within the EVEREST project will also be applied for the spent fuel study. However it has to be verified if some characteristics which are specific for the case of spent fuel disposal cannot give rise to the selection of other scenarios or to considerable modifications of the scenarios which were already selected. Each feature, event or process mentioned in the FEP catalogue /4/ has been systematically reexamined in order to check if that FEP can become more important in the case of spent fuel disposal than in the case of disposal of reprocessing waste.

REFERENCES

/1/ Marivoet, J. and Bonne A., "PAGIS : Disposal in Clay Formations", C.E.C. Report EUR-11776 (1988)

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CONSIDERATION OF ENVIRONMENTAL CHANGES IN LONG-TERM RADIOACTIVE WASTE DISPOSAL SYSTEM EVALUATIONS.

Contractors :	CIEMAT, Spain - ENRESA, Spain
Contract Nº :	FI2W-CT92-0123
Duration of contract :	1 December 1992 to 30 June 1994
Period covered :	1 December 1992 to 31 December 1992
Project Leader :	Mr. F. Recreo (CIEMAT; coordinator), Ms. C. Bajos (ENRESA).

A. OBJECTIVES AND SCOPE

The objective of the work is a state-of-the-art analysis consisting basically in a well-founded, critical discussion of the phenomena of long-term environmental changes, their possible consequences on the biosphere of the EC countries, their basis and the existing or foreseeable scientific and technological capacity for suitable consideration in the safety evaluation of radioactive waste disposal systems, and of a comparative analysis of regulations, guidelines and tendencies on the post-closure timescales issue. The study will also include a comparative analysis between what is indicated above and the actual consideration given to climatic changes within the EVEREST project. So, a suitable hierarchization of the effects of environmental variations and their relevance to the safety of the repository would be an interesting complement to the efforts currently being made in the EVEREST project to evaluate the sensitivity of the different elements involved in safety evaluation methodologies for deep geological repositories.

B. WORK PROGRAMME.

This study will comprise the implementation of the following steps :

B.1. Basis for safety evaluation of high-level radioactive waste disposal systems.
B.2. Environmental variation and its effect on the disposal system.
B.3. The human capacity to predict environmental evolution.
B.4. Consideration of environmental change to disposal system safety evaluation.
B.5. Comparative analysis with the EVEREST project.
B.6. Conclusions and recommendations for subsequent development.

Title: "EVEREST: EValuation of Elements Responsible for the dose Equivalent associated with the final STorage of radioactive waste".
Contractors: CEA/IPSN* - ANDRA ** - CEN / SCK ° - ECN°° - GRS°°°
Contract n°: FI2W CT 90-0017
Duration: 01/04/91 - 30/09/94
Period covered: from 01/01/92 to 31/12/92
Project leader: M. GOMIT (CEA/IPSN coordinator) - M. RAIMBAULT (ANDRA) - M. MARIVOET (CEN/SCK) - M. PRIJ (ECN) - M. MARTENS (GRS) -

A- OBJECTIVES AND SCOPE

The general objective is the evaluation of the sensitivity of the radiological consequences associated with deep nuclear waste disposal to the differents elements in the performance assessment. The following geological formations are taken into consideration: clay, granite and salt and for HLW and MLW.
This work will be realized in four phases 1-elaboration of the methodology, 2- model description and data collection, 3- calculations, 4- interpretation of results.

B- WORK PROGRAMM

B.I - Methodology: this phase will be divided into four steps: identification of main features controlling the radionuclide transfer to human beings, scenarios, definition of calculations to be performed and reflexion on different approaches and techniques of sensitivity analyses.
B.II - Model description and data collection: documentation and presentation of the models and codes to be used, compilation of the site data and of the other data (waste inventory, package, repository design...)
B.III - Calculations: deterministic and stochastic calculations for normal and altered selected scenarios for each site. The results obtained will be used for sensitivity analyses.
B.IV - Interpretation of the results: the final phase will lead to a hierarchized list of the most influential elements (scenarios, phenomena, RN..) for each site; this list can contribute to the definition of future orientation of the R&D programmes.

* Commissariat à l'Energie Atomique - ** Agence Nationale pour la gestion des Déchets Radioactifs - ° Centre d'Etudes pour l'énergie Nucléaire / Studiecentrum voor Kernenergie - °° Stiching Energieonderzoek Centrum Nederland - °°° Gesellschaft für Reaktorsicherheit mbH -

C- PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The Working Group 1 has specified the methodology to identify the most important elements of the repository system to be studied through sensitivity analysis, to improve the performance assessment.

The Working Group 2 has finalized the scenario selection procedure and the detailed description of selected scenarios (/1/ and /2/).

The Working Group 3 has fixed the main elements for the strategy and approaches (deterministic/stochastic) for evaluating the sensitivity.

Further, a first selection of data in terms of inventory, waste package, design, site and geochemical data is available for the three formations (clay, granite and salt) and an estimated planning from January 1993 to June 1993 has been established for the reference calculations.

Progress and results

B.I - Methodology

A performance assessment of a geological repository for the disposal of radioactive waste packages involves the application of mathematical models that simulate the processes in the various compartments: near field, geosphere and biosphere. The EVEREST project covers the evaluation of the sensitivity of the results (individual annual dose equivalents or other indicators) with regard to the different elements involved in the performance assessment: phenomena, physico-chemical parameter values, scenario characteristics. The sensitivity of the model for the convergence/compaction of backfilled openings in rock salt will be performed by GRS, GSF and ECN.

The calculations may cover different times scales:

- 0 - 500 years : records on the existence of the repository subsist and human intrusion is not considered,
- 500 - 10000 years : with geological stability and possibility of human intrusion,
- 10000 - 60000 years : during which a Würm type glaciation can be expected,
- >60000 years : where severe glaciations may occur.

In these different time steps, increasing uncertainties with time and widening in the range of the parameters may be taken into account.

In the framework of the EVEREST project, climatic changes and their influences on modifications of the biosphere and the geosphere states may be considered, which will imply the study of a set of reference biospheres. A set of conversion factors may have thus to be defined.

The Working Group 2 has produced final lists of the scenarios considered as important for each type of rock formations. For the scenario selection, three methodologies have been chosen and used by the parties involved in the project:

- the Independent Initiating Events (I.I.E.) methodology (ANDRA/IPSN) based on the production of a limited list of about 20 independent initiating events with associated induced events;
- the PROSA methodology (CEN/SCK, ECN) starts from a comprehensive list of about 150 Features, Events and Processes (FEP's) and selected FEP's are associated to specific states of the barriers composing the repository system;
- the Transport Mechanism Methodology (T.M.M.) (GRS) is based on nuclide transport mechanisms combined with the entities which have an influence on these transport mechanisms.

The scenarios selected for clay, granite and salt are shown respectively in Tables I, II and III. In the framework of the EVEREST project, these scenarios can be treated in a qualitative or semi-quantitative manner or can be analyzed in detail with the associated sensitivity analysis studies.

Sensitivity aspects in the EVEREST project have been discussed. Two calculational approaches have been distinguished:
a) deterministic calculations with single value of input parameters which lead to a reference value for the radiological consequences;
b) the stochastic calculations with parameters sampled from probability functions which allows to obtain a distribution function of the considered output variables.

Three kinds of sensitivity studies will be elaborated with respect to:
- model parameters: sensitivity coefficients, stochastic sensitivity studies,
- models: phenomena, alternate models, model interfaces,
- future states of the repository system: scenarios, evolution with time (degradation of engineered barriers, climatic changes,...).

The stochastic sensitivity calculations will be done with PREP and SPOP (or deriving from them) or LISA computer codes by IPSN, ANDRA, CEN/SCK, ECN, and with the SAMOS computer code by GRS.

B.II - Model description and data collection

. IPSN/ANDRA

IPSN and ANDRA will use a common inventory data issued from CEA. Waste package and design data will be issued from the ANDRA concepts for clay, granite and salt formations. A first preliminary version of data report for the French sites has been provided. A revision of this document concerning in particular the geochemical data (solubility limits and sorption coefficients) is in progress. It takes into account a critical analysis of litterature data. For necessary but not available data, the solution will be to use PAGIS and PACOMA data.

For both sites, clay and granite, ANDRA will use the DIMITRIO computer code issued from the general finite element fluid mechanical code TRIO. In the case of the normal evolution scenario in granite, a 3D hydrogeological calculation will be carried out with TRIO, leading to the determination of a 2D cross-section for groundwater and transport calculations for the best-estimate case (crystalline version of DIMITRIO). ANDRA plan to perform the multi-parameter sensitivity calculations with an unidimensional model built on results of the previous 3D modelling. The undetected fault scenario will be investigated using the MIGRAN transport code. In the case of clay, the normal evolution scenario and the exploitation drilling scenario will be analyzed with the clay version of DIMITRIO. For the salt formation, two specific models are available: the analytic code AQUADEF for the sealing defect scenario (water intrusion) and the quasi-analytical code AQUASEL for the solution mining abandoned cavity scenario.

For both sites, clay and granite, IPSN will use the MELODIE computer code; for the normal evolution scenarios, a quasi-3D modelling leads to determine a 2D cross-section for the groundwater and transport calculations, the altered scenarios such as human intrusion, will be investigated using the quasi-3D modelling. For the salt formation, a specific model has been developed for the solution mining scenario.

. CEN/SCK

CEN/SCK has reexamined the data which has been used in the earlier performance assessment studies PAGIS and PACOMA; this has led to an updating of the data bases by considering results which have been obtained recently from the Belgian R&D programme on radioactive waste disposal in the Boom clay. The basic data that will be used in the EVEREST calculations for the Mol site is collected in three topical reports: geological and hydrological characteristics, repository concept and input data.

The mathematical models for the assessment of the normal and some altered evolution scenarios have been developed. A number of alternative computer codes are now available to perform calculations for the main components of the repository system; the components that will be considered are the near field, the host clay layer and the aquifer. For the fourth repository component, i.e. the biosphere, the model development and the updating of the available parameters will start in 1993. The first step of the calculations consists of the elaboration of a number of sensitivity studies with regard to one component of the repository system in order to evaluate which phenomena play an essential rôle in the performance of the considered component. The results of these sensitivity studies which allow to select the most appropriate computer codes to be used in the final assessment. For the selection of computer codes which will be used in stochastic calculations, the aspect computer time also has to be taken into consideration.

. ECN

ECN will use the data defined in the Dutch safety study performed in the OPLA phase 1A project. Most element and nuclide specific parameters are based on PAGIS and PACOMA. The determinictic analyses will be performed with the code EMOS ECN. This code is based on the code EMOS developed at GSF. The main modifications are:
- the model of convergence of openings in the salt formations is based on the transient convergence instead of stationary,
- the effect of the compaction of the backfill is modelled with a constitutive relation instead of a reduction factor only based on porosity,
- the numerical groundwater compartment THROUGH has been changed in the model MASCOT which is based on an analytical solution,
- the dose conversion factors are based on analyses with th miniBIOS code.

The stochastic analyses will be performed with the code PANTER. This code is based on EMOS with the following modifications:
- the subrosion rate is stochastic and depth dependent,
- the internal rising rate of the salt is a stochastic parameter,
- the leaching rate of the nuclides from the glass is a stochastic parameter,
- the effective surface of the glass particles is determined with the assumption that the particles are spheres with a stochastic radius,
- the particle velocity with the groundwater is stochastic and due to the combined effect of subrosion and halokinesis depth dependent. The distribution function is calculated with METROPOL analyses,
- the dose conversion factors are stochastic parameters calculated with miniBIOS.

. GRS

In the framework of the EVEREST project, GRS has choosen the reference site of Gorleben in Germany and the associated data which has been used in the performance assessment studies PAGIS and PACOMA.

The model area is subdivided into three components: the near-field, the geosphere and the biosphere. Whithin the near-field, the calculation of selected scenarios will be done with the MARNIE computer codes, whereas for the geosphere, the MODFLOW computer code will be used. The MARNIE code is a coupled one dimensional modular network code which described the transport within the near-field. The MODFLOW code is a three dimensional modular groundwater model developed by USGS. The flow calculations will be limited in two dimensions. In the biosphere model, all relevant exposure pathways will be taken into account.

D- REFERENCES

/1/ EVEREST project
Working Group n° 2 - Scenario selection
2nd Preliminary Version - September 1992

/2/ RAIMBAULT, P., and al., International Symposium on Geological Disposals of Spent-fuel, High-level and Alpha-bearing Wastes, Antwerp, 19-23 October 1992

CLAY SCENARIOS

Scenario Nr		Type of analysis		
		CEN/SCK	IPSN	ANDRA
1	Normal evolution (including Würm type glaciation)	TT	TT	TT
2	Riss type glaciation (-> erosion, hydrogeology)	TT	TP	no
3	Earthquake / neotectonics (inner geodynamics) Belgium : near field effects and fault activation France : fault activation	TT	TP	no
4	Exploratory drilling	TP	no	no
5	Exploitation drilling	TT	TT	TT
6	geologic barrier bypassed Belgium : non detected faults France : sand lenses	TP	no	no
7	Sealing failure	TT	no	no

TABLE I

TT : Total treatment (evaluation including radiological consequences)
TP : Partial treatment (qualitative or semi-quantitative evaluation)
no : not treated in EVEREST

GRANITE SCENARIOS

Scenario Nr		Type of analysis	
		IPSN	ANDRA
1	Normal evolution	TT	TT
2	Altered natural evolution (Riss type glaciation, ...)	TP	TT
3	Sealing defect of the engineered barrier	no	no
4	Undetected fault	TT	TT
5	Exploitation of water (associated with a detected and conductive fault)	TT	TP

TABLE II

SALT SCENARIOS

Scenario Nr		Type of analysis			
		GRS	ECN	IPSN	ANDRA
1	Normal evolution .diapirism .subrosion	TT	TT	TP	TP
2	Altered natural evolution	TT	TT	no	no
3	Water intrusion .anhydrite vein .sealing defect	TT	TP	TP	TT
4	Water intrusion + brine pocket migration	TT	TP	TT	no
5	Solution mining for salt consumption	no	no	TT	TP
6	Solution mining abandoned cavity	TT	TP	TP	TT
7	Exploratory drilling	no	no	no	no

TABLE III

PART B

Construction and/or operation of underground facilities

PART B

CONSTRUCTION AND/OR OPERATION OF UNDERGROUND FACILITIES OPEN TO COMMUNITY JOINT ACTIVITIES

Project B1 "The underground facility in the Asse Salt Mine (FRG)"

FI2W/0002 The HAW project : test disposal of highly radioactive canisters in the Asse salt mine

FI2W/0006 Retrievable emplacement experiment with ILW and spent HTR fuel elements in the Asse salt mine

FI2W/0068 In-situ investigation of the long-term sealing system as a component of a dam construction

FI2W/0069 Active handling experiment with neutron sources

FI2W/0120 Thermo-mechanical study of the area in the vicinity of a storage borehole in salt formations (CPPS)

Project B2 "The underground facility HADES in the argillaceous layer under the Mol Site (B)"

FI2W/0003 Preliminary demonstration test for disposal of high-level radioactive waste in clay (PRACLAY, CERBERUS, Mine-by-test)

FI2W/0001 Characterization of the clay under thermal loading for underground storage - CACTUS project

FI2W/0098 Demonstration of the in-situ application of an industrial clay-based backfill material (BACCHUS)

FI2W/0033 102 Modelling and validation of the thermal, hydraulical, mechanical and geochemical behaviour of the clay barrier

FI2W/0117 Acquisition and regulation of water chemistry in an argillaceous medium (ARCHIMEDE)

FI2W/0116 Evaluation of hydraulic transfers between the argillaceous rock and the excavations (PHEBUS)

Project B4 "Underground validation facility at Sellafield (UK)"

FI2W/0114 Hydrological characterisation of fractured rock (Sellafield)

PART B: CONSTRUCTION AND/OR OPERATION OF UNDERGROUND FACILITIES OPEN TO COMMUNITY JOINT ACTIVITIES

A. Objectives

The main objective of this part of the programme is the construction and the operation of underground facilities to develop and demonstrate emplacement techniques and to validate site and design criteria of deep geological repositories. All these facilities have been declared, by the responsible bodies in the Member States on which territories the facilities are build, open to scientists of the Community for joint R&D activities.

B. Research performed under the programme 1985-1989

In the programme 1985-1989 joint research acvtivities were already started at the Asse salt mine (FRG) and in the HADES underground facility at Mol (B). The research in the Asse salt mine concerned mainly the preparation of the test disposal of simulated vitrified HLW (HAW) project. In the underground facility at Mol a Test Drift was excavated and various lining systems tested. Moreover, a combined heating/radiation experiment (CERBERUS) was started.

C. The present programme 1990-1994

Research activities at the facilities in the Asse salt mine and in the HADES facility in clay at Mol (Project B1 and B2 respectively) started during the previous programme were continued. Additional research projects have been initiated as described below. However, in December 1992 the Federal Government in Germany decided not to continue with the HAW project.
The construction of underground facilities in France (Project B3) has been delayed and the planned budget has been allocated to research activities on clay and salt, complementary to the investigations in Mol and Asse.
Site characterization work at Sellafield (UK) (Project B4) has started.

Project B1: The underground facility at the Asse salt mine (FRG)

At the facility at Asse the Commission supports experiments involving emplacement of simulated high-level waste, the test emplacement of genuine medium-level waste, the long-term sealing of galleries in salt, and investigating backscattering effects with neutron sources in a salt environment.

The HAW project concerns test disposal of 30 radioactive canisters simulating vitrified high-level waste in six 15m deep boreholes. Handling equipment has been developed, manufactured and tested. Electrical heaters installed in two additional boreholes since November 1988, provide data on the thermo-mechanical behaviour of the salt. In parallel irradiation experiments are being carried out on salt

samples at irradiation facilities at Saclay (F) and Petten (NL) to investigate both radiolysis effects and radiation damage phenomena.
However, in December 1992 the Federal Government in Germany decided not to continue with the HAW project. It is planned to shut down the electrical heaters in 1993 and to retrieve corrosion specimen for analysis.

The MAW/REV project concerns a retrievable emplacement experiment with intermediate level waste and spent fuel (HTR fuel) elements. Six 200 litre drums with cemented cladding hulls, fuel hardware and dissolved sludge from the WAK-Karlsruhe reprocessing plant and four 220 litre stainless steel canisters with 950 spherical spent fuel elements are to be emplaced for a maximum of five years in three unlined boreholes. The Federal Government in Germany decided in December 1992 to postpone this project.

Within the DAM project a multicomponent dam is being developed, constructed and tested in the Asse mine for use as an engineered barrier in galleries. The CEC is participating in a subproject concerning an in-situ experiment on the tightness of a long-term sealing component consisting of salt bricks. The seal will be tested on tightness first against gas and then against brine.

The AHE experiment (Active Handling Experiment) with neutron sources aims at studying the effect of neutron back-scattering on the overall neutron- and neutron induced gamma-dose rates during handling of highly active material in a repository in a salt formation.

The CPPS project, performed in the Amélie potash mine (F), concerns investigation of the thermo-mechanical behaviour of the near-field of waste emplacement boreholes in salt.

Project B2: Experiments at the HADES underground facility at Mol (Belgium)

In the HADES underground facility in the Boom clay beneath the site of Mol, the following large projects are being carried out.
The PRACLAY project is a preliminary demonstration test for disposal of HLW canisters in horizonal mini-tunnels in clay. It will feature a full scale simulation, over a length of 20m of the cross sectional configuration of the waste environment, complete with heat generation (electrical heaters).

The combined heating-radiation test (CERBERUS) aims at investigating the near-field effects in an argillaceous environment of a HLW canister. It uses a Co-60 radiation source of 397 TBq and two electrical heating elements each dissipating 365W.

In a mine-by test the response of the clay on the excavated Test Drift is monitored.

In the CACTUS project, the near-field thermo-hydro-mechanical behaviour of clay around boreholes with high-level waste is being investigated using electrical heaters.

The BACCHUS-2 project aims at optimizing and demonstrating an installation procedure for a clay based backfill material. The instrumentation of this experiment will be optimized in such a way that it can be used as a validation experiment for a hydromechanical model being developed.

The ARCHIMEDE project aims at the investigation of the water chemistry in clay and the PHEBUS project concerns the study of the hydrous behaviour of clay around ventilated excavations.

Project B3: Underground facilities in France

The construction of underground facilities in France has been delayed. The planned budget has been allocated to research activities on clay (ARCHIMEDE and PHEBUS) and salt (CPPS) (see above B1 and B2). Furthermore the CEC is participating in the underground laboratory at Tournemire (see Task 4).

Project B4: Underground facilities in the United Kingdom

The Commission is participating in some parts of the site characterisation programme carried out by UK Nirex Ltd. at Sellafield (UK).

THE HAW-PROJECT: TEST DISPOSAL OF HIGHLY RADIOACTIVE RADIATION SOURCES IN THE ASSE SALT MINE

Contractors: GSF-IfT/ Braunschweig-Germany, ECN/Petten-The Netherlands, ANDRA/Fontenay-aux-Roses-France, ENRESA/Madrid-Spain
Contract No.: FI2W-0002-C(MB)
Duration of Contract: from May 1990 to December 1994
Period covered: January - December 1992
Project Leaders: T. Rothfuchs, L. Vons, M. Raynal, J. C. Major

A. OBJECTIVES AND SCOPE

In order to improve the final concept for the disposal of high-level radioactive waste (HAW) in boreholes drilled into salt formation plans were developed a couple of years ago for a full scale testing of the complete technical system of an underground repository. To satisfy the test objectives, thirty highly radioactive radiation sources were planned to be emplaced in six boreholes located in two test galleries at the 800-m-level in the Asse salt mine. A duration of testing of approximately five years was envisaged.

A system, necessary for handling of the radiation sources was developed and installed in the Asse salt mine. Two non-radioactive reference tests with electrical heaters were started in November 1988. These tests serve for the investigation of thermal effects in comparison to the planned radioactive tests. An accompanying scientific investigation programme performed in situ and in the laboratory comprises the estimation and observation of the thermal, radiation-induced, and mechanical interaction between the rock salt and the electrical heaters and the radiation sources, respectively. The laboratory investigations are carried out at Braunschweig (FRG), Petten (NL), Saclay (F) and Barcelona (E).

On Dec. 3rd, 1992 the German Federal Government, represented by Bundesministerium für Forschung und Technologie (BMFT) and Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit (BMU), has declared its decision to renounce from the test disposal of the 30 radiation sources and that all related preparatory activities of the GSF are to cease as of immediately.

B. WORK PROGRAMME

B.1 In-Situ-Activities
- B.1.1 Completion and Testing of the Handling System for the Radiation Sources
- B.1.2 Emplacement of the Radiation Sources and Periodical Retrievability Tests
- B.1.3 Maintenance of Instrumentation: Electrical Heaters, Gap Monitoring System, Data Collecting System etc.
- B.1.4 Irradiation Experiments in the Dummy Canisters
- B.1.5 Performance of a Radiological Measuring Programme
- B.1.6 Thermomechanical and Geochemical Analysis

B.2 Laboratory Activities
- B.2.1 Radiolysis Effects in Salt
- B.2.2 Geochemical und Petrophysical Characterisation of Salt Samples
- B.2.3 Development, Calibration, and Testing of High-Dose Measuring Systems
- B.2.4 Gamma Fields and Gamma Spectra Calculations

B.3 Desk Studies
- B.3.1 Development of a Post-Test Plan
- B.3.2 Description of the Mineralogical and Geochemical Properties of the Test Field

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The test disposal of highly radioactive radiation sources in the Asse salt mine was planned in regard of the design and licensing of a HAW repository in Germany.

In May 1991 the handling system for the radiation sources was approved by the mining authorities and by the Technischer Überwachungsverein (TÜV). Since late 1988 two preceding electrical reference tests are in operation at the test sites A1 and B1 in the test galleries A and B. Corresponding thermomechanical and geochemical investigations as well as laboratory investigations on radiolysis effects in salt are underway since beginning of the project. The results obtained until the end of 1991 were reported in /1/, /2/, /3/.

Progress and results

1. In-situ-activities

1.1 Completion and testing of the handling system for the radiation sources

In 1992 some improvements of the system were made under consideration of the experiences gained from cold trainings. In general the system can be considered as being successfully tested and hence the goal of developing and providing a suitable handling system for high level waste has been achieved.

1.2 Emplacement of the radiation sources and periodical retrievability tests

As pointed out under point A the emplacement of the radiation sources will not be performed. Hence, no work was performed in this regard.

1.3 Maintenance of instrumentation: electrical heaters, gap monitoring system, data collection system

The maintenance of intrumentation was carried out continuously. In January 1992 a computer failure, caused by aging of the system, led to a four-days-interruption of the heater experiments. Plans were, therefore, developed for a replacement of the computers. This, however, will not be done because of the early termination of the test and hence, an increased maintenance effort is to be expected in 1993.

1.4 Irradiation experiments in the dummy canisters

The ECN part of the preparation of the salt samples and sample holders necessary for the irradiation experiments in the dummy canisters inside the radioactive emplacement boreholes in the HAW test field /4/ was finished in 1990 /5/. However, experiences gained in irradiation experiments performed with the holders made it advisable to modify the design. Amongst other modifications, research into the mass production of golden holders to substitute the silver wrapping /6/ of the samples is being carried out first.

1.5 Performance of a radiological measuring programme

The radiological measuring programme comprise measurements of gamma dose rates and doses in the above ground transfer station, in the dummy canisters, and in the salt surrounding the emplacement boreholes. The measurements would have been only performed parallel to the emplacement of the radioactive canisters.

1.6 Thermomechanical and geochemical analysis

Already at the end of 1987 most of the instrumentation for monitoring stresses, stress changes, rock displacements, temperatures and gas release had been installed. The set of instruments at the heater boreholes A1 and B1 was connected to the data collection system (DCS) in summer 1988, and the instruments at the remaining emplacement boreholes in summer 1989. From then onwards the complete data set is being monitored continuously.

The walls of the heater boreholes A1 and B1 have reached temperatures of about 225 °C after approximately 300 days of heating and are rather constant since that time.

Stress measurements using straingaged stressmeters are performed in order to investigate specific stress components developed in the salt pillar in the region between the test sites A1 and B1. The measured vertical and horizontal stress components are about 16 MPa and nearly constant since 1989.

Since six years the vertical stress component measured in the pillar at the Monitoring Station already instrumented in 1985 for long term observation of stress components with Glötzl cells shows a nearly constant value of 20 MPa, superimposed by minor fluctuations. The radial measuring Glötzl pressure cells, installed in boreholes adjacent to the heater boreholes A1 and B1 at a depth of 12.1 m and a distance of 7.5 m to them indicate an in situ stress of 10 to 11 MPa at these locations, as was measured already in 1991.

The displacement measurements consist of gallery closure and extensometer measurements and of floor leveling observations.

Since start-up of heating at test sites A1 and B1 the deformational behaviour of the whole test field is affected by the local thermally induced stresses in the surrounding rock mass and the related rock mass movements, directed to both galleries.

The local heat input at the test sites A1 and B1 gradually increased
- the pillar creep deformation between both galleries
- the creep deformation of the rock mass in the abutments of both galleries
- the floor heave in both galleries.

The gallery roof sag is affected inferior.

Already at the end of the year 1991 in both galleries horizontal and vertical closure rates at all test sites were smaller compared to those observed at the end of the isothermal phase before the heaters were turned on.

During the second half of 1992 the average vertical closure rates in gallery A ranged between 15 mm/yr and 22 mm/yr. The corresponding horizontal rates at the different test sites ranged between 22 mm/yr and 26 mm/yr. In gallery B the vertical closure rates ranged between 16 mm/yr and 22 mm/yr.

Since May 1992 a slight rise of the horizontal and the vertical closure rates could be observed at all test sites. Compared to the previous rates observed in 1991 the closure rates in both galleries increased by 6 % to 23 % in horizontal and by 10 % to 18 % in vertical direction. The reasons for these unanticipated effects are not yet understood and have to be analyzed in more detail.

Twelve ultra-sensitive tiltmeters have been installed by the Institut de Physique du Globe Paris (IPG) in three locations around the HAW test field to survey the movements of salt. The measurements carried out in 1992 are satisfactory and confirm the previous results /7/, except for 2 units, which have been replaced in February. Results are consistent with modelling and with other geomechanical measurements.

The magnitude of the values measured at the location close to heated borehole A1 is much higher than at the two other stations. The inclination rate is slowly decreasing without any asymptotic state of evolution. Heating does not seem to affect the two stations located outside the experimental galleries, since the values obtained there are in the same order of magnitude as those recorded near A1 before heating.

An important aim of the HAW experiment is the use of the measurements for the validation of thermo-mechanical codes used for the assessment of the potential of rock salt as a host rock for radioactive waste. The validation process adopted at ECN is a stepwise approach. The first step is formed by the pre-test analyses which have been performed before the start of the experiment. The second step is a confrontation of the pre-test results with the experimental data. The final step is the evaluation which can also contain some new predictions of the behaviour with a better model. The pre-test analyses, performed at ECN on the thermo-mechanical behaviour of the HAW test field, have been finalized in 1990 and reported in /8/. The analyses have been made with plane strain models for the pillar; axi-symmetric models for the boreholes and a three dimensional model for the central part of the HAW test field. The programs used are TASTE and ANSYS for the temperature analyses while ANSYS and GOLIA-FAME have been used for the deformation and stress analyses.

Important data to be used in the analyses are the constitutive relations which are derived from experiments in a 300 m hole in the ASSE and the initial pressure in the HAW field. For this pressure a value of 11 MPa has been used which is based on measurements in the 300 m hole, simplified analyses of the stress state in the ASSE, and convergence measurements of the galleries of the HAW test field.

The predictions of the deformations, temperatures and stresses are presented for a period before the start of the heat input and for 5 year long heated situation. In the presentation of the results attention is given to the role of the different modelling assumptions. The results for the heated situation were based on the assumption that all eight boreholes in the test galleries A and B are heated.

In 1992 most of the work was devoted to a further elaboration of several assumptions in the pre-test analysis and the start of the comparison of measurements and analyses.

Previous plain strain, axisymmetric and three-dimensional analyses of the HAW test field /8/, /9/, /10/ have shown that the maximum thermally induced compressive stresses in the field are not very sensitive to the number of boreholes. For the development of the compressive stresses over longer time periods the analyses show that the boundary conditions, and therefore the number of heated boreholes, have a large influence on the evolution of the stresses. Based on this finding a full three-dimensional model has been set up of the HAW test field with only two (electrically) heated boreholes. The results of this analysis have been reported in /11/. The main conclusions are:

i) In the case of two heated boreholes, A1 and B1, there is one symmetry plane between these boreholes parallel to the galleries. In case of a completely heated field there also are several symmetry planes perpendicular to the galleries; this will result in more heat and salt flowing into the gallery. This explains the significantly higher stationary value for the compression on the liner in the case of two heated boreholes compared with the completely filled field.

ii) The analysis has shown that the effect of the heaters in A1 and B1 is noticeable at rather large distances. At the location of the boreholes A2 and B2 the horizontal compressive stress increases by about 1 MPa.

The effect on the other stress components and on all stress components at larger distances is smaller.

iii) The analysis has shown that the ovality of the liner is predominantly caused by the circumferential variation in the compression of the rock salt on the liner and to a much lesser extent by bending of the liner. The numerical results presented clearly show a large difference between the time history of the horizontal movement of the heated boreholes which causes the bending of the liner and the circumferential variation in the compression on the liner. The resulting ovality nicely corresponds with the measurements, not only in absolute sense but also in the time history.

Following the finite element analysis presented in /12/ some analytical work has been done on the heater interruption that occured in early 1992 /13/. It appears that due to the heater interruption the drop in the temperature ΔT leads to a rise in the radial stress $\Delta\sigma_{rad}$:

$$\Delta\sigma_{rad} = \frac{2G\alpha_s}{1 + \frac{2GR}{E_s\delta}} \Delta T$$

where:

G	Shear modulus of the rock salt.
α_s	Coefficient of thermal expansion of the steel liner.
R	Outside radius of the liner, or radius of the borehole.
E_s	Young's modulus of the steel liner.
δ	Thickness of the liner.

The rise in the tangential stress is twice the rise in the radial stress. This analytical expression nicely corresponds with the finite element analyses and holds when during the reduction of the temperature the creep effects of the salt can be neglected. This will be worked out further with respect to a smooth shut-down of the heaters which is foreseen in 1993 because of the early termination of the project.

In cooperation with GSF work has been started to compare the analyses with the measurements.

Measurement data of temperatures, displacements and stresses in the surroundings of the two electrically heated boreholes are now available for more than four years. The test field data were compared by GSF in a former analysis /14/ with an axisymmetric finite element model, which considers only one borehole. The comparison turned out that measurement and calculation of temperatures agree very well, but in the mechanical performance this model is somewhat stiff because of the axisymmetric formed gallery and because primary creep of rock salt has not been taken into account.

To get better results now a 3D-model of the HAW test field has been set up by GSF after programming a 3D-mesh-generator for handling of the spatial twenty-nodes-elements. The results of the thermal calculation are in agreement with measurements and the mechanical part of calculation shows clear indications of an interaction between the two heated boreholes, which could not be given by the former axisymmetric model. The spatial distribution of stresses is not very accurate and this is caused by the roughness of the model which consists of 1173 nodes and 204 twenty-nodes-elements.

Future calculations should use a finer grid to get accurate stress results. This seems to be very important, because recent calculations of ECN have shown that there might be fundamental problems of measuring stresses in rock salt, and therefore, calculation is perhaps the better way to get an overview of the time dependent stress fields in rock salt.

The measurements on the in situ gas release have been continued after all 48 boreholes have been rinsed with pure nitrogen in summer 1991 in order to reduce the concentration of the various gas components. Afterwards gas samples have been taken after 1; 10; 100 and in 1992 about every 100 days. The previous plateau values of the gas concentration have been reached again more or less in all boreholes.

As a consequence of the interruption of heating in January 1992 the temperature of the salt decreased, which led to the generation of fissures and additional gas release in a distance of about 2 m surrounding the heater borehole. The concentrations of methane, carbon dioxide and hydrogen increased up to 1 Vol %.

The programme to determine the adsorption enthalpies of CO_2 and CH_4 on the salt crystal surfaces have been finished. The enthalpy of adsorption on the 100-NaCl-surface is about 29 kJ/mol for CO_2 and about 10 kJ/mol for CH_4.

2. Laboratory Activities

2.1 Radiolysis effects in salt

The French laboratory investigations on radiolytic gas formation and liberation from Asse salt were dedicated to develop the analysis methods, especially Fourier-Transform-Infrared-Spectroscopy (FTIRS), and to improve the irradiation procedures /15/, /16/, /17/. Osiris spent fuel elements could not provide integrated doses exceeding 10^7 Gy, which is not sufficient to simulate the dose accumulated in rock salt surrounding vitrified wastes in a repository. This was achieved in 1992 using ^{60}Co sources: four months of irradiation led to a total dose of $1.3 \cdot 10^8$ Gy.

The concentrations of the major components of the gas phase (CO_2, N_2O, H_2 and CH_4) corresponding to samples conditioned in synthetic air (N_2/O_2 = 80/20) and irradiated with ^{60}Co are given in figure 1 together with previous results. The residual amount of oxygen in the containers was 0.1% after irradiation.

The amount of CO_2 formed at maximum dose (32 ppm) corresponds to the calculated value (30 ppm) for total combustion of organic matter present in the salt (TOC = 8 ppm). Cobalt irradiation gives slightly higher levels of CO_2 due to a greater thermal desorption of gases caused by the higher operation temperature.

Air radiolysis, illustrated by the N_2O evolution, is reduced at high irradiation level because oxygen desappears.

Formations of H_2 and CH_4 are similar. However, the concentration of H_2 grows faster at the beginning because of the radiolysis of water. CH_4 is the last organic compound originated by the degradation of organic matter before its transformation into CO_2. The increase in concentration at 10^8 Gy results from the transition to a reducing medium (oxygen disappears) which cancels the last combustion step. The absence of CO indicates that every oxydation reaction is eliminated.

Formation of HCl in amounts which vary with time had been observed at 10^7 Gy. The higher concentration obtained at 10^8 Gy (0.7 %) may indicate the formation of more complex compounds that will be investigated further on.

As far as the improvement of FTIRS is concerned, a software for spectra analysis of complex mixtures of gases was worked out, using selected lines for each compound and a proper deconvolution technique which

enables to identify and quantify compounds whose concentrations in the sample are very different. A specific data base of spectra of standard compounds has been constituted and a suitable sampling cell with a variable optical path between 0.2 and 1 meter has been built. This cell may be heated in order to study compounds originated by thermal desorption and enables analysis of corrosive gases.

It is evident that very high integrated doses affect the composition of the gases formed under irradiation. It is therefore important to go thoroughly into the investigation of gas evolution, especially as regards corrosive ones, discriminate irradiation and thermal effects and improve detection of reactive intermediate compounds: on line analysis would provide very useful information. These will be the main lines of our future work.

Radiation damage development in rock salt and pure NaCl crystals has been studied by means of irradiations performed in the Gamma Irradiation Facilities (GIF) of the High Flux Reactor (HFR) at Petten.

Irradiations in GIF A of unpressurized samples of Asse Speisesalz from the 800-m-level, take place at 100 °C, variable dose rates (40 to 240 kGy/h), and up to different (accumulative) total doses. Due to an experimental failure this experiment was restarted, the samples are now contained in gold holders and the highest achieved integrated dose amounts to 390 MGy. Small Angle Neutron Scattering (SANS) experiments on three pure NaCl-samples irradiated in this facility (before experimental failure) suggest that the colloids are not fractals /18/. More experiments are proceeding.

Another set of irradiations, in GIF B, of samples both pressurized and unpressurized and of the same pure NaCl and natural rock salt planned to be used in the dummy canisters /19/ proceeded at 100 °C but at constant dose rate of 4 kGy/h and up to doses of 4.6 ± 0.8 MGy. A new experiment is proceeding under the same conditions but with a planned total dose of 43.8 MGy.

Many of the samples irradiated in experiments performed in previous periods at identical conditions as those described for GIF B (except for dose rate which was 15 kGy/h) have been studied during this period /18/ (see also section 2.2). Stored energy measurements showed that before extensive colloid development the agreement with the Jain-Lidiard predictions was very poor. Therefore the Jain-Lidiard model is being extended in order to include the nucleation process. Comparison of the stored energy yields of pure single crystals with that of the most damaged (non-recrystallized) parts of natural rock samples simultaneously irradiated showed that at least in our experiments, natural rock samples (even in absence of recrystallization and of the endothermal effect of polyhalite) do not develop more stored energy than pure NaCl /18/.

Laboratory analysis performed at the University of Barcelona on natural rock salt irradiated at the GIF B, have provided useful information about the influence of several parameters (total dose, confining pressure, brine content and geochemical and mineralogical composition) on the radiation damage. The following progress and results were obtained:

a) Factors effecting radiation induced defects formation

In order to explain the interrelationship between the radiation induced defects and the geological parameters, Principal Component Analysis (PCA) using the correlation matrix has been performed with the data coming from the cylindrical shaped samples. The aim of PCA is to explain these multivariate data set in terms of as few factors as possible. Moreover, the measurement of radiation induced defects on tablet-shaped samples has provided the basis to test the favourability of certain salt formations to develope those defect using the Kruskal-Wallis test.

The increase of total dose controls the production of colloidal sodium, keeping the molar fraction of F-centers constant. The mineralogical impurity of the rock salt enhances the development of radiation-induced defects. Therefore mineralogically pure rock salt formations can be more suitable to host radiactive waste than impure rock salt. This information can be very helpful in site characterization. The influence of brine content and pressure in the radiation damage is weak.

Quantitative microstructural analysis on PLL samples (coming from the Sallent Mine) has shown that there is a positive correlation between white material (recrystallized) and intragranular brine while the correlation is negative with solid impurities and pressure. Moreover, the time of irradiation, time under pressure and intergranular brine have a negligible effect. The negative correlation between solid impurities and white material suggests that impurities may act as physical barrier, hindering the movement of grain boundaries.

b) Maximal expected dose at the repository

The comparison between experimental data and the Jain-Lidiard model have shown that the radiation damage values obtained by the Jain-Lidiard simulations performed by ECN, are slightly higher than the 95th percentile of risk based on the experimental results (see figure 2).

Moreover, the extrapolation of these data to doses up to 400 MGy, induces to expect the maximal value of F-centers to not exceed 10^{-4}. For colloidal sodium the 95th percentile risk follows a quasilinear trend ranging between 10^{-6} to 10^{-3}. The extrapolation to doses up to 400 MGy induces to expect a maximal value of colloidal sodium below 1 %.

c) Decay of the amount of the radiation induced defects

The decay of the amount of the radiation induced defects, due to back reactions, has been studied as a function of storage time. After irradiation at dose rate of 34 kGy/h, light absorption measurements were performed several times during a period of 50 days in order to know the evolution of the irradiated sample. The results of this study have shown that the amount F and M-center decreases due to recombination of defects. This decay is very fast in the first 10 days, slowing down afterwards.

d) Radiation induced defects in samples irradiated at dose rate of 4 kGy/h

The starting material used in this experiment are cores of natural and synthetic rock salt. The determination of the amount of radiation-induced defects has been performed by light absorption. In the studied samples three types of defects have been detected: In Harshaw monocrystals, only F-centers are present, while in polycristalline rock salt F-related centers (F_A or F_Z) as well as sodium particles of colloidal size have been measured. The amount of colloidal particles ranges between less than 10^{-6} mol in Harshaw monocrystals, which is the detection limit of the light absorption measurements to 10^{-4} mol für polycristalline rock salt. The size of the colloidal sodium particles ranges between 40 and 60 nm. The amount of F- and F-related center is around 10^{-5} mol.

2.2 Geochemical and petrophysical characterization of salt samples

Microstructural analysis of the sample fabrics developed during irradiation in GIF B combined with light absorption measurements and with hydrogen yield experiments have shown that fluid assisted recrystallization of already recrystallized parts of a polycrystalline salt aggregate takes place during irradiation and that solution of irradiated NaCl does not decompose the brine present at the grain boundaries as long as colloids are not developed. Therefore fluid assisted recrystallization can continuously proceed under repository conditions provided it is quicker in eliminating colloids than radiation is in developing them /19/. Research into recrystallization rates in natural rocks is proceeding which - combined with H_2 content determinations - is expected to give an answer to the

question if brine would still be available for recrystallization during the first 500 years after emplacement of sources in a repository. Should this be so, the amount of colloids to be expected in repositories will not exceed a few tenths of a mol % /20/. It has also been proven that fluid-assisted recrystallization can proceed even if brine is in a vapour state /19/.

2.3 Development, calibration and testing of high-dose measuring systems

ANDRA has developed two separate dose measuring systems based on ion chamber detectors and thermoluminescent dosemeters, aiming to record dose rates at various locations of the test field as well as in the transfer station. The first is completed and partly delivered to Asse, partly stored in Saclay. The second system, which has needed intense development works for high temperature applications, is also completed. In 1991, a low level experiment (the so-called INHAW-experiment) has been successfully carried out in the HAW test field /21/, showing that the procedures developed for the project are ready for operation.

In 1992 a second field experiment was performed in the Morsleben salt mine to test the dosimetry system developed by GSF-ISS. As a reference 5 different dosemeters (TL, Alanin-ESR etc.) were used. The maximum dose rate was 20 Gy/h, which is significantly lower than the minimum dose rate expected in the HAW test. Preliminary results can be best explained by assuming a dose rate dependency of the LiF dosemeters scheduled for the HAW project, which was not found earlier under laboratory conditions. Further experiments are going on to prove this; final results will be available in 1993. This phenomenon does not put the principal applicability of the system into question.

A new method of evaluation of the LiF dosemeters was developed using the radiophotoluminescence (RPL) of the crystals. It was shown that this way of determining the dose is reproducible and applicable under laboratory conditions in the range from 0.1 kGy to 10 kGy. Various influencing factors, which prevented the use of the RPL method in the past such as geometry, optical diffraction, ambient temperature and UV-light could be excluded. The method is considered for individual calibration. Furthermore, in 1992

- the precision of the determination of the temperature dependence of the LiF samples was improved,
- the TL properties of the LiF crystalls were investigated in more detail and
- the TL-predose-method was found to be a possible technique to indentify the properties of the quartz used for HAW dosimetry.

Two different types of gamma ionization chambers are available at GSF-IfT in Braunschweig: the MGFK 61 (manufacturer Kraftwerk Union/Germany) for high dose rates (upper limit 10^5 Gy/h) and the RS C4-1606-237 (manufacturer Reuter Stokes/USA) for low dose rates (upper limit 5 Gy/h). In order to determine experimentally the sensitivity of the ionization chambers some calibrations were performed in 1992 at the GSF secondary standard dosimetry laboratory (SSDL). The irradiations was carried out using Co 60 and Cs 137 gamma sources and x-rays from 150 kV and 300 kV generator. The sensitivities of the ionization chambers are largely influenced by lower photon energies.

2.4 Gamma-fields and gamma-spectra calculations

Dose calculations have been carried out in France /22/ to give a predictive map of gamma dose distribution in the salt surrounding the testfield. Preliminary analysis determined which radiative transition may have significant effect and have to be considered : one gamma transition for each Cesium and Strontium plus Bremstrahlung for the latter were thus

pointed out. Calculations with Mercure-5 attenuation code were carried out for canisters loaded with 1 Ci of each isotope and for a limited number of points (125). And additional (custom-usable) software permits to obtain the result at any point in salt and for any kind of loading or arrangement of the HAW canisters.

GSF-ISS calculated dose rate and photon fluence distributions around the emplacement boreholes of the HAW test field. For canister No. 12 in the emplacement borehole A3, height profiles of dose rates and photon spectra were calculated at the outside wall of the canister and of the borehole liner with improved accuracy.

In the salt region, the dose rates and photon spectra were evaluated in radial direction up to 80 cm distance from the borehole axis in steps of 1 cm and in 1.65 cm steps in height. For the dummy canister used in the INHAW experiment, improved dose rate distributions were calculated for the guide tube and the borehole "DL001" in the emplacement borehole B3.

3. Desk Studies

3.1 Development of a Post Test Plan

On the basis of the table of contents developed in 1991 the first chapters of the Post Test Plan were written. Most emphasis was given to the determination of the objectives of the post test activities. First plans were developed in regard of a possible marking of fractures which could develop during shut-down of the heaters. Further plans were developed for a retrieval of measuring sensors in order to investigate their in-place-behaviour for later improvement of the measuring techniques.

3.2 Description of the mineralogical and geochemical properties of the underground test field

The SEM-survey of a representative number of rock salt samples, aiming at the investigation and characterization of the rock pores, was continued and finished in 1992. It revealed again a great variety of shapes and structures which roughly can be classified into a few groups of pore spacings partly related to crystallographic properties and directions, as to be described in more detail in the final report which was started now.

Also concluded was the analytical survey of texture and fabric of the rock salt of the test field. It revealed a generally poor orientation of the halite grains which might be in accordance with the relatively flat lying and weakly deformed (domed) structure of the entire rock salt of the test field.

A special study was aimed at the investigation and description of monocrystal halite layers often occuring parallel to the anhydrite layers.

The compilation and comparison of trace element profiles through the test field showed an unexpected and unexplainable behaviour for the Fe, Ni, Co and Mn-contents in the upper part of the B4-profile. That requires a repetition of sampling and analysis for about 15 samples.

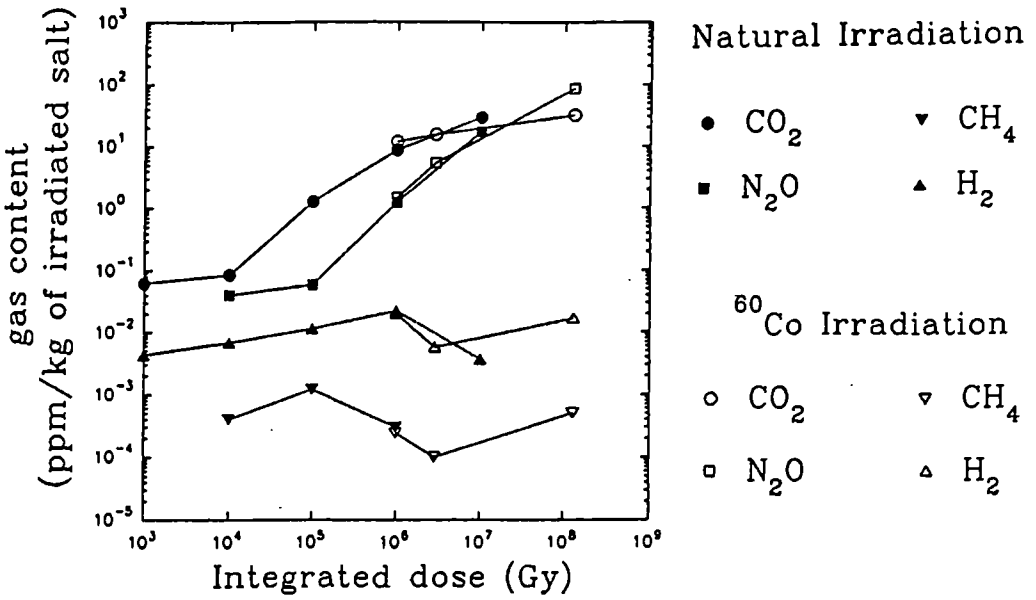

Figure 1: Irradiation of Asse Salt Samples: Generated Amounts of Gas Versus Integrated Dose

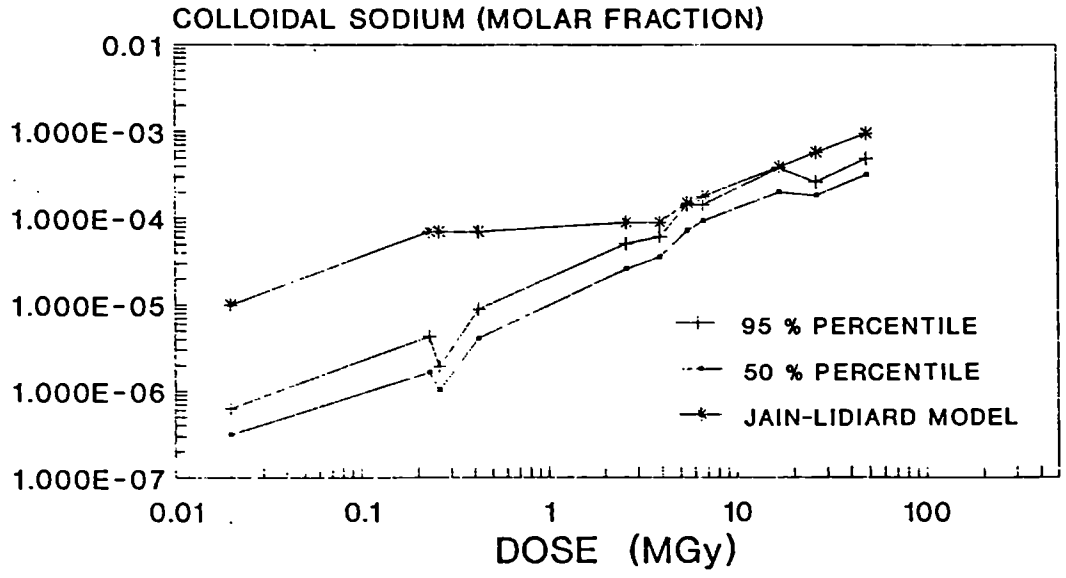

Figure 2: Comparison of the Amounts of Colloidal Sodium Obtained from Experimental Results (50th and 95th Percentile Risk Data) and Jain-Lidiard-Simulations

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Title:	Retrievable Emplacement Experiment with ILW and Spent HTR Fuel Elements in the Asse Salt Mine (REV project)
Contractors:	Forschungszentrum Jülich (KFA) GmbH and GSF- Forschungszentrum für Umwelt und Gesundheit GmbH (Federal Republic of Germany)
Contract No.:	F12W/0006
Duration of contract:	July 1990- December 1992
Period covered:	January 1992 - December 1992
Project leaders:	D. Niephaus (KFA) and K.Wieczorek (GSF)

A. OBJECTIVES AND SCOPE

In the Federal Republic of Germany, radioactive waste forms of pronounced decay heat generation shall be disposed of in deep vertical boreholes in the final repository at Gorleben site. The disposal technique for heat generating intermediate-level waste and for spent HTR fuel is under development in the R & D project, entitled "Intermediate-Level Waste and Spent HTR Fuel Element Test Disposal in Boreholes" (MHV project) . The MHV project is divided in two subprojects /1/ and is supported by the Bundesminister für Forschung und Technologie (BMFT) since 1983. In the subproject "Retrievable Emplacement Test" (REV) /2/, which is additionally supported by the Commission of the European Communities since 1990, an emplacement experiment with available waste packages will be conducted in the Asse salt mine. The objectives of the REV project are to characterize the available waste packages within a hot cell investigation programme at KFA, to demonstrate basic handling and emplacement operations, to show that emplacement boreholes can be operated safely with respect to radiation protection, to investigate the interactions between waste packages, borehole atmospheres and surrounding salt rock by monitoring, and in particular, to study the effects on gas release and generation. The duration of the emplacement experiment itself is intended to be up to a maximum of five years.

Work is done by KFA, Jülich and GSF, Braunschweig under coordination of KFA.

B. WORK PROGRAMME

1. Preparation of the experiment
1.1 Coordination of work between GSF and KFA
1.2 Assembly, installation and test of components
1.3 Licensing
1.4 Installation of radiation protection instruments
1.5 Staff training for emplacement and retrieval

2. Implementation of the experiment
2.1 Coordination of work between GSF and KFA
2.2 Transport of the waste packages to the Asse mine
2.3 Emplacement of the waste packages
2.4 Measurement of dose rate, temperature, gas composition and borehole convergence
2.5 Maintenance of equipment
2.6 Radiation protection measurements
2.7 Staff training for retrieval

C. PROGRESS OF WORK AND RESULTS

State of Advancement

The basic reliability of operating boreholes with ILW and spent HTR fuel packages emplaced will be demonstrated with respect to safety engineering and radiation protection aspects within a retrievable emplacement test. The waste packages foreseen for this emplacement test have been investigated for the release of gaseous radionuclides, and in particular, intermediate-level waste for hydrogen generation due to radiolysis. Apart from this, the other characteristic data such as waste content, total activity, decay heat generation, surface dose rate etc. have been made available from measurements and theoretical calculations. Emplacing will take place in a drift EV, which has been excavated at the 800-m level of the Asse salt mine. Five large boreholes (EV1-EV5) were driven into the drift floor and instrumented to carry out precursory tests and the emplacement test (Fig.1a,b).

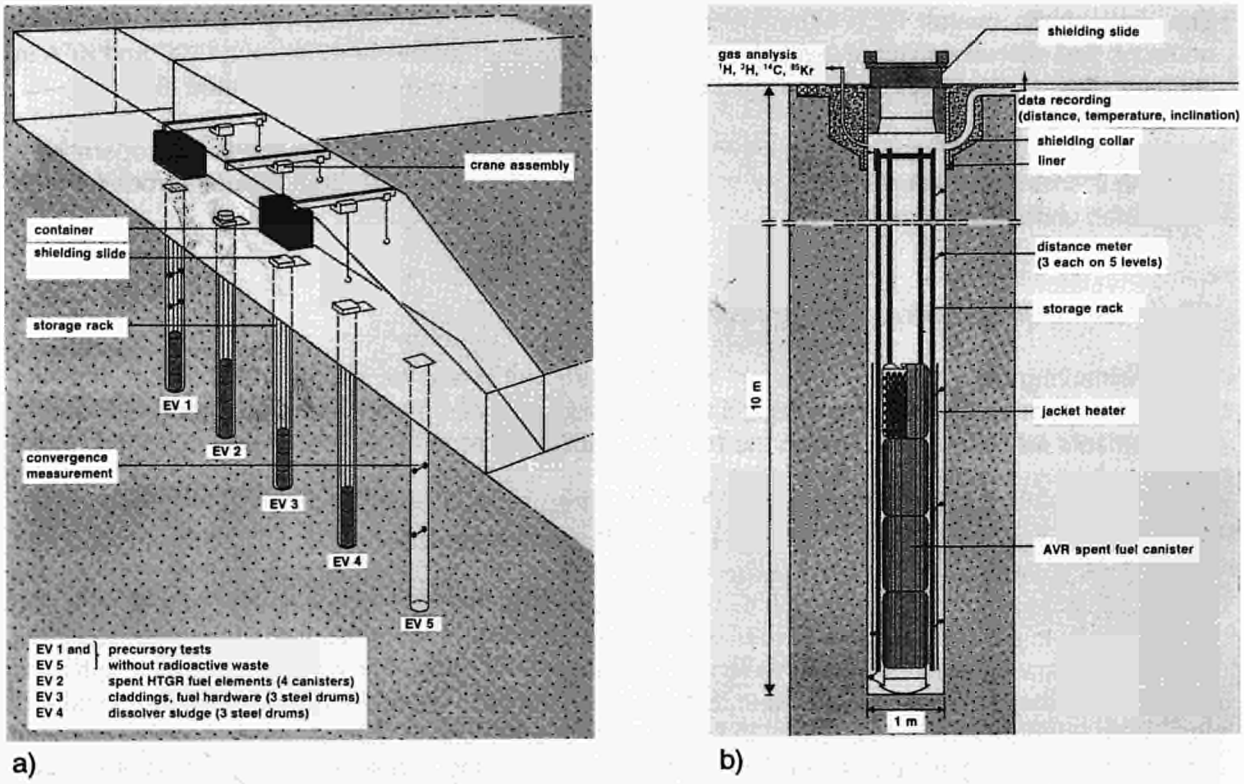


Fig.1: (a) Schematic view of the drift EV and (b) of the EV2 borehole set up instrumented accordingly to the boreholes EV1, EV3 and EV4

An accompanying geomechanical programme to measure deformations, stresses and temperatures in the vicinity of the boreholes and the drift EV was initiated and supplemented in the course of the precursory test programme by convergence and temperature measurements directly located in the boreholes EV1 and EV5. The installation work was completed in mid-1988 and April 1989, respectively and the programmes are fully operational. Additionally, a geological mapping and probing of the drift and a moisture measuring programme on the boreholes EV3 and EV5 has been carried out in previous phases of the project /3,4/.

During the period covering the year 1992, a gas control and analysis station has been installed and work on connecting the data lines from the emplacement boreholes EV2-EV4 to the central measuring and data collection system has been completed.

Manufacturing and cold testing of the engineering equipment neccessary for shipping, handling, emplacing and retrieving operations except the service cabinets, control systems and boards for the different hoisting assemblies have been completed, too.

With regard to the experimental borehole internals installed and the properties of the waste packages to be emplaced some theoretical considerations and assessments have been carried out, focussing on the problem of gas generation and release during the emplacement test /5/.

Due to delay in the licensing procedures, complete assembly and installation of the engineering equipment at the Asse mine is still lacking and thus the emplacement of the waste packages could not be performed in 1992.

1.1 Coordination

The draft of the overall REV experiment description has been reviewed by GSF/IfT. Remarks, additions and alterations requested have been discussed and coordinated between GSF and KFA in January 1992. Work on revising the report correspondingly has been nearly completed /6 /.

In agreement with GSF the revised report is intended to serve as the basis for further operational planning licensing procedures pursuant to the Federal Mining Act and for the licensing procedures to be initiated under the Atomic Energy Act.

1.2 Assembly/ test of components/ installation

The engineering equipment for transport, handling, emplacing and retrieving as well as borehole set ups and monitoring systems are adapted to the waste packages available, to the statutory licensing requirements for retrievability and to the technical facility equipment and conditions at the Asse salt mine.

The four canisters containing 950 spent HTR fuel elements each will be packed into type B licensed single AVR shipping casks (Fig.2) and transported individually to the Asse mine by rail. Prior to this the leak tightness of the canister closure must be demonstrated according to a type-B licensing requirement. In order to fulfil this requirement, a special unit was manufactured for plug replacement at the canisters as well as determination of the leak rate on canister plugs by He leak tightness testing. This plug replacement and leak testing unit was installed and tested as a preparational and necessary step in a KFA Hot Cell (Fig.3a,b) /7/. A second unit of almost equal design has been constructed; it will be installed in the "Hot Cell" of the Asse mine and kept ready for canister retrieval at the end of the experiment.

The transport and handling of the fuel canisters at the Asse mine will be conducted with these AVR shipping casks. The casks will be hoisted directly to the shaft station at the 800-m level, transported to the test drift EV and be placed onto the EV2 borehole. The spent fuel canister then will be lowered individually into the borehole after coupling and opening the sliding bottoms of the AVR cask and the AVR borehole slide by a 720-kg hoisting gear equipped with a coupling link compatible to the canister grab inside the cask.

The six ILW 200-l drums will be packed into the type B-licensed single CASTOR-MTR-F shipping casks at the KFA (Fig.4a) and transported to the Asse mine in pairs by rail. The drums will be reloaded from the two CASTOR casks into two E2 transfer casks (Fig.4b). This will take place in the shaft house at the Asse mine with the aid of the ILW reloading station and a 720-kg hoisting gear equipped with a special coupling link compatible to the different grabs inside the AVR and E2 casks. The E2 casks then will be hoisted to the shaft station at the 800-m level, transported to the drift EV and placed onto the EV3 and EV4 borehole, respectively. The drums will be lowered into the

boreholes after coupling and opening the sliding bottoms of the E2 casks and E2 borehole slides by 720-kg hoisting gears equipped with coupling links compatible to the drum grabs inside the casks.

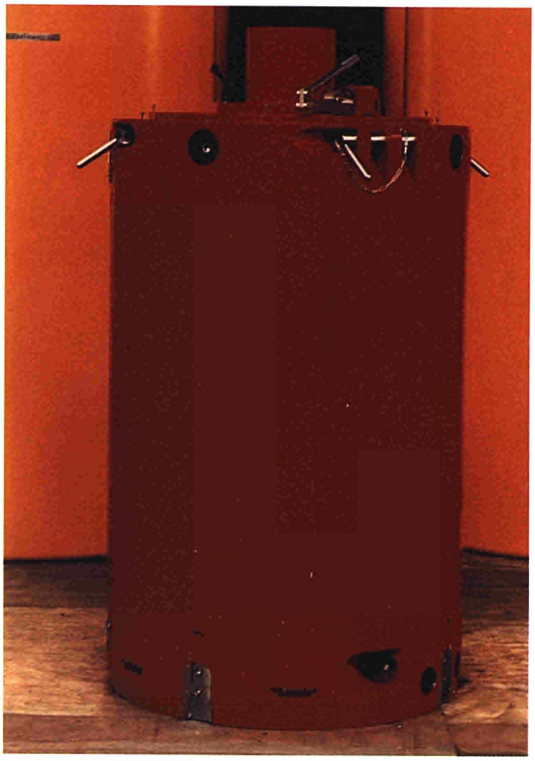
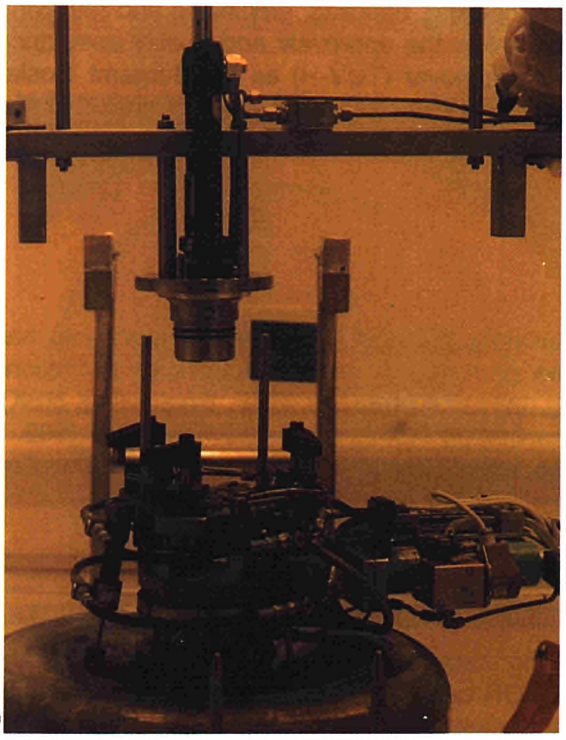


Fig. 2: AVR shipping cask

a)



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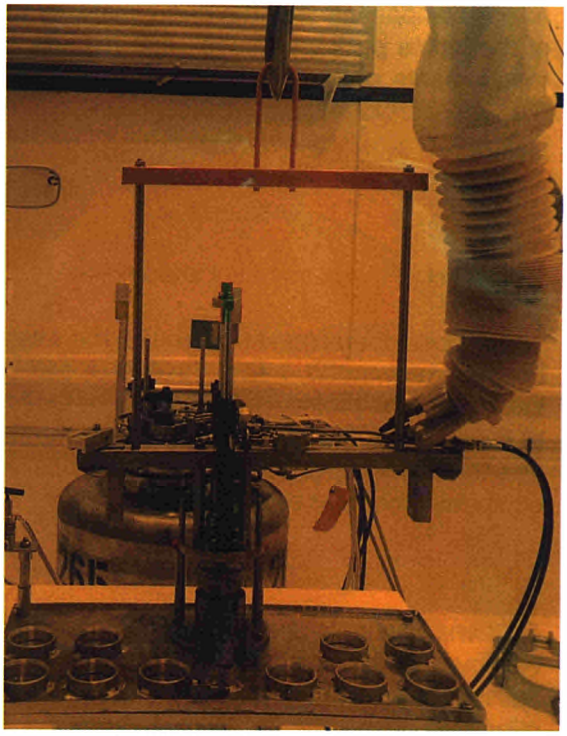
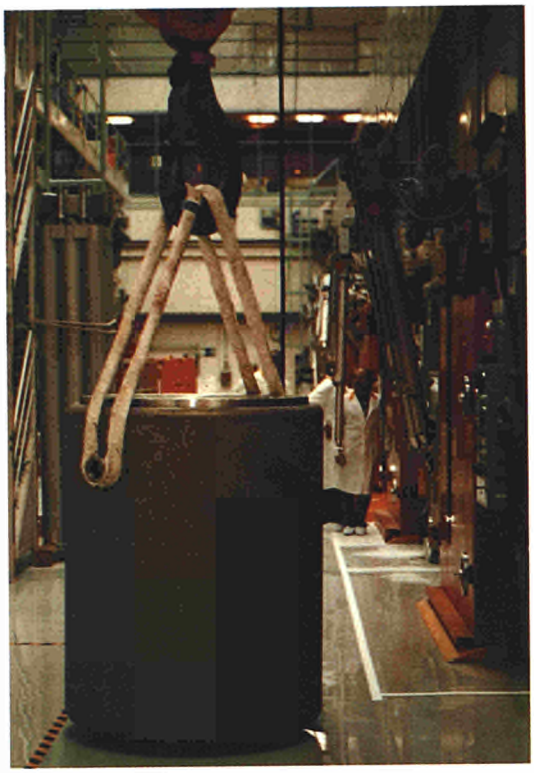


Fig.3: (a) Withdrawn canister plug attached to the spindle and (b) taking the plug off the spindle on an plug replacement set up



a)

b)

Fig.4: (a) CASROR-MTR-F shipping cask and (b) E2 transfer cask

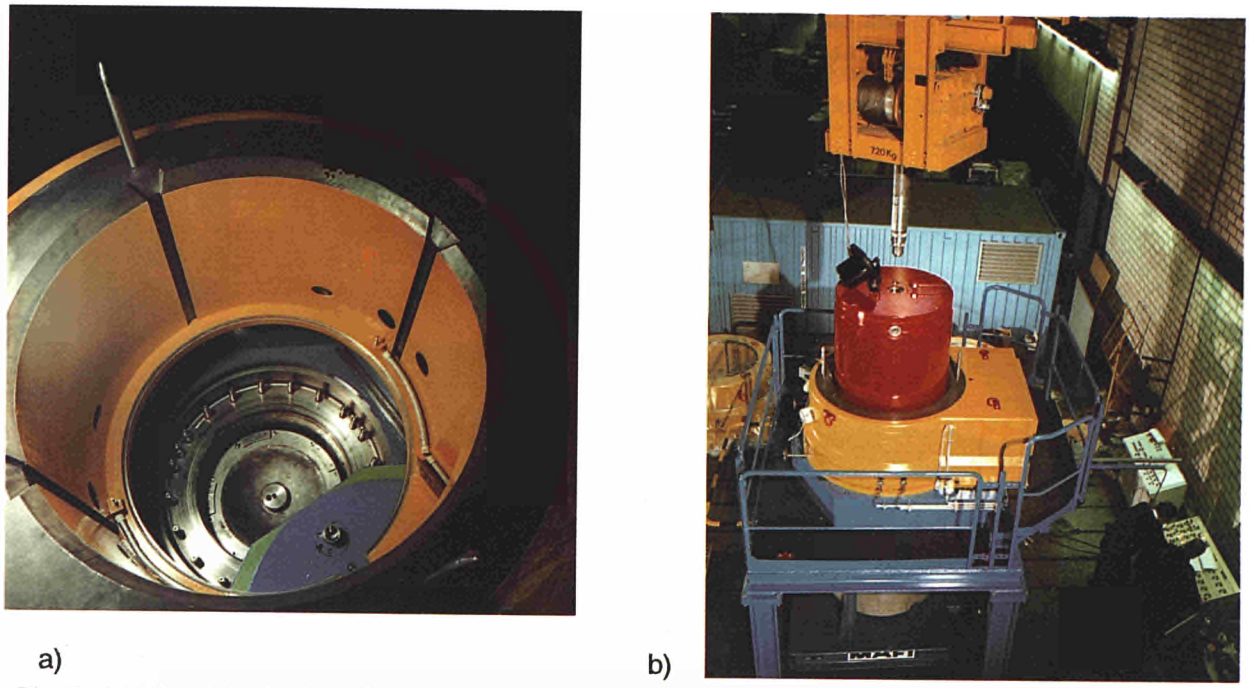
1.2.1 Assembly

All the components and devices necessary for shipping, hoisting, handling, emplacing and retrieving of the waste packages have been manufactured pursuant to the approvals and quality assurance requirements of the Technische Überwachungs-Verein Hannover (TÜV-H) as the Bergamt Goslar (BA-GS) consultant. Assembling of the different components has been completed for checking and testing at the manufacturer sites.

1.2.2 Test of the component assemblies

The proper operating, in particular the interactive functioning of the large scale components has been demonstrated within three test set ups in the presence of representatives of institutions involved in the project (GSF, BGR), of those advising on the project (BfS, DBE, GNS, GRS, HBK), of the Bergamt Goslar (BA-GS) and of the Bergamt consultant TÜV-H one final time in May 1992. It was thus possible to successfully conclude, as a whole, the cold test phase of the essential handling equipment, components and sequences.

Systems Test I
Removal of the lid of the CASTOR-MTR-F shipping cask in the ILW reloading station and subsequent reloading of a 200-l drum from the CASTOR cask into an E2 transfer cask and also reloading of the CASTOR cask from the E2 transfer cask and subsequent replacement of the CASTOR lid was implemented several times (Fig.5a,b)

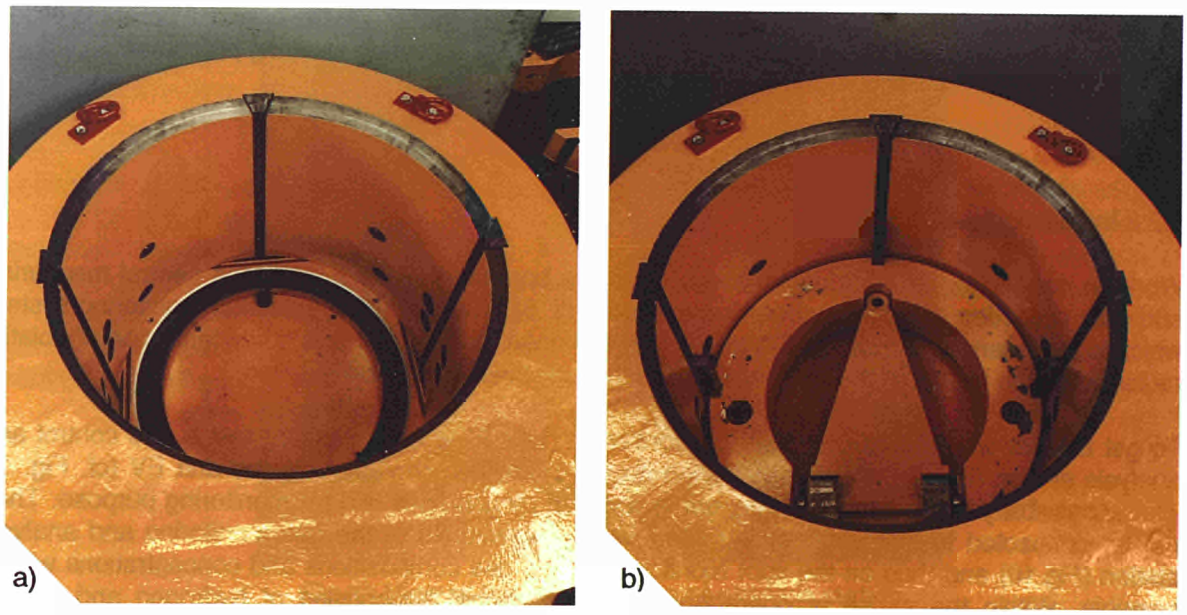


a) b)

Fig. 5: (a) View into the transfer opening of the shielded casing of the ILW reloading station onto the lid of a 200-l drum and (b) of the overall systems test set up during lowering of the link to be coupled with the package grab inside the E2 transfer cask

Systems Test II

Positioning of an E2 transfer cask and an AVR shipping cask in the shielded casing envisaged for the radiation protection slide of the "Hot Cell" was similarly repeated several times with subsequent opening and closing of the coupled sliding bottoms (Fig.6a,b).The slide is stationary imbedded in the floor of shaft house of the Asse mine. Therefore the test set up has been erected by using the second E2 borehole slide constructed in the same way as the radiation protection slide.

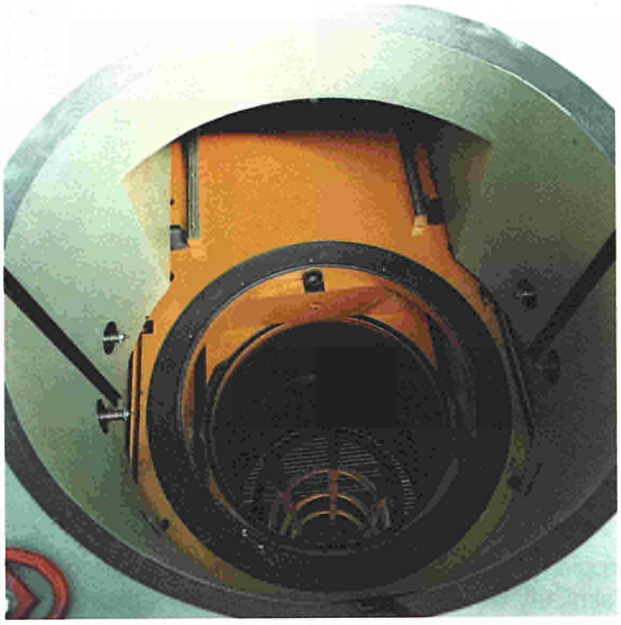


a) b)

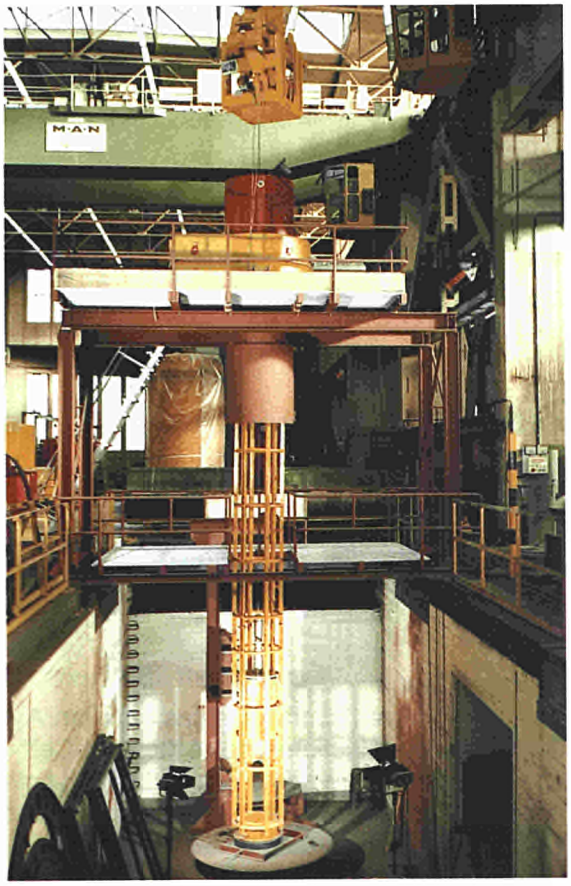
Fig. 6: Assembly of the shielded casing and an E2 borehole slide prepared for positioning (a) an E2 tranfer cask and (b) an AVR shipping cask into the transfer opening
(Similar to the arrangement envisaged for the "Hot Cell" at the Asse mine)

Systems Test III

Emplacing a 200-l drum from an E2 transfer cask deposited in the shielded casing of an E2 borehole slide into a storage rack (borehole) with subsequent retrieval of the drum has been performed several times (Fig.7a,b).



a)



b)

Fig. 7: a)View into the transfer opening of the shielded casing through the open E2 borehole slide onto a storage rack and (b) of the overall test set up during lowering procedure

1.2.3 Installation

Work on connecting the test desks allocated to the boreholes EV2 - EV4 to the central measuring and data collection system has been completed (Fig. 8). The radiation protection monitoring system which is to undertake operational monitoring of the dose, the dose rate and concentration of volatile radionuclides in the air of the EV test drift and the boreholes has been installed.

To get familiar with the gas release and formation during the emplacement test a gas control and analysis station (Fig. 9) has been installed in one of the two containers in the drift EV (cf. Fig. 1). The accessibility to the borehole interiors is ensured by gas lines laid for monitoring purpose. They will be connected to identically constructed measuring circuits of the gas monitoring and analysis station (Fig.10) and thus on-the-spot monitoring of the gas compositions and concentrations will be possible. Within the sense of operational safety addtional supervising of hydrogen and activity concentrations can be carried out by gas sampling and external analysing. To avoid the formation of explosive gas mixtures and to keep hydrogen concentrations below a required limit of 0.8 vol % hydrogen can be oxidized to water in a copper oxide bed.

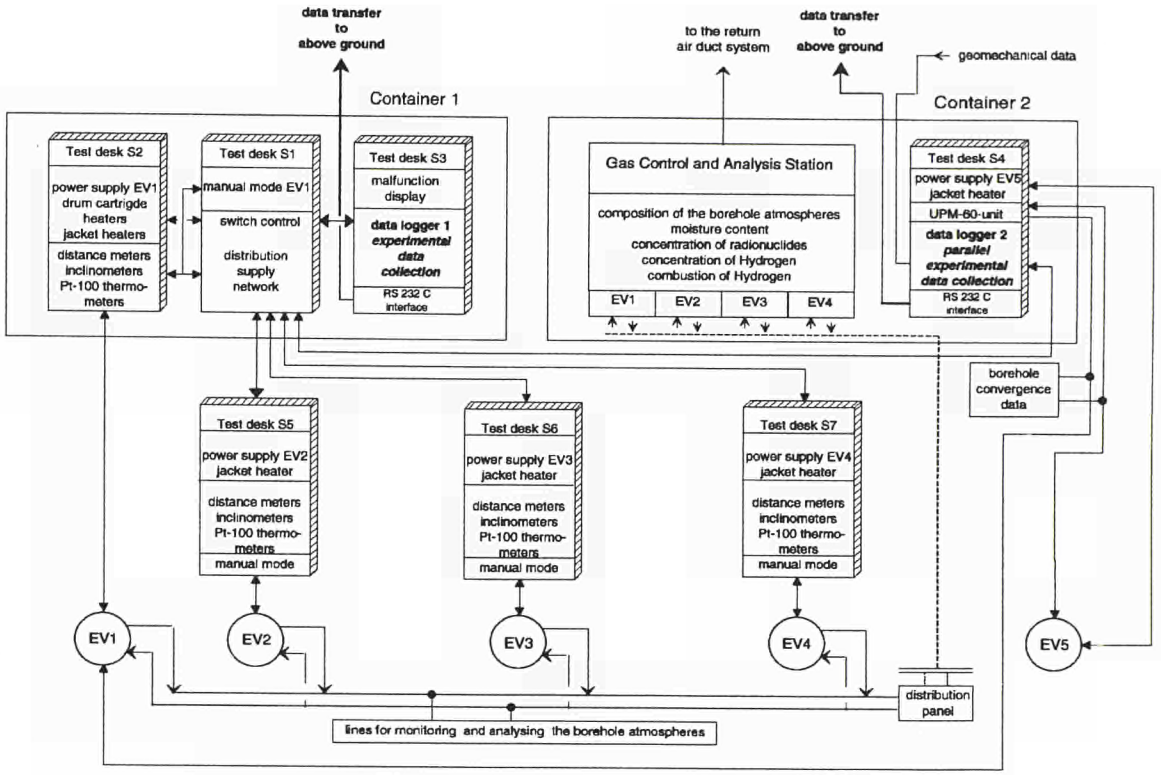


Fig. 8 :Scheme of the measuring and data collection systems and of the gas control and analysis equipment installed

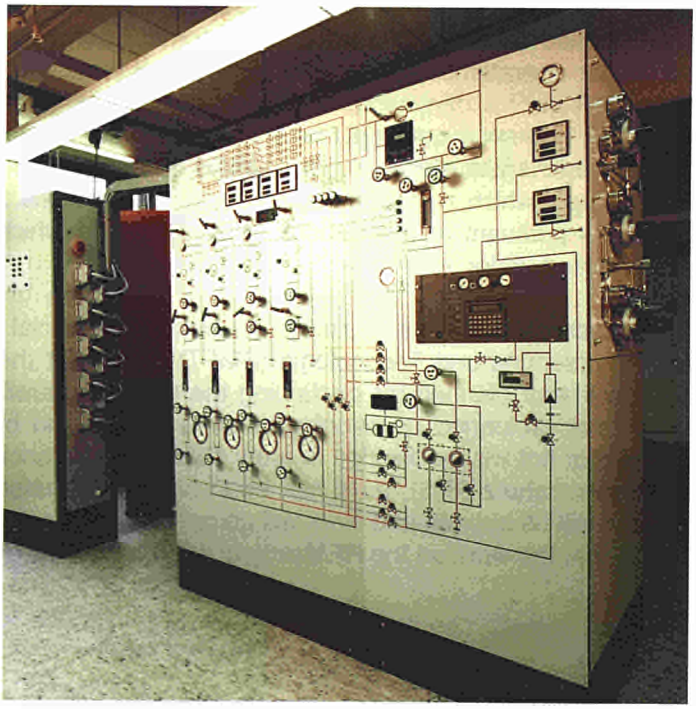


Fig. 9: View of the gas control and analysis station

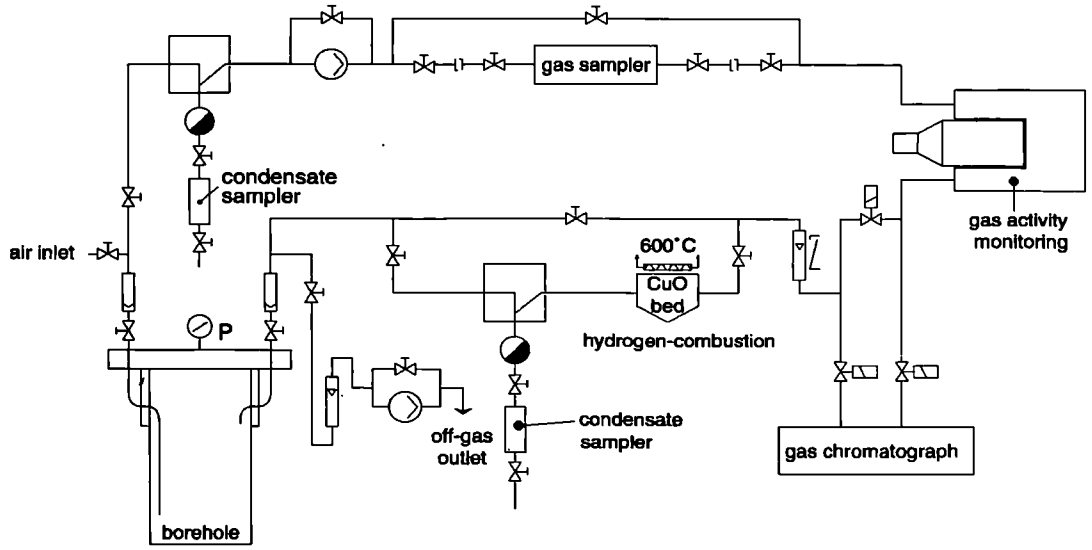


Fig. 10: Gas circuit for monitoring, sampling and analysing the borehole atmosphere

1.3 Licensing

In December 1990 the Bundesminister für Umwelt, Naturschutz und Reaktorsicherheit (BMU) has decided, that the Retrievable Emplacement Test will have to be licensed pursuant to §9 of the Atomic Energy Act instead of §3 of the Radioation Protection Ordinance, as it was discussed before. Due to this the responsibility for the licensing procedure has changed from the Bergamt Goslar (BA-GS) to the Niedersächsisches Umweltministerium Hannover (NMU). Regarding this, the Bergamt Goslar in June 1992 has notified GSF and KFA, that the Atomic Energy Act licensing procedure must be started before further operational plans could be licensed pursuant to the Federal Mining Act.

In compliance with a former requirement of the Bergamt Goslar a draft of an overall REV experiment description has been drawn up , which was intended to serve as the basis for further operational planning licensing procedures pursuant to the Federal Mining Act and which now is intended for licensing procedure to be initiated under the Atomic Energy Act.

Nevertheless, licensing procedure has not been started yet because financial support of the project by the Bundesminister für Forschung und Technologie (BMFT) expires at the end of 1992 and no prolongation is foreseen as it was planned for continuing the work. In parallel, the CEC contract, which also was intended after prolonged questioning, expires at the end of 1992. The question wether the work is continued or not will be decided in early 1993. If the financial support is taken up by the Bundesamt für Strahlenschutz (BfS), as it has been already discussed between BMU and BfS, the licensing procedure will be opened and work will go on. However, reflecting the first inofficial statements one can expect that the work on the REV project will probably be ceased.

List of publications

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/2/ Niephaus, D.; Retrievable Emplacement Experiment with ILW and Spent HTR Fuel Elements, in: Pilot tests on radioactive waste disposal in underground facilities, Proceedings of a workshop held in Braunschweig 1991, edited by Haijtink, B., Commission of the European Communities, Report EUR 13985, Brussels 1992

/3/ Niephaus, D.; Kreutz, F., Wieczorek, K.; Untersuchungen an Großbohrlöchern im Salz im Hinblick auf den sicheren Betrieb bei der Einlagerung radioaktiver Abfälle, Beitrag zum GSF-Seminar "Herstellung von Großlochbohrungen in Salzformationen und ihre Nutzung zur Endlagerung umweltgefährdender Stoffe", Braunschweig, 5. und 6. März 1992

/4/ Niephaus, D., Kreutz,F., Wieczorek,K.; The REV project- Investigations on Large Boreholes in Salt with Respect to Safe Operation During the Emplacement of Radioactive Waste Packages, paper prepared for and presented on the third meeting of the CEC-Project Commitee B1:Asse, Colmar/France 25. - 26. June 1992

/5/ Niephaus, D.; The REV project- Experimental installations with a view to measurements of gas release and formation during radioactive waste package emplacement in large boreholes at the Asse mine, in: Proceedings of a CEC-progress meeting of the PEGASUS project , Brussels, Belgium, June 11-12, 1992, edited by Haijtink, B., McMenamin, T., to be published in the EUR series

/6/ Niephaus, D.; Teilprojekt "Rückholbarer Einlagerversuch" (REV)- Versuchsauslegung und Handhabungstechnik zur zeitlich befristeten Einlagerung von radioaktiven Abfallgebinden in Bohrlöchern auf der 800-m-Sohle der Schachtanlage Asse- Technical Report ICT-TB-8/90 (Rev. 1), in Vorbereitung

/7/ Niephaus, D. ,Printz, R.; Operational Experiences with a Plug Replacement and Leak Testing Unit for Spent HTR Fuel Element Canisters- One step towards the retrievable emplacement of radioactive waste packages in salt-, Extended Synopses, IAEA-SM-326, Antwerp, Belgium, 19-23 October 1992

Title:	**IN SITU INVESTIGATION OF THE LONG-TERM SEALING SYSTEM AS A COMPONENT OF A DAM CONSTRUCTION**
Contractors:	Deutsche Gesellschaft zum Bau und Betrieb von Endlagern für Abfallstoffe mbH (DBE) GSF - Forschungszentrum für Umwelt und Gesundheit GmbH Agence Nationale pour la Gestion des Déchets Radioactifs (ANDRA) Empresa Nacional de Residuos Radiactivos, S.A. (ENRESA)
Contract No:	FI2W - CT 90 - 0068
Duration of contract:	April 1, 1991 - March 31, 1995
Period covered:	January 1, 1992 - December 31, 1992
Project Coordinator:	W. Bollingerfehr

A. OBJECTIVES AND SCOPE

Dam constructions represent an essential component of the multibarrier safety concept for a repository for radioactive waste in salt formations. Within the scope of the dam project the long-term seal, which is responsible for the long-term safety of a dam construction is subjected to an in situ test. Main objectives of the scientific investigation programme are:

- to provide proof of the tightness of the long-term seal as a dam construction component by means of experimental investigations to obtain essential data concerning the effectiveness and
- to prognosticate its functioning (tightness) over long time periods (up to approximately 500 years) via model calculations.

The long-term evolution of permeability and porosity will be considered, investigating the chemical stability and the petrophysical behaviour.

The state of the art on calculations and codes for multiple-phase flow will be analyzed, adequate mathematical models and computer codes developed and verificated.

B. WORK PROGRAMME

According to the Technical Annex of the contract, the work programme consists of the following tasks:

for DBE and GSF

I/1. Conception, numerical preliminary investigations and detailed planning of the long-term seal test in the Asse Mine
I/2. Preliminary and parallel laboratory and in situ (borehole) tests
I/3. Instrumentation of the long-term seal construction
I/4. Performance of the large scale test long-term seal with gas and brine
I/5. Evaluation of the test results
I/6. Hydraulic modelling

for ANDRA

II/1. Physicochemical and petrophysical characterization
II/2. Evaluation of the solubility of materials
II/3. Dissolution kinetics
II/4. Laboratory batch experiments
II/5. Laboratory open system experiment
II/6. Pilot study in mine gallery (Amelie Mine)
II/7. Geochemical modelling
II/8. Petrophysical modelling
II/9. Interpretation and final modelling of the coupled system

for ENRESA:

III/1. Analysation of the state of the art on calculations and codes for multiple-phase flow

III/2. Conceiving laboratory experiments for measuring the permeability of the long-term seal against brine

III/3. Development of adequate mathematical models and computer codes for the numerical simulation of multiple-phase flow

III/4. Code verification

III/5. Interpretation of the in situ test measurements using the developed codes

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Due to budgetary problems BMFT (Federal Ministry for Research and Technology) prolonged DBE' and GSF' contracts for the dam project at a stand-by (low) level for half a year up to the and of 1992. Finally BMFT decided to stop further funding of the dam project. From the beginning of 1993 BfS (Federal Office for Radiation Protection) will be responsible for R&D-projects which are considered as final waste disposal facility related. The negotiating procedure for the dam project with BfS has been started at the end of 1992. Regarding these circumstances the DBE/GSF-programme in 1992 for the long-term seal has been reduced to planing and laboratory works. A modification of the planing for one long-term seal component has been done (I/1.). Preliminary laboratory and in-situ handling-tests with salt briquettes and an appropriate mortar have been performed (I/2.). The instrumentation for the long-term seal construction has been specified and ordered and is now available for installation. The development of hydraulic model to describe the long-term seal behaviour within the test field has been continued and first calculations were made (I/6.).

Within the project ANDRA is in charge of investigating the geomechanical behaviour of salt briquettes and its interaction with saturated brine. Taken into account the unsatisfying results an available mortar recipes in 1992 ANDRA performed additional laboratory experiments with mortar and salt briquettes (II/2. to II/5.). The feasibility study on the pilot test (II/6.) as well as the petrophysical modelling (II/8.) have been continued.

ENRESA focussed it's interest on further developing a computer code describing the multiple-phase flow phenomena. In addition to that laboratory experiments with salt samples have been performed.

Progress and results

1. Conceptional, numerical preliminary investigations and detailed planing of the long-term seal test in the Asse Mine (I/1.)

Taking into account the above mentioned financial restrictions DBE's activities in 1992 were focussed on a modification of the planing of the long-term seal observation chamber and on handling experiments with the mortar for the salt briquettes brickwork.

1.1 Modification of the observation chamber

The requirements and the technical layout of the observation chamber has been described in the 1991 progress report. One main point of interest was the joint between the rock salt surface of the excavated drift and the steel plates of the observation chamber. The joint should be completely filled with bituminous material. A free convergence of the adjacent rock was assumed to be approx. 10 mm/a. In the meantime measures of drift convergence near the Asse test field delivered values of approx. 50 mm/a regarding free convergence. In order to avoid high radial stresses for the observation chamber it's integration in the adjacent rock has been modified. The spherical inter-

space between observation chamber and adjacent rock was extended, and will be filled with a very compressible plastic material. Regarding the free convergence also the construction method of the chamber was slightly modified.

1.2 Handling experiment for investigating underground processability of salt mortar

1.2.1 Objectives of the handling experiment

General construction sequence for building the salt brickwork is planned in a way that the brickwork is built step by step in separate phases from the retreating. A brickwork without uninterrupted horizontal and vertical joints in flow direction of charging media was selected to guarantee the necessary low seal permeability. The brickwork has to be adapted to sides and roof of the drift, i. e., salt bricks have to be formed optimizing the joint between bricks and rock with regard to mortar and free space.

Laboratory tests carried out by GSF resulted in a mortar which seems to have the necessary consistency to reach a minimal joint thickness of 0,5 cm.

The time which is necessary for building the brickwork seal underground significantly depends upon mortar hardening time, time needed for pointing up the bricks and number of bricklayers who can work at the same time.

Therefore the mortar which was developed under laboratory conditions has to pass underground tests with respect to:

- verification of mortar mixture and properties developed under laboratory conditions with regard to transferability to underground conditions considering the brickwork construction (e. g., higher temperature and lower humidity of the air in the mine)
- verification of practical handling of mortar and salt bricks when building the planned brickwork bond
- possible modification of mortar mixture with respect to workability in the mine
- determination of construction sequence with respect to progress in volume and time.

1.2.2 In-situ experiments

In order to achieve the objectives criteria for the investigations have been defined (i. e. workability, hardening time, achievable strength). The handling experiments included three main steps:

- production and test of mortar mixture
- erection of brickwork blocks and
- material tests

Mortar tests have been performed determining in experiments in the Asse Salt Mine under in-situ conditions:

- necessary mixing time obtaining homogenous mortar mixture,
- mortar consistency as a function of mixing time (by slump tests),
- workability of mortar (by walling up tests),
- achievable thickness of vertical and horizontal joints with regard to complete filling.

The construction of a test brickwork in the Asse dam test field is shown in fig. 1. During the brick-laying activities the progress of brickwork strength and stability have been investigated as well as different manufacturing methods.

1.2.3 Results

The performed in-situ tests with the mortar composed salt powder and brine showed on the one hand the general feasibility to reproduce in-situ the quality which has been achieved in laboratory. The workability of the mortar could be demonstrated and a complete filling of the vertical and horizontal joints is possible. On the other hand there remained open questions concerning the hardening process and the time necessary to wall up a

brickwork. Additional investigations will be performed in 1993.

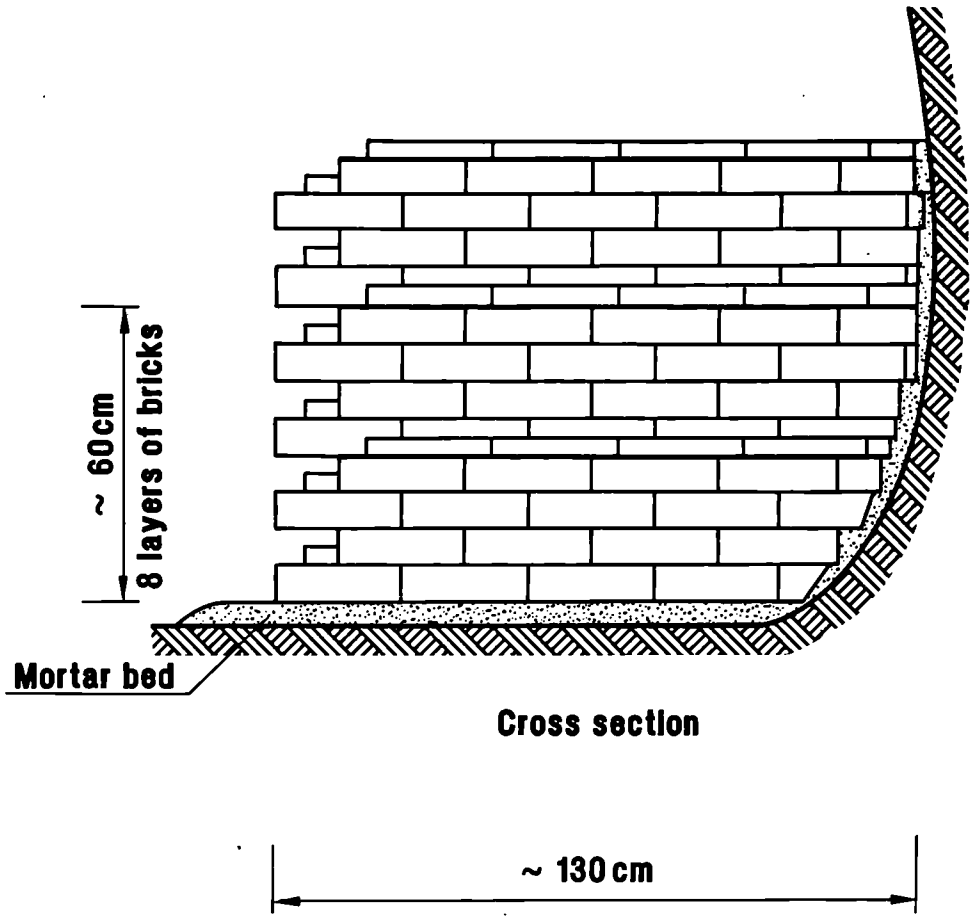


Fig. 1: Long-term seal handling-test; design of the test brickwork

2. Preliminary and parallel laboratory and in-situ tests (task I/2.)

In 1992 GSF has concentrated the scientific works at laboratory tests investigating salt mortar containing saliferous clay. In-situ tests for determining the permeability on rock salt around the test drift have been performed.

2.1 Laboratory tests

For the constructing of the long-term seal it is necessary to combine the bricks with a dense and tight complex. This should be achieved by binding the bricks with mortar.

To reduce the mortar permeability, saliferous clay may be added. The undermentioned laboratory programme investigated the preparation of such mortars, their porosity, permeability and swelling and provides initial information on their compressive strength.

2.1.1 Material description and investigation programme

As raw materials for mortar production fine-grained K&S halite powder and broken, ground saliferous clay from the Bleicherode salt mine in the southern Harz mountains were available.

The mortar was mixed manually. Its clay content (salt powder + saliferous clay = 100 %) ranged from 0 to 50 %. Liquids were added until workability had been obtained. Saturated brine (containing approx. 0.2643 kg salt/kg brine at 20 °C) as well as water (cf. Table 1) were used as liquid additives.

Subsequent to molding the samples were further consolidated by

vibration. The brine mixtures were recalculated to salt and water using the relation of salt/brine = 0.2643.

Content [weight-% Solids]		
Clay	Salt	Water
0	100	21
10	90	19
20	80	19
30	70	19
40	60	19
50	50	18

Content [weight-% Solids]			
Clay	Salt	Water	Brine
0	100.000	21.714	29.503
9.238	90.762	21.080	28.648
18.572	81.428	19.818	26.935
27.935	72.065	19.175	26.076
37.340	62.660	18.540	25.202
46.781	53.219	17.897	24.322

Table 1: Mixing ratios for saliferous clay, salt powder and water resp. saturated brine in order to attain good workability. The brine mixtures were recalculated to salt and water using the relation of salt/brine = 0.2643.

The samples were dried for 8 days at 100 °C. Saliferous clay mortar might be considered for combining individual salt bricks into a dense and tight long-term seal. At the Institut für Tieflagerung of the GSF a specific laboratory programme was started to test mortars consisting of halite powder and grey saliferous clay of the Staßfurt from the Bleicherode salt mine. Clay fractions between 0 and 45 % were subjected to the investigation. In addition to the description of the materials involved the interest focused upon obtaining good workabilities of the mixtures as well as upon the permeability and compression strength of the dried mortar samples.

2.1.2 Results

The test results may be summarized as follows:

- Without loss of quality the mortar can be mixed using fresh water. Approx. 18 to 20 weight-% of the solids must be added as mixing water.
- The porosity and the permeability of the mortar samples increases distinctly when equally coarse-grained salt powder is used for mixing.
- The mean grain size and the grain size distribution of the saliferous clay and the salt powder should be very similar to form a useful mortar.
- The permeability of the mortar samples decreases with increasing clay fraction from $2 \cdot 10^{-12}$ m^2 to $2 \cdot 10^{-14}$ m^2. The investigated samples, however, were large and dried at 100 °C.
- The uniaxial compressive strength of the clay mortar equals, at an average, only 4 MPa and decreases clearly with increasing clay fraction. Moist mortar samples did not show any measurable compressive strength.
- Moistened saliferous clay mortar may show little temporary swelling.

2.2 In-situ pressure tests for determining the permeability on rock salt around the test drift

These tests are intended for determining whether the excavation of a drift causes alterations in the permeability as a result of loosening of the rock salt in the vicinity of the drift. For this purpose, well pressure test have been conducted before, during, and after excavation of the southern dam construction test drift.

2.2.1 Test methods

Pressure test provide the possibility of determining various parameters of a formation, such as permeability or skin factor. In performing pressure tests, the flow rate and pressure variations are observed in the boreholes as functions of time. One of the two quantities is thereby controlled (for instance, by maintaining a constant flow rate), and the reaction of the system (for example, the pressure variation in the well) is measure. The pressure tests have been conducted in three phases:

- April to June 1991
- January to March 1992
- March to May 1992

The results of the evaluation are summarized in fig. 1.

2.2.2 Summary of results and conclusions

The initial phase of the second test series from April 1991 to June 1992, as well as the first test series in August 1989, were conducted before the excavation of the southern test drift. No effect was detected during the excavation.

Additional investigations are necessary for explaining the permeability changes which do not depend systematically on the distance from the roof.

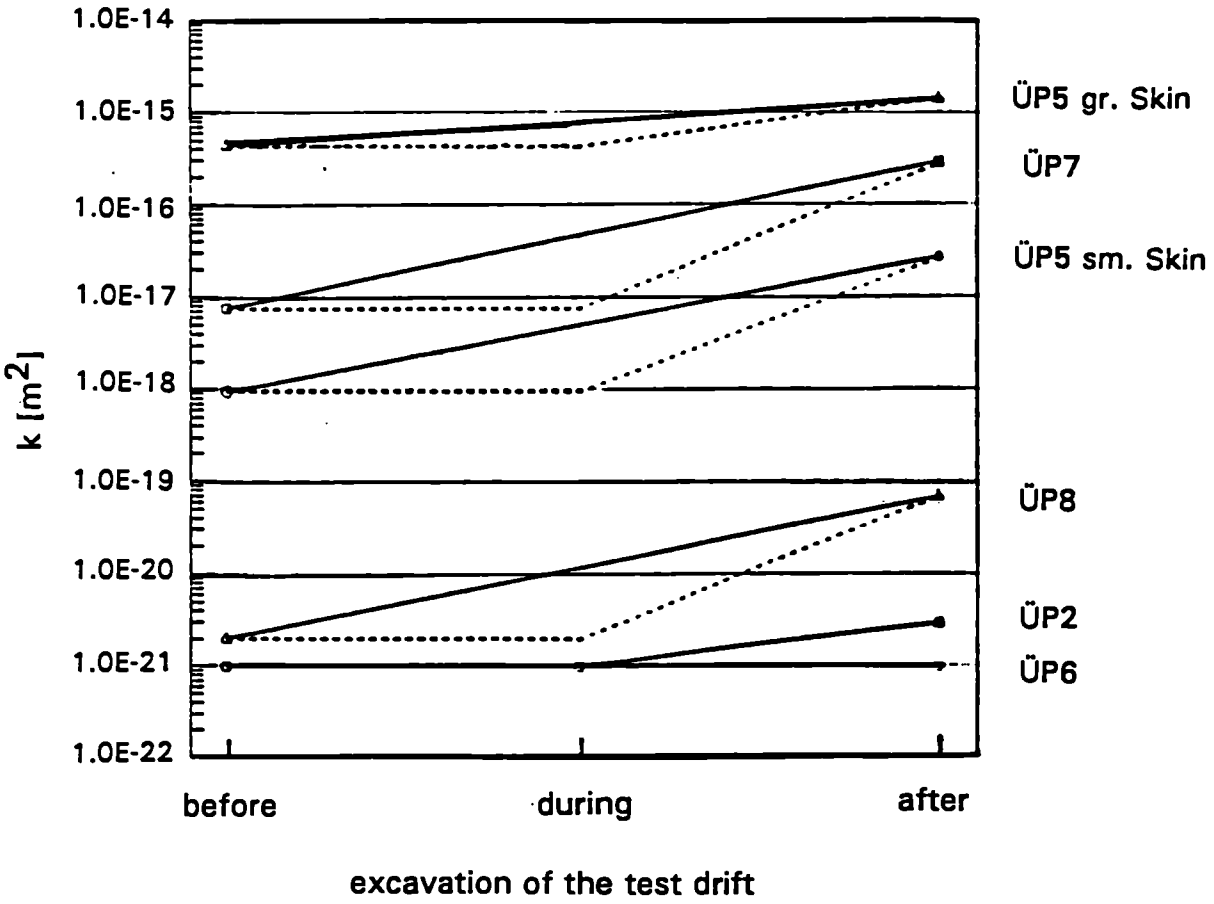


Fig. 2: Changes in permeability before, during and after excavation of the test drift

3. Geochemical investigation on salt briquettes

3.1 Evaluation of the solubility of the materials (II/2.)

The dissolution rates and migrations of the major impurities (KCl, $MgSO_4$, $CaSO_4$) through the porosity of the briquettes have been measured by putting a briquette in an agitated NaCl saturated solution and following the grade of these impurities in the solution. After 2000 hours most of the impurities were in the solution.

3.2 Dissolution kinetics study (II/3.)

The purpose of this study was to determine the value of the dissolution rate constant K according to the relation

$$\frac{dm}{dt} = K \times S \times (C_s - C_k)$$

The value of this rate is depending on the following parameters:

- temperature of the system,
- relative circulation rate of salt solvent,
- area exposed to the solvent,
- surface condition of the salt.

The measures have been made according to two settings:

- in a cell allowing a laminar straight flow along a sample,
- by rotation of a cylinder in a reactor of suitable shape and volume.

3.3 Brine penetration experiments (II/4., II/5.)

The aim of these experiments was the study of the interaction between a salt briquette and a NaCl saturated brine. This type of experiment allows the direct visualization of brine penetration by using X-rays transmission. These experiments have shown that the capillary strengths are the main factors which cause the brine penetration.

3.4 Petrophysical modelling (II/8.)

This consists of :

- study the problems of natural convection in a parallelepipedic cavity both numerically and experimentally,
- study the theory of imbibition of a passive porous material by a wetting fluid,
- analyze briefly the dispersion of components dissolved during the imbibition of the briquettes by the brine,
- giving order of magnitude of the main parameters of the in situ pilot test.

3.5 Mortar tests

Several test walls (see figure 3) have been built in order to test the different mortars to be used for the in situ pilot test. The leakages flowrates through them have been registered.

Twenty one mortars have been tested belonging to the following families : sodium chloride mixed with brine, industrial double components adhesives, sealing products, tile sealants and sodium silicate.

Only the two mortars containing sodium silicate have shown a good efficiency during a six months test. Further investigations (thin slices) lead to the conclusion that these joints do not affect the transfers through the wall.

Conclusions of these works

During all these works we have noticed that the imbibition of a briquette by a brine caused swelling of approximately 5 %, loss of mechanical consistency, and probably increased the permeability.

At this moment, it was obvious that we needed a feasibility study of the in situ pilot test.

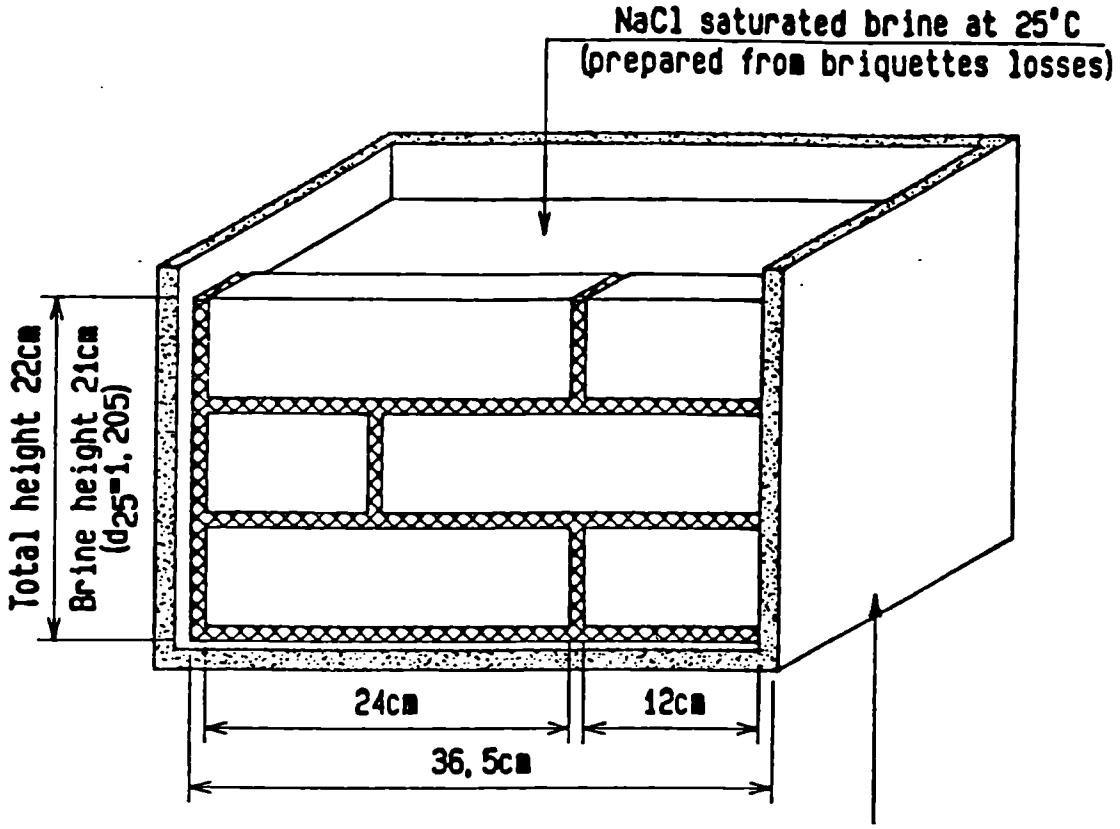


Fig. 3: Test configuration to test different mortars

3.6 Pilot study in mine gallery (Amelie Mine) (II/6.)

Feasibility study of the pilot test

This study has been done in the last four months of 1992.

Its three aims were :

- understand the brine migration mechanisms and their effects on the permeability,
- try to build a physical model consistent with the experiments,
- make predictions about the behaviour of the construction.

Experiments made for this study

- Two horizontal experiments of brine migration with free or closed outlet.
- One vertical experiment of brine migration with variable pressure and open outlet.
- Tests walls with mortars of sodium silicate and sodium silicate + kaolin.

Interpretation of the results

A model of imbibition by capillarity has been built.

The forces considered are :

- capillary pressure,
- viscosity of water and air,
- increase of air pressure in the briquette,
- gravity,
- additional pressure.

It has not been possible to obtain with this model a coherent interpretation of these experiments. That leads to the conclusion that a good understanding needs to take into account the changes of the internal geometry of the porous medium.

Nevertheless some conclusions could be drawn :
- after imbibition the permeability of the briquettes is approximately 10^{-14} m^2 (10^{-16} m^2 before migration),
- the brine will cross the wall in a few hours,
- the brine flow could reach 100 liters per day.

Other tests

Uniaxial compressive tests of impregnated briquettes have shown that the values decrease from 30 MPa (dry medium) to 1 MPa when totally impregnated.

Conclusion of the feasibility study

The feasibility of the in situ pilot test has not been demonstrated.

According to our investigations there are major risks of high leakages through the wall and very poor mechanical stability, that could lead together to a collapse. Therefore it is not possible to carry on the project as initially foreseen.

4. Analyzing of the state of art and developing models and computer codes for the numerical simulation of multiple-phase flow

ENRESA's theoretical work has continued during this year following the project tasks and the research work performed during 1991. At the beginning of the investigation, the mechanical constitutive model of granular aggregates was studied with special emphasis. When trying to reproduce laboratory mechanical tests obtained from the reviewed literature, some new aspects of mechanical behaviour have been observed. Therefore, the preliminary developed model should be improved in order to take into account these new features.

The governing equations for multiphase flow of brine and gas in deforming saline media have been put into the corresponding numerical representation using the finite element technique. An extensive work analyzing numerical procedures has been performed in order to optimize numerical computations, in order to develop an efficient computer code. A preliminary version of the code is already working and the first simulations for uncoupled problems will be presented at the next project meeting.

Experimental work includes the establishment of the test types designed in connexion with theoretical developments, the design of the cell to perform hydromechanical tests and, the results of some preliminary tests.

4.1 Constitutive modelling (III/3.)

At the Second Half Annual Report, a model for creep behaviour of porous granular aggregates of salt was presented. This model was developed using a simple geometry for grains and pores and applying the theoretical concepts of two different mechanisms of deformation. Advances on modelling are in progress in two different aspects. The first one refers to the adequate combination of these two mechanisms. Despite the fact that from theoretical point of view they act independently, their relative relevance depends on the physical conditions and characteristics prevailing in the medium, specifically temperature, stress, fluid pressures, brine content and grain size.

The second aspect of modelling refers to the existence of viscoplastic effects on the deformation of porous aggregates. Even though for rock salt and probably for low porosity aggregates, irreversible strain can be explained solely by creep mechanisms, granular aggregates in general develop deformation behaviour due to granular structure rearrangement. This means, that viscoplastic or plastic effects will appear as stresses change. This will lead to a more comprehensive model for porous granular aggregates of salt of a wide range of porosities.

Results of the experimental work on granular aggregates will provide a useful information in this regard.

4.2 Discretization of governing equations and computer code development (III/3.)

After development of governing equations for multiphase flow of brine and gas through deforming saline media, the corresponding numerical representation has been obtained. Our methodology has been to extensively study the numerical aspects until a clear procedure of coding has been obtained. When dealing with coupled problems, this previous work is important because it allows to optimize numerical computations and, at the same time, future difficulties are avoided. For this reason the development of the computer code has been delayed until all aspects, which come from our previous experience on numerical modelling, have been cleared.

There are some basic tasks of the computer code development that can be viewed as independent. These are:

- Constitutive relationships.
- Mechanical constitutive model.
- Interpolation functions and space integration.
- Element matrices: stiffness, coupling, storage, conductance, ...
- System matrix and residual.
- Boundary conditions.
- Dependent variables (porosity, stress, ...) updating.
- Input/output subroutines.

These tasks have been coded in a preliminary version of the program. Using this version, simple simulations of uncoupled problems are in progress.

4.3 Experimental work (III/2.)

Based on our experience and also on some theoretical aspects found during the previous research, the planning of experimental work has led to establishing the main test types that are considered necessary. These types are:

- Oedometric tests without suction control. Permeability against brine or gas.
- Suction controlled oedometric tests for low suction ranges. Permeability against brine or gas.
- Suction controlled oedometric tests for high suction ranges.
- Tests to obtain the suction-water content relationship.

A compaction procedure to manufacture specimens of salt aggregates has been developed. The raw material used comes from the Suria Mine in the Barcelona province.

On the other hand, as was shown in the Third Half Annual Report (October, 1992) the oedometric cell to perform the experiments has been designed. Some units have been manufactured according to the requirements of the tests and the particular characteristics of the material to be tested.

4.4 Ongoing work (III/2. and III/3.)

Current work is concentrated in the following three topics:

- Improvement and checking of the mechanical constitutive model will be performed. New experimental data will be useful to provide adequate parameters to characterize stress-strain behaviour.
- Using the first version of the computer code, simulations on uncoupled problems are currently performed to check its performance. This work will continue towards the simulation of more complex problems closer to laboratory and field conditions.
- Current experimental work is devoted to perform oedometer tests at low stress levels using high porosity samples without suction control. This preliminary tests have also the objective of developing the testing methodology.

Title:	**ACTIVE HANDLING EXPERIMENT WITH NEUTRON SOURCES**
Contractors:	Deutsche Gesellschaft zum Bau und Betrieb von Endlagern für Abfallstoffe mbH (DBE) Agence Nationale pour la Gestion des Déchets Radioactifs (ANDRA) Kernforschungszentrum Karlsruhe GmbH (KFK)
Contract No:	FI2W - CT 90 - 0069
Duration of contract:	01.04.91 - 30.09.94
Period covered:	01.01.92 - 31.12.92
Project Coordinator:	K. D. Closs

A. OBJECTIVES AND SCOPE

The Active Handling Experiment with Neutron Sources (AHE) is a demonstration test which will be performed by DBE and ANDRA/CEA in the Asse mine with KfK acting as coordinator. Besides the CEC, the DBE contribution is supported by the Bundesminister für Forschung und Technologie (BMFT) under contract 02 E 8472 7.

The objective of the AHE experiment is to investigate radiological aspects of handling high level waste (either spent fuel or vitrified high level waste) in an underground repository. Neutron dose rates are measured resulting from direct radiation and from neutrons scattered by the surrounding host rock (rock salt). Computer codes and model calculations are to be verified by these experiments. Thus, an experimentally validated tool will be available for future detailed repository planning with emphasis on minimizing the radiation exposure of the operating personnel.

B. WORK PROGRAMME

According to the Technical Annex of the contract, the overall programme consists of the following formal items

Design planning	1991/1992
Implementation planning	1992
Construction and acquisition	1992/1993
Execution and disposal	1993/1994
Evaluation and description	1994.

From a more practical point of view, the programme can be broken down into the following activities:

1. Shielding and backscattering calculations for a POLLUX cask with spent fuel and a transfer cask with vitrified high level waste
2. Design and construction of shielding casks which simulate a POLLUX cask and a transfer cask
3. Planning of test programme with shielding casks
4. Planning and design of instrumentation for experiment
5. Execution of the measurements

5.1 Above-ground measurements

5.2 Underground measurements in the ASSE mine

6. Evaluation and documentation of the results.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Up to now, items (1) to (4) of the work programme were dealt with, the main emphasis lying on items (1) and (2).

Numerous calculations have been performed to investigate the influence of neutron backscattering on the radiation exposure of the operating personnel during underground handling of a POLLUX cask. At a distance of 1 to 3 m from a POLLUX cask, the total neutron dose rate is doubled due to neutron backscattering. At a longer distance from the cask, the contribution of the backscattered neutrons to the total neutron dose rate is even larger, but the absolute value of the dose rate decreases, of course. The effect of secondary gammas to the total dose rate is almost negligable. Calculations for a transfer cask with vitrified high level waste have been postponed in order not to delay the lay out of the shielding cask for the active experiment.

The lay out and design of the shielding cask with a Cf 252 line source has been finished, and the cask is under construction now. As far as neutron dose rates and neutron spectra are concerned, the shielding cask simulates the POLLUX cask quite well. The shielding cask weighs something like 7.5 t. It can be handled in the Asse mine with existing equipment. The shielding cask will be loaded with a Cf 252 neutron line source in Great Britain. After termination of the experiment, the source will be taken back by the supplier.

The above and underground measurement programme will be performed by Physikalisch Technische Bundesanstalt (PTB) under subcontract to DBE. A detailed description of the experimental programme is under way. First official discussions with the licensing authorities identified a way how to proceed with the license application.

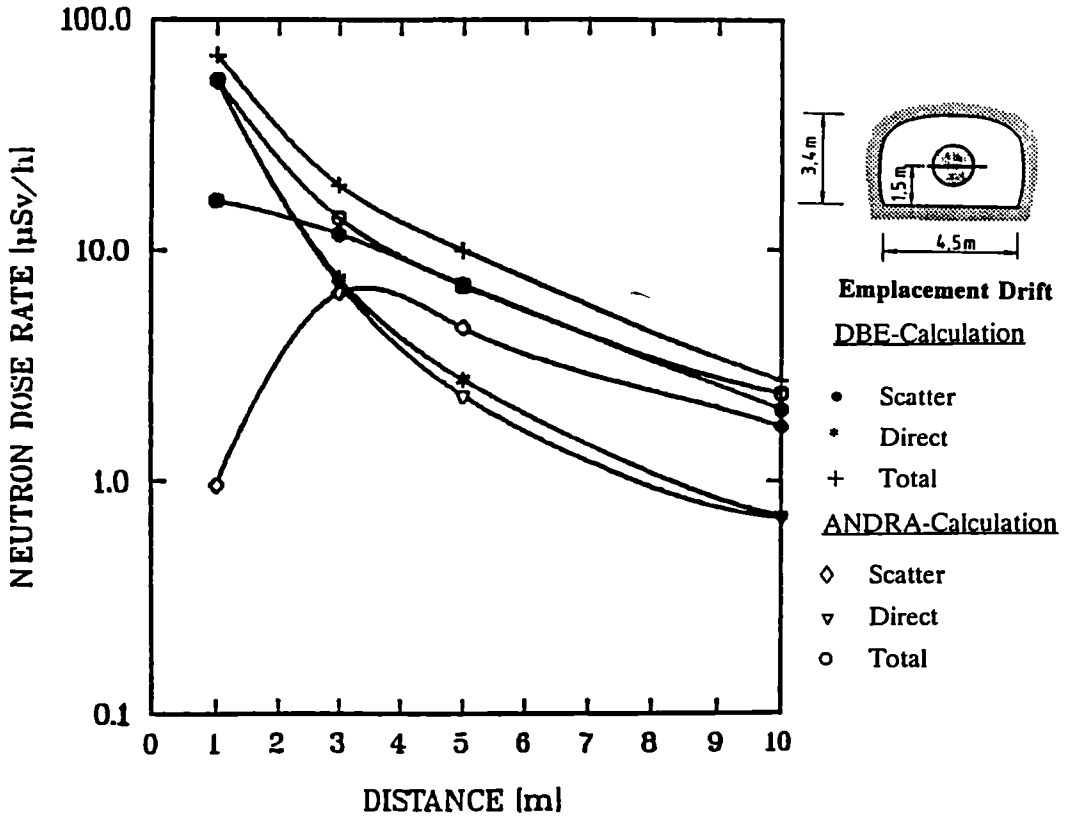
Progress and results

1. Neutron dose rates for the POLLUX cask in transport and emplacement drifts

The activities mainly concentrated around radiation aspects during underground handling of a POLLUX cask which was designed in the Federal Republic of Germany for direct disposal of spent fuel. Calculations for a transfer cask with vitrified high level waste have been postponed in order not to delay the lay out of the shielding cask for the active experiment. The final model of the POLLUX geometry was introduced in the last annual progress report. In the meantime, quite a number of neutron dose rate calculations have been performed by DBE and ANDRA/CEA for the POLLUX cask to investigate the effect of neutron backscattering in the narrow dimensions of the transport and disposal drifts. Calculations were performed for two drift geometries and two positions of the POLLUX cask within the drifts: The emplacement drift is 4.5 m wide and 3.7 m high, the transport drift 7.0 m wide and 4.3 m high. As far as the position of the POLLUX cask within the drift is concerned, the cask is either lying on the floor or it is in a 1.5 m lifted position.

As an example, the dose rates from direct and scattered neutrons as well as the total neutron dose rate at the bottom of the POLLUX cask situated at 1.5 m height in the emplacement drift is shown in Fig. 1. For

the DBE calculations the Monte-Carlo-programm MORSE/SGC-S was used, whereas the ANDRA/CEA calculations were performed with the TRIPOLI-2 code.



Distance [m] from top of the POLLUX cask

Fig. 1: Comparison of the neutron dose rates evaluated by the MORSE (DBE) and the TRIPOLI-2 (ANDRA/CEA) codes. POLLUX at 1.5 m height in the emplacement drift

The direct neutron dose rates calculated by the MORSE and the TRIPOLI-2 codes, resprectively, agree very well. Certain discrepancies exist in the neutron dose rates from scattered neutrons mainly near the surface of the POLLUX cask. But in this region the direct neutrons by far exceed the backscattered neutrons, thus, the total neutron dose rates even near the surface of the POLLUX cask are very similar in both calculations.

The discrepancy in the dose rates due to backscattered neutrons near the surface can be explained as follows: ANDRA/CEA calculates the backscattering contribution from the difference of total neutron dose rate with salt surrounding and neutron dose rate in vacuum. The difference is very small and the statistical error is large. On the other hand, DBE calculates the dose rate of the direct neutrons as well as the dose rate of the backscattered neutrons. Each value is known with a relatively small statistical error. It is therefore not necessary to take the difference of two values.

Another example for the neutron dose rates during underground handling of a POLLUX cask is given in Fig. 2. In this figure the neutron dose rates are given along the POLLUX jacket at a distance of 1 m from the surface when the POLLUX is lying on the floor of the emplacement drift. It is interesting to note that the dose rate originating from direct neutrons is almost 30% higher at the bottom than at the top of the POLLUX cask. This is due to the special POLLUX design, using more shielding material in the top than in the bottom of the cask. Taking also the scattered neutrons into account, this difference in dose rate between the bottom and the top reduces to merely 14%. Moreover, the axial distribution of the neutron backscattering: the ratio of the neutron dose rate in the middle and the top/bottom of the POLLUX is reduced from 4.7/3.7 for the direct neutrons to 2.6/2.3 for the direct plus scattered neutrons.

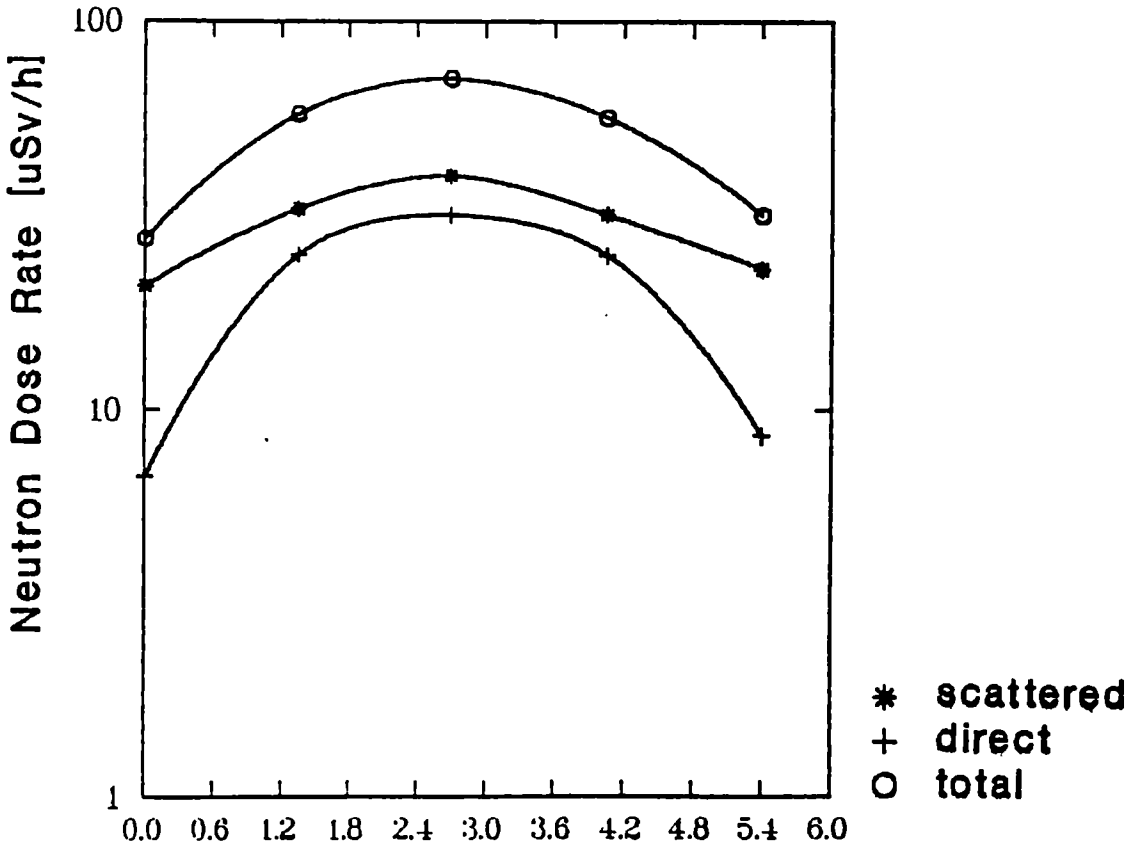


Fig. 2: Neutron dose rates along the POLLUX jacket at a distance of 1 m from the surface. POLLUX lying on the floor of the emplacement drift

Besides the neutron backscattering investigations in very long drifts, the neutron dose rate inside an emplacement drift was evaluated taking into account neutron backscattering phenomena at the dead end of the drift. The configuration studied is shown in Fig. 3. The calculated dose rates are listed in Tab. 1. As can be seen from the table, the presence of the end-wall of the drift modifies the neutron dose rates somewhat but does not change the order of magnitude.

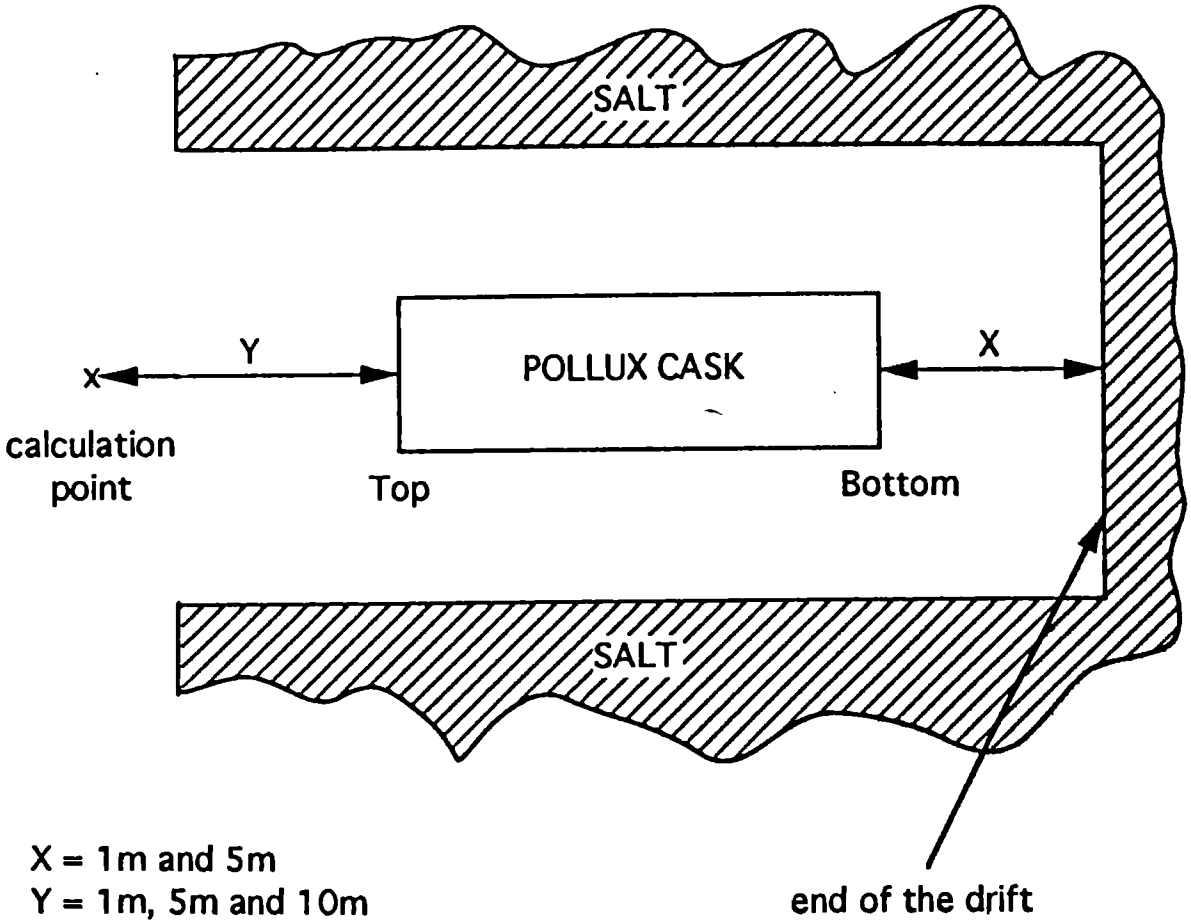


Fig. 3: Configuration of the POLLUX cask at the dead end of the emplacement drift

Distance from top	Neutron dose rate [µSv/h]					
	without dead end		dead end at 1 m		dead end at 5 m	
	D	%	D	%	D	%
1 m	34.95	12.1	42.23	17.1	29.80	22.1
5 m	6.369	12.6	8.529	12.5	4.851	15.3
10 m	1.367	12.7	2.493	13.0	1.668	16.2

Tab. 1: Influence of the dead end of the emplacement drift on the total neutron dose rates D at various distances from the POLLUX top. Term % means standard deviation.

As can be seen from the table, the presence of the end-wall of the drift modifies the neutron dose rates somewhat but does not change the order of magnitude.

From all the calculations performed up to now it can be concluded that the backscattered neutrons play an important role during underground handling of nuclear waste. At a distance of 1 to 3 m from a POLLUX or a transfer cask the dose rate of the scattered neutrons equals that of the direct neutrons. The longer the distance from the cask the higher is the contribution of the backscattered neutrons to the total neutron dose rate.

2. Effect of secondary gammas

So called secondary gammas will be produced by activation of the shielding material. The total neutron and secondary gamma dose rates (i.e. backscattering included) for the POLLUX-cask in the emplacement drift in 1.5 m height is given in Fig. 4. The secondary gamma dose rate is only 1 to 4% of the neutron dose rate, depending on the distance from the POLLUX cask. The standard deviation for the gamma calculation is about 20% compared to less than 10% for the neutron calculations. It can be concluded that the contribution of the secondary gammas to the total dose rates is almost negligible.

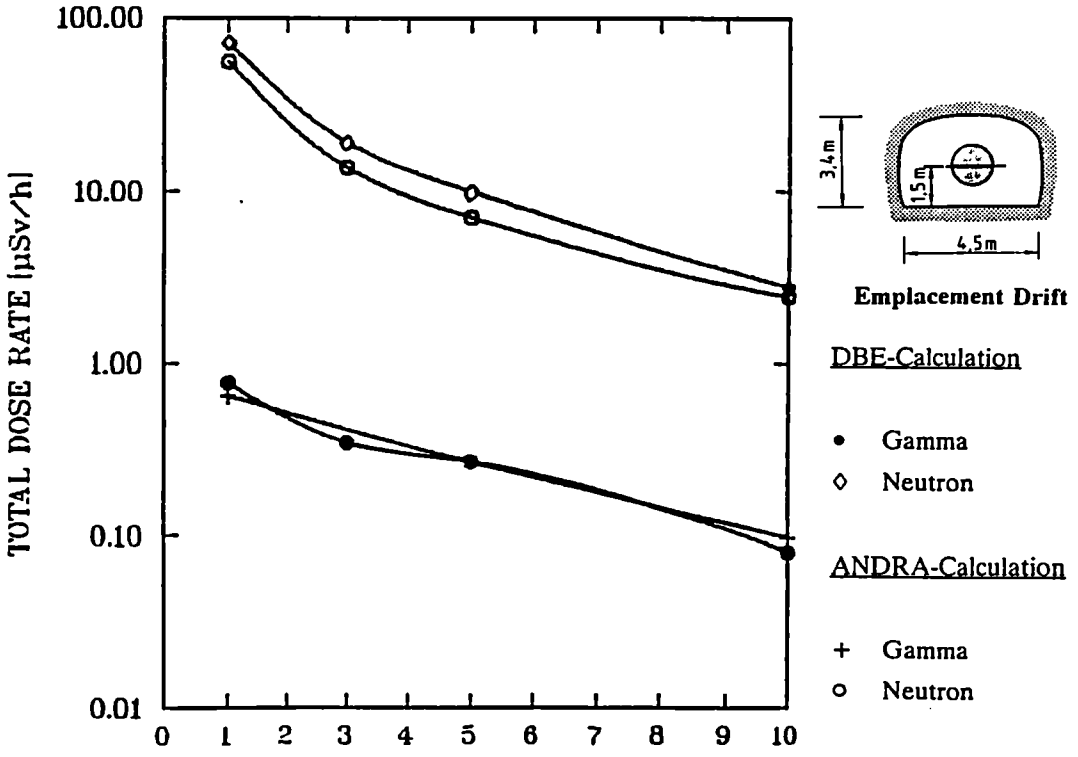
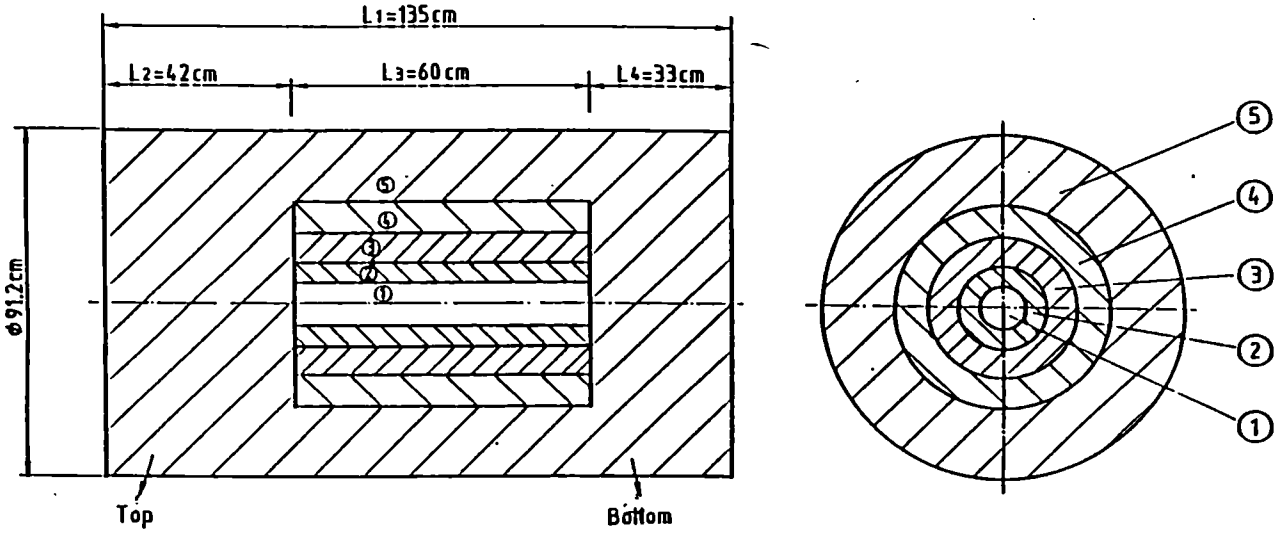


Fig. 4: Comparison of the total neutron and secondary gamma dose rates evaluated by the MORSE (DBE) and the TRIPOLI-2 (ANDRA/CEA) codes. POLLUX at 1.5 m height in the emplacement drift

3 Layout and design of the shielding cask

The POLLUX cask cannot be handled in the Asse mine due to his weight and dimensions. Therefore, a shielding cask with a Cf-252 neutron source has to be used for the experiment to study the influence of neutron backscattering in the narrow drift dimensions of a repository mine.

The geometry of the shielding cask is given in Fig. 5, and the various material zones are specified more precisely in Tab. 2. The data from this figure and table, respectively, are used for the calculations outlined in chapter 4.



	Material	φ(cm)
①	Fe (matrix)	0,8
②	GGG 40.3	1,6
③	Stainless steel	31,2
④	Polyethylene	51,2
⑤	GGG 40.3	91,2

Fig. 5: Geometry of the shielding cask

The design of the shielding cask is reproduced in Fig. 6. It is designed such that it can be used in a horizontal and vertical position, simulating a POLLUX cask or a transfer cask with spent fuel, respectively. The shielding cask weighs something like 7.5 t. It can be handled in the Asse mine with existing equipment. Some structural parts have to be manufactured to hold the cask in its position during the measurements. The shielding cask will be sent to Great Britain to be loaded there with a neutron line source which consists of 40 neutron capsules with 2 µg Cf-252 each. The shielding cask has a type A qualification. After termination of the experiment, the line source will be taken back by the supplier.

Zone 1: Source material

Nuclide	Particles/ccm	Weight%
Fe	8.41 E 22	100

Neutron spectrum of Cf-252 (source strenght: 1.8 E 8 n/s)

Zone 3: Stainless steel 15 Mn Ni 63

Nuclide	Particles/ccm	Weight %
C	7.0459 E 20	0.18
Si	5.8538 E 20	0.35
Mn	1.4108 E 21	1.65
Ni	6.8034 E 20	0.85
Fe	8.1565 E 22	96.97

Zone 4: Polyethylene

Nuclide	Particles/ccm	Weight %
H	7.7757 E 22	14.3
C	3.91374 E 22	85.7

Density 0.91 g/ccm

Zone 2+5: Nodular cast iron GGG 40.3

Nuclide	Particles/ccm	Weight %
C	1.3598 E 22	3.8
Si	3.65377 E 21	2.4
Mn	4.66970 E 20	0.6
Ni	9.47135 E 20	1.3
Fe	7.03630 E 22	91.9

Density 7.1 g/ccm

Tab. 2: Specification of the material zones

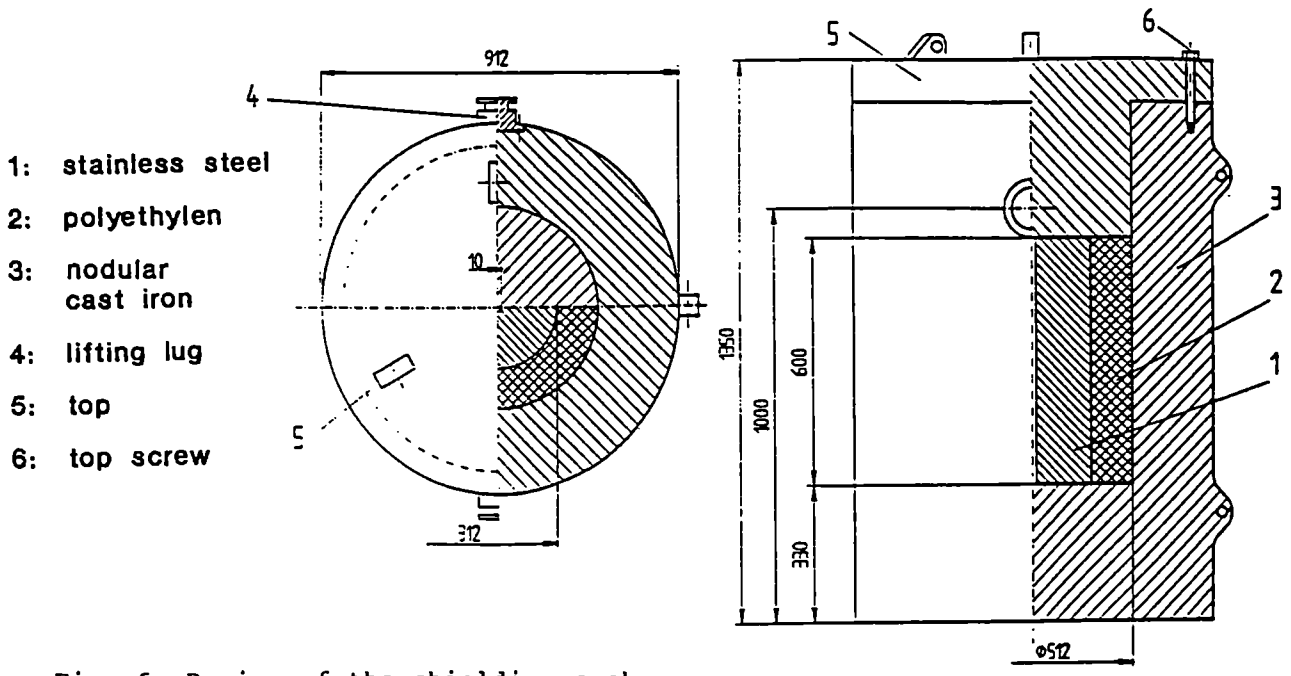


Fig. 6: Design of the shielding cask

4 Comparison of neutron dose rates and neutron spectra for the POLLUX and the shielding cask

The neutron dose rates for the POLLUX and the shielding cask in the transport drift (bottom side of casks, casks at 1.5 m height) are compared in Fig. 7. It can be stated that the dose rates of the POLLUX and the shielding cask agree very well for the direct neutrons and agree fairly well for the scattered neutrons. The small differences with respect to the scattered neutrons are due to the different geometries, mainly the difference in length between the POLLUX and the shielding cask. But in general, the shapes of the curves are comparable.

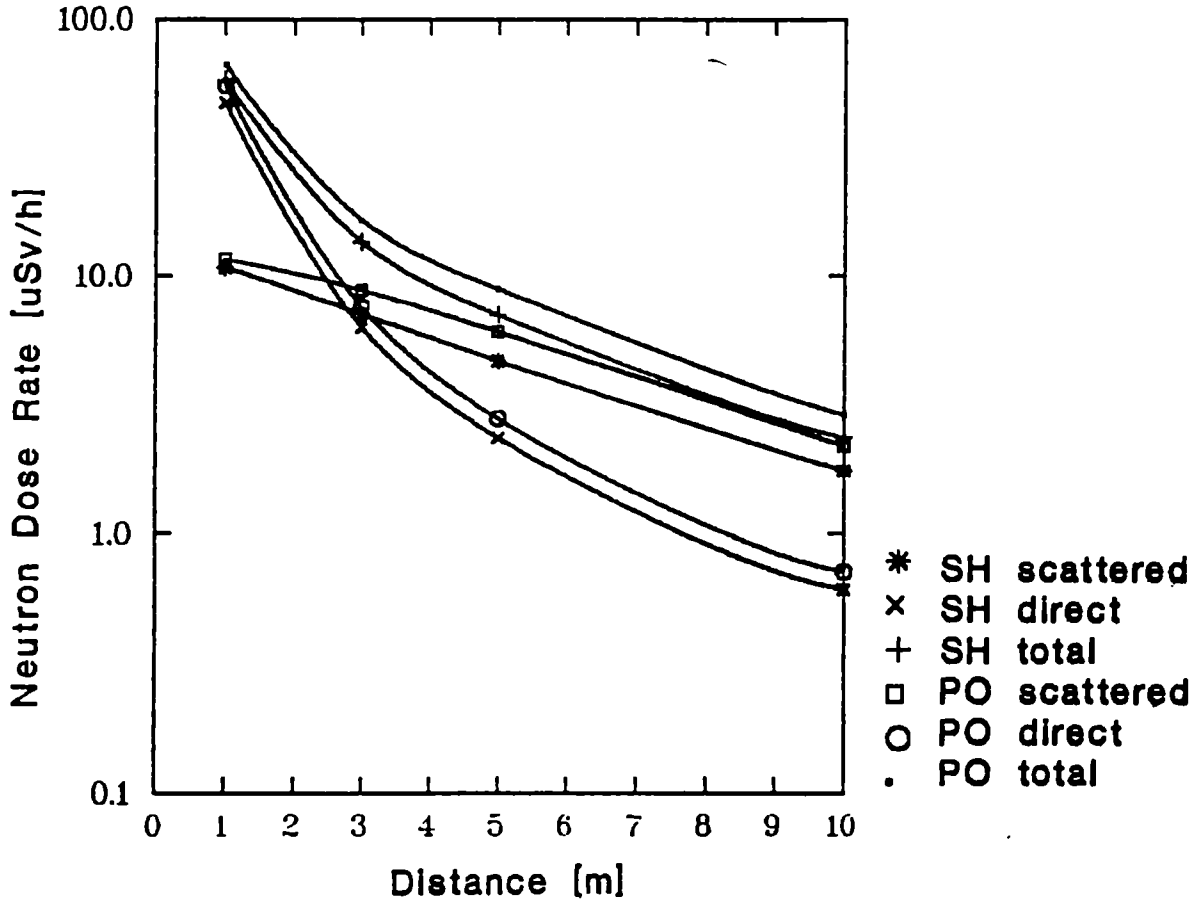


Fig. 7: POLLUX and Shielding Cask in the Transport Drift, at 1.5 m height (SH ● Shielding Cask; PO ● POLLUX)

The shapes of the neutron spectra are compared in Fig. 8 for the POLLUX and the shielding cask. As can be seen, the spectra are nearly identical.

It can be stated that the shielding cask simulates the POLLUX cask quite well.

List of publications

No publications in 1992.

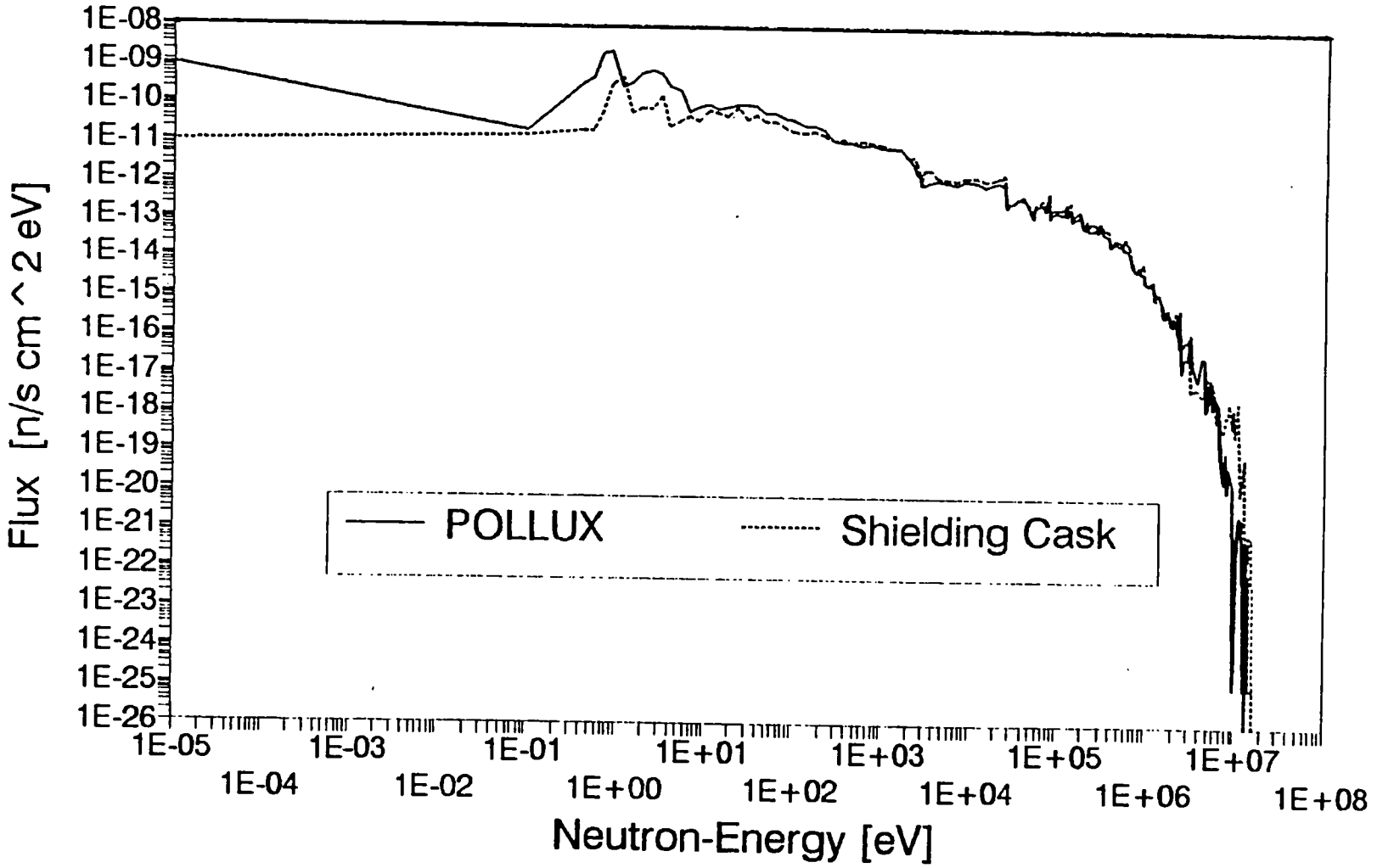


Fig. 8: Neutron spectra for the POLLUX and the shielding cask. Emplacement drift, casks lying on the floor, 1 m distance. (Values of the shielding cask are divided by 10)

THERMOMECHANICAL SIMULATION OF THE NEAR FIELD OF AN EMPLACEMENT BOREHOLE IN A SALT FORMATION (Amélie Mine France)

"CPPS TEST"

Contractors CEA/ANDRA - Fontenay-aux-Roses - France
G.3S (Groupement pour l'étude des structures souterraines de stockage) - Palaiseau - Fance

Contrat n° FI2W-C92-0120

Duration of contract from april 92 to march 95

Project leaders M. RAYNAL, JF. LAURENS

A/ OBJECTIVES AND SCOPE

The aim of "CPPS" test is to study the near field thermomecanical behaviour in deep layered salt around a borehole waste emplacement under thermal loading. This is of major importance for predicting the behaviour of radioactive waste storage particularly as regards to the temperature and the pressure that the canisters will have to withstand. The influence of marno anhydritic layers will be studied too.
The experiment is planed to include three tests in separate boreholes at Mine Amelie underground facilities, with identical heating probes but different types of thermal loadings and backfilling materials. The scientific interpretation of the results will be made by the G.3S (see figure 1).

B/ WORK PROGRAM

1. CPPS ONE : Emplacing of a prototype heater with an annulus between the heater and the borehole as small as possible (< 5mm) and heating after having observed the borehole convergency.

2. CPPS TWO : Emplacing of a heater with the annulus filled with crushed salt and immediate heating.

3. CPPS THREE : Emplacing of a heater with an empty annulus and heating after having observed the borehole convergency.

C/ PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

CPPS 1 probe was installed in December 1991. After a period of observation of the borehole creeping, the heater has been turned on in May 1992. The heating power was 2.4 KW. After two months the heating power has been raised up to 4 KW in order to speed up the borehole creeping.

The fact that no major power cut happened during this six months heating, will facilitate the scientific interpretation.

The CPPS 2 and 3 probes are under construction new developments aiming to improve their pressure sensors are on progress.

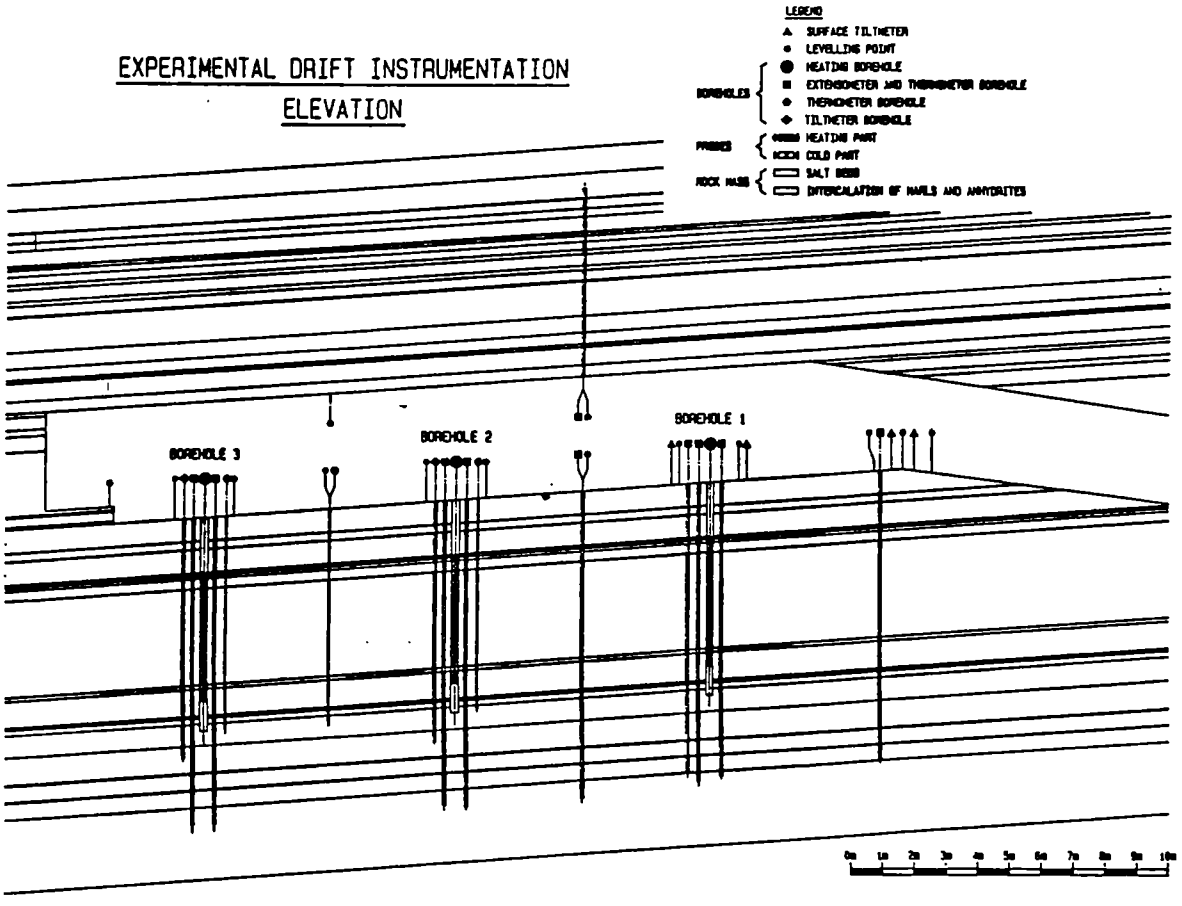


Figure 1

Progress and results

1) Results obtained before the heating period

The mechanical behaviour of the gallery in which the tests are conducted has been observed. The convergency measurements of the gallery are strongly dependent on the air temperature.
For example a five degrees increase of temperature multiplies by a factor 6 the convergency rate (see figure 2).

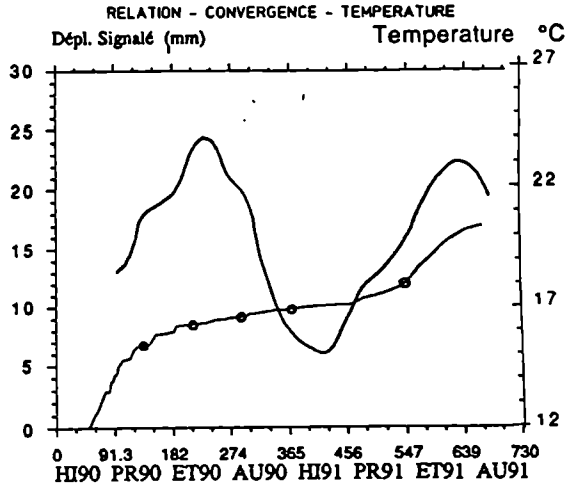


Figure 2

The horizontal and vertical displacements of the rocksalt surrounding the experimental gallery have been measured in several places (see figure 3). Their difference can probably be explained by the influence of the horizontal marno anhydritic layers.

BOREHOLE EXTENSOMETER MEASUREMENTS
RESULTS BEFORE HEATING

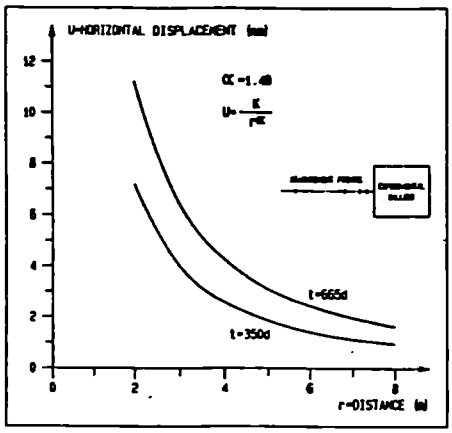


Figure 3

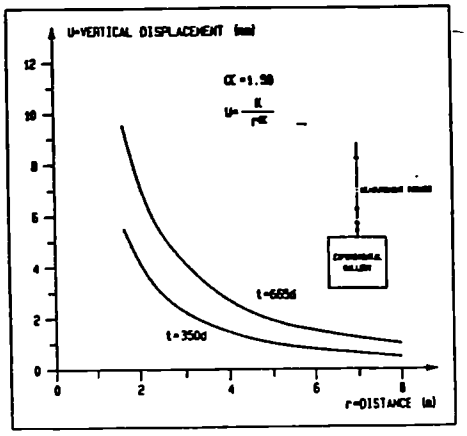


Figure 3 bis

2) Results obtained during the heating

Heating power (see figure 4)
After nearly two months at 2,4 KW the power has been raised up to 4 KW.

HEATING POWER

PROBE # 1

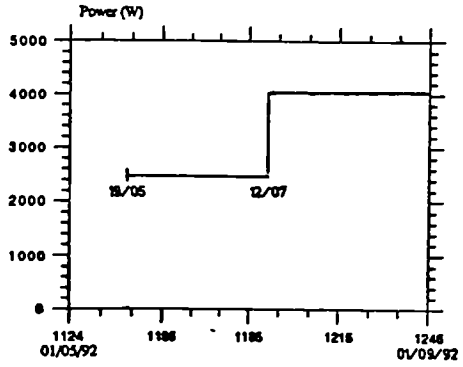


Figure 4

BOREHOLE # 1

CLOSURE

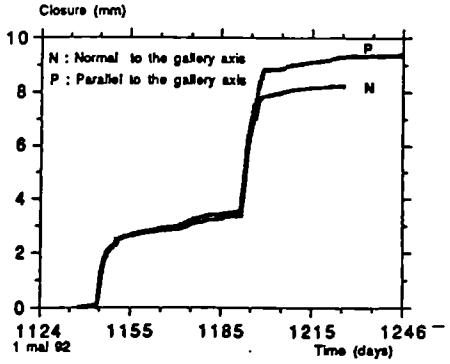


Figure 5

Borehole closure (see figure 5)
At the end of the first heating step the closure rate was very low.
Three days after the increase of power the borehole was in contact with the probe.

Temperature (see figure 6)
During the first step the maximum temperature was 120°C on the surface of the probe.
During the second step the temperature has reached 200°C at this place and it's nearly stabilised.
At a distance of 70cm from the axis of the probe the temperature reaches 70°C.

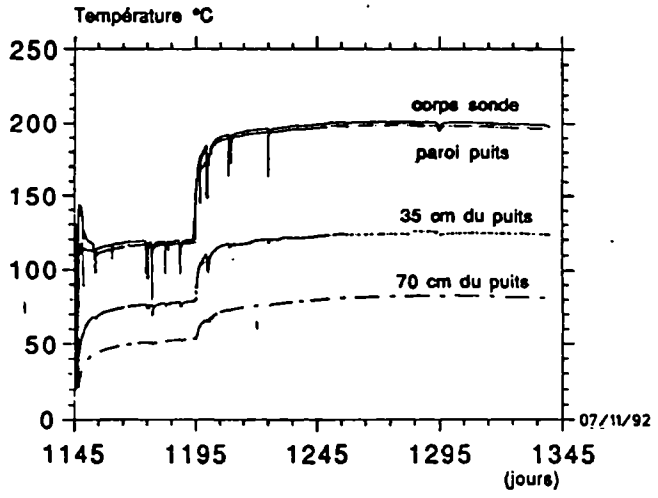


Figure 6

Displacements around the borehole (see figure 7)
The displacements of the rock salt reaches 8mm in surface whereas 4mm at a depth of 2.65 meters and nearly 0 at a depth of 4.65 meters.

DISPLACEMENTS

AROUND BOREHOLE # 1

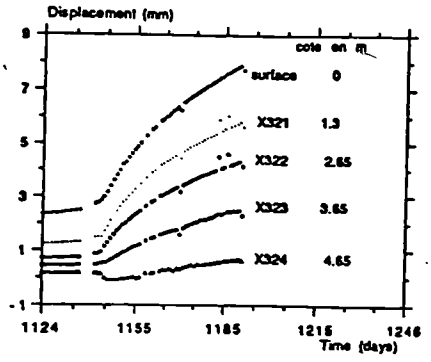


Figure 7

Dip angle of the floor around the borehole (see figure 8)
One can clearly see the two heating steps. The angle varies according to the directions. Due to the effect of the wall of the gallery the angle measured perpendicularly to the gallery axis is much greater than the one measured parallely.

DIP ANGLE AROUND

BOREHOLE # 1

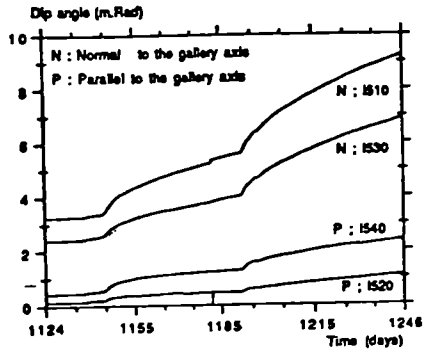


Figure 8

PRESSURE MEASURES

ON PROBE # 1

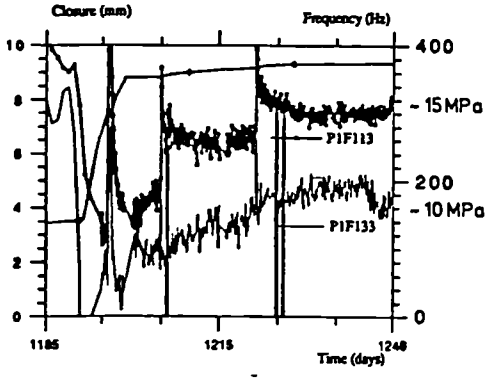


Figure 9

Pressure (see figure 9)
Though the measurements must be carefully interpreted, it seems that the pressure on the probe varies beetween 10 and 15 MPa.

Publication
KAZAN Y., BAZARGAN B., GHOREYCHI M.
Premiers résultats thermomécaniques de l'essai CPPS sur le puits P1.
Rapport interne ANDRA n° 624 RP G.3S 92-009

PRELIMINARY DEMONSTRATION TEST FOR DISPOSAL OF HIGH LEVEL RADIOACTIVE WASTE IN CLAY (PRACLAY / CERBERUS / Mine-by-Test)

I. PRACLAY

Contractor : ONDRAF/NIRAS, Brussels, Belgium

Contract N° : FI2W/0003

Duration of contract : 01-07-90 / 31-12-94

Period covered : 01-01-92 / 31-12-92

Project leader : J. VAN MIEGROET

A. OBJECTIVES AND SCOPE

PRACLAY aims at demonstrating the constructive and operational soundness of the Belgian Disposal Facility for High Activity Vitrified Waste in the Boom clay layer, 230 m under the surface in North-Belgium, with the following four steps :

a) excavate a mini-tunnel similar, except in length, to the contemplated disposal galleries, using the industrial techniques that would have to be dealt with for the full-size repository.
b) erect and support a large connecting chamber of the type needed at the intersection between main and disposal galleries.
c) install and operate a dummy gallery geometrically identical, except in length, to an actual disposal gallery.
d) monitor the thermal and mechanical behaviour of the clay layer, gallery concrete lining, filling material and metal shroud surrounding the dummy waste.

B. WORK PROGRAMME

- Carry the engineering work needed for detailed design of the experiment
- Review the multiple experience gathered in the Boom clay with the needed monitoring devices
- Erect a large connecting chamber
- Establish the detailed instrumentation program
- Excavate the mini-gallery and install the equipment (dummy waste, instrumentation, ...)
- Operate and monitor the experiment
- Proceed with interpretation of results

C. PROGRESS OF WORK AND OBTAINED RESULTS

- State of advancement
  During the period under review, the project has proceeded along two lines :
  1. further development of instrumentation programme
  2. investigation of the criteria and solutions for design and installation of the central tube

- Progress and results
  1. further development of instrumentation programme
  1.1. goals and priorities

The PRACLAY operational phase centers around an extensive monitoring of the thermal, hydraulic and mechanical behaviour of the clay layer, gallery concrete lining, filling material and metal shroud surrounding the dummy waste. Among these protective barriers, only the clay layer and the concrete lining behaviour needs an in-situ environment to be credibly demonstrated : the mechanical protection provided by the lining indeed relieves the filling material and the metal shroud of any significant interference from the geological surroudings ; these two barriers could thus be easily and validly investigated in a laboratory environment, if needed.

The clay layer - safety-wise the concrete lining is a barrier of lesser importance - will consequently be given top priority for the allocation of the available monitoring capability.

Even so, the limited space availability (for boreholes, a.o.) and construction - induced limitations have led to concentrate the available means on the most essential measurements : it was consequently decided not to develop any "chemical" monitoring (E_h, pH, water composition, ...) : one has indeed no reason to believe that a linkage of some significance - from a safety standpoint - exists between the mechanical and thermal perturbations that are central to Praclay, and the above-mentioned "chemical" parameters.
By the same token, no effort will be made to assess the degree of crack formation in the clay area surrounding the concrete lining nor its evolution during the heating and cool-down phases : in spite of their potential importance, those cracks are so tricky to quantify and the investigation methods so preliminary that it could easily develop into a programme within a programme, unduly complicating and jeopardizing the whole effort of PRACLAY.

1.2. nature of the measurements

1.2.1. measurements to be performed in the clay

The measurements in the clay are mainly aimed at validation of one or several (hydro-) thermomechanical models. Since the models are complex, it is important to keep the numerical simulation under control, and to select the simplest possible geometry. The measurements will therefore be concentrated in the 10 meter long central area where the geometry is two-dimensional - possibly one-dimensional if the clay is considered isotropic - and boundary conditions do not need to be taken into account, provided one does not move too far from the centerline.

The second goal of the measurements is to gain insight into the mechanical loading of the clay, primarily in the central 10 meter area and close to the PRACLAY centerline where the clay experiences the most severe loading.

Measurements will thus all be performed in the central "monitored region" at distances shorter than 4 meters from the centerline (see fig.).

Interpretation and prediction of the clay hydro-thermomechanical behaviour require a detailed knowledge of the total stresses, the pore pressure, the temperature and the permeability at various locations and also the deformations and/or displacements ; validation of the mathematical models describing the clay behaviour under various mechanical and thermal loads requires such information to be available prior, during and at the end of each perturbation of any significance generated within the system.

1.2.2. measurements to be performed in the near field

- on the shroud, to evaluate the swelling pressure and homogeneity of the backfill, by assessing the total radial stress distribution before, during and after heating
- water content and thermal conductivity of the backfill, before, during and after heating
- on the lining, monitor the total radial stress and pore pressure applied externally by the clay layer and internally by the backfill.

1.2.3. measurements to be performed in the lining near the connection chamber, to clarify the nature and amplitude of
- the stress anisotropy in the clay layer
- the interaction between the gallery and the connection chamber when heat - thus thermal expansion - is generated in the gallery.

1.3. continuation of the screening process set-up for selection of the sensors and installation procedures

Reception and calibrations procedures have been set for each of the sensors selected, on a preliminary basis, at the end of the previous phase :

- Sensors for total ground pressure
  Piezoresistive pressure transducers (KISTLER)
  Embedment vibrating wire stressmeter (GEOKON)
  Hydraulical flatjacks with pressure transducer (GEOKON, ROCTEST)

- Pore water pressure sensors
  Piezoresistive pressure transmitter (DRUCK)
  Vibrating wire pressure transducer (GEOKON)

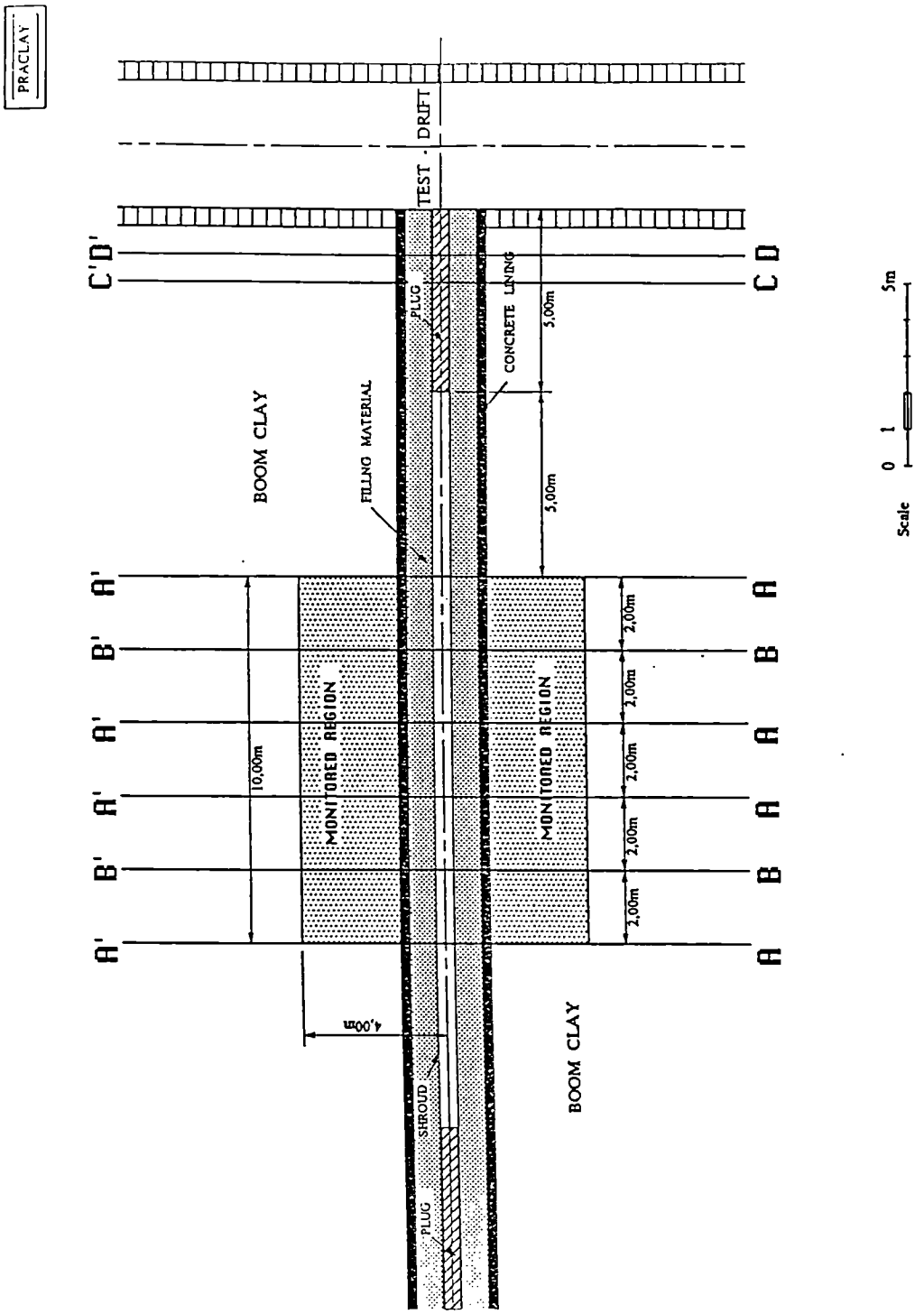
- Deformation sensors (strain gages)
  Vibrating wire strain gage (GEOKON, ROCTEST)
  Resistance strain gage (GEOKON)

- Displacement sensors
  Deflectometer (GEOKON)

2. investigation of the criteria and solutions for design and installation of the central tube

A major effort has been under way during the second half of the period to better identify and quantify the functional criteria of the central tube and to solve the feasibility problems associated with its installation :
step 1, having first assessed the tube thermo-mechanical loading, then derives its main dimensional requirements and suggests a number of standard piping materials that will satisfy them.
step 2 examines in details how the canister is going to reach its final position inside the tube and develops the functional criteria to be met.
step 3 analyses a variety of potentially feasible procedures to assemble the tube elements and screens them on basis of the functional criteria.

step 4 further elaborates on the selected method (welding) and derives a detailed recommendation on the procedure and equipment to be used.
step 5 discusses the assembly procedure (together with the associated problems of handling and transportation) for the tube elements and derives a number of practical recommendations for selection of the operational sequences and equipment technology.



THE CERBERUS TEST

Title :	The CERBERUS Test
Contractor :	ONDRAF/NIRAS, Brussels, Belgium
Contract n° :	FI2W/0003
Duration :	from 01-07-1990 to 31-12-1994
Period covered :	from 01-01-1992 to 31-12-1992
Project leader :	ONDRAF/NIRAS : J. Van Miegroet
	CEN/SCK : B. Neerdael, L. Noynaert

A. OBJECTIVES AND SCOPE

The CERBERUS Test aims at investigating the near-field effects produced by a HLW Cogema canister after 50 years cooling time by means of a combined heat and radiation source emplaced in the Boom clay.

B. WORK PROGRAMME

Measuring programme

1.- measurement of the radiation level with an ionisation chamber, LiF and $CaSO_4$:Dy dosimeters;
2.- measurement of temperature as a function of time, following a measuring frequency which allows the study of temperature variation;
3.- in-situ measurement of the permeability coefficient (once every 3 to 6 months);
4.- measurement of total stress and pore-water pressure as a function of time, following a measuring frequency which allows the study of pressure variation;
5.- measurement of the pH/Eh and detection of radiolysis effects in the near-field as well as the presence of radiolysis products (H_2, O_2 and H_2O_2).

Interpretation work

1.- validation of the existing computer model DOSEGEO by comparison of calculated values with radiation and dose-rate in situ data;
2.- validation of the existing heat transfer model MPGSTN on basis of the field temperature measurements and research regarding the heat transfer parameters before and after the heat and radiation treatment;
3.- study of the hydraulic field which must allow to point out in case of hydrological changes (fractures ...) the corresponding indicative values for the radiation intensity and temperature;
4.- mathematical interpretation of total and interstitial pressures by application of simple analytical methods as the TEMPPRES program in order to precise the relation between the induced effective stress and the temperature;
5.- analysis of the pH and Eh measurements, in order to detect, in case of drastic changes, corresponding values for temperature and dose rate and investigations on the qualitative relation between radiation and the amount of radiolysis products.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

The Cerberus Test is fully operational since the end of November 89. Periodic measurements are performed and a preliminary interpretation is available since 1991. The efforts were mainly devoted to the characterization of the hydraulic and chemical field.

Progress and results

Hydraulic field

A third campaign to determine from *in situ* measurements the permeability was performed. The results compared with the previous campaign (see Table 1), indicate an average decrease of the permeability of roughly 12 % (time interval = 12 months).

Table 1 : Observed and expected evolutions of the permeability coefficient (E-12 m/s) at various temperatures(°C)

	1st campaign		2nd campaign		3rd campaign				
sensor	T_0	k_0	T_{t1}	k_{t1}	k_{t1}/k_0 obs.	t_{t1}/k_0 cal.	T_{t2}	k_{t2}	decr. (%)
PSS2742	16.5	2.40	50	4.26	1.78	1.93	50	4.0	7.0
PSE2742	16.5	2.53	82	10.50	4.20	2.86	79	8.0	24.
PSE3262	16.5	(3.74)	80	8.07	(2.17)	2.80	77	7.5	7.4
PSW3002	16.5	2.25	92	11.20	5.06	3.15	88	10.2	9.0

A new campaign has to be launched to investigate if the decrease is due to long term effects or to consolidation effect as a consequence of the temperature variation during a power shutdown.

Using the programme SOURCE (2) and simulating the pressure drops registered in the near field of the screen PSS2742 during the permeability campaigns, a hydraulic diffusivity of 3.0-4.0 m^2/y can be assumed at 50 °C which corresponds to a value of 1.0-2.0 m^2/y at 16.5 °C.

Chemical field

After 30 months running, the pH has decreased from 8.5 to 6.9[1] while the redox potential still remains reducing i.e : -93 mV versus SHE. A similar value of the pH was already observed after 12 months. During the same campaign, the observed Eh value was -202 mV versus SHE.

The main inorganic constituents are the sodium (720 ± 20 mg/l) and the sulfate (240 ± 40 mg/l). The sulfate concentration decreases progressively from ~ 300 mg/l to ~ 200 mg/l as a function of time. The presence of large quantities of borate and silicate in solution is observed and could give some indications on the dissolution extent of the glass (measuring electrode) in direct contact with the clay water. This dissolution could be rather high if the clay water is not yet saturated with respect to these elements. The earth-alcaline elements seem also rather stable from one sample to the next one.

The first campaign to measure the hydrogen produced by radiolysis was performed. A volume of 287 ml of interstitial clay water was collected into a glass bottle with a needle to avoid evaporation. The mean water flow over

[1] value obtained after recalibration of the pH electrode

the whole period is 0.0143 ml/min. The analysis using the Macleod method resulted in the detection of 1.8 µl of hydrogen corresponding to a concentration of $5.2*10^{-7}$ g/kg H_2O.

List of publications

(1) BONNE A. et al.
The HADES demonstration and pilot project on radioactive waste disposal in a clay formation. CEN/SCK, Final Report, Contract FI1W/0004 B, EUR 13851, 1992

(2) NOYNAERT L. et al.
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MINE BY TEST

Title :	Mine by Test
Contractor :	ONDRAF/NIRAS, Brussels, Belgium
Contract N° :	FI2W/0003
Duration of contract :	01-07-90 / 31-12-94
Period covered :	01-01-92 / 31-12-92
Project leaders :	ONDRAF/NIRAS : J. Van Miegroet CEN/SCK : B. Neerdael, D. De Bruyn

A. OBJECTIVES AND SCOPE

The Mine-by-Test deals with the long-term behaviour of the so called *Test Drift* of the HADES Underground Research Facility. The measurements on the concrete lining and on the terminal shotcreted front are recorded and analysed to follow their stability. Monitoring of the surrounding clay mass gives reliable data for assessing its rheological behaviour.

B. WORK PROGRAMME

Acquisition of field data and interpretation exercises are the two main items of the programme.

Measurements in the clay mass around the Test Drift are gathered from :

- one settlingmeter and one inclinometer device installed above the Test Drift before the 1987 construction phase;
- six piezometer nests, one series of pore water pressure cells and one multiple-point extensometer installed from the Test Drift.

Monitoring of the concrete lining is ensured by :

- 34 load cells installed between the liners and 42 total pressure cells embedded in these liners;
- diametrical convergence measurements of seven instrumented sections.

Follow-up of the terminal shotcreted front occurs through :

- one multiple-point extensometer installed from the front up to 10 m depth in the clay mass;
- 15 reflectors installed on the surface of the shotcreted shell.

Interpretation of the collected data occurs with simple analytical elasto-plastic models or with finite-element analysis.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

The Mine by test is now in a phase of long term survey.

Progress and results

Measurements in and around the Test Drift do not show major differences with regard to the information described in the last annual report :

- the total pressure on the lining ranges from 1.7 to 2.4 MPa when calculated from load-cell measurements; pressure-cell measurements show some more scattering (from 0.4 to 3.1 MPa);
- the average convergence of the lining amounts 1.2 %, 1800 days after installation;
- all four sensors of the multiple-point extensometer installed from the front have reached their measuring limit;
- fracturing in the shotcreted shell increases significantly, restraining the entrance in this part of the underground facility.

Interpretation task deals this year with the following topics :

- comparison between pressure-cell measurements depending on the cell position in the section;
  Numerical simulations were launched, taking into account the Test Drift excavation method and the results were compared to the field measurements; the pressure acting on the lining is systematically lower at the bottom part (*bench*) and this conclusion is consistent with the excavation method.
- follow-up of the disturbance on the piezometer nests and on pore water pressure measurements due to a borehole drilling in their vicinity;
  The influence of this borehole, drilled in the framework of the MEGAS project (FI2W-0076), remains limited. The pressure dropped of a maximum of 10 % and returns in 3 months time to its original value.
- update of the comparison between pressure measurements and of the convergence-confinement curves for the different instrumented sections;
  The comments given in previous reports remain valid : the pressure-cell measurements are systematically lower than the load-cell measurements but the pressure build-up is similar; the concrete lining has still an average stiffness of 200 MPa.
- further analysis on the long-term convergence of the concrete lining.
  The four instrumented sections (rings 15 to 52) in the first part of the Test Drift behave differently from the three remaining sections (rings 71 to 105) : the convergences of these sections were higher immediately after installation but are now stabilizing. On the other hand, the convergences of sections 71 to 105 were limited in the beginning, but are still increasing.

CHARACTERIZATION OF CLAY UNDER THERMAL LOADING FOR UNDERGROUND STORAGE (MOL, BELGIUM)

"CACTUS" PROJECT

Contractors CEA/ANDRA - Fontenay-aux-Roses - France

Contrat n° FI2W-0001-F (CD)

Duration of contract from Septbember 1990 to march 1993

Project leaders M. RAYNAL, F. PLAS, B. VIGNAL

A/ OBJECTIVES AND SCOPE

The aim of CACTUS project is to study the near field thermo-hydro-mechanical couplings in deep clay around a waste emplacement borehole, under thermal loading. This is of major importance for predicting the behaviour of radioactive waste storage, particularly as regards to the irreversible phenomena due to the effect of heating on stresses and pore pressure. The experiment is planned to include a number of tests conducted in separate boreholes at Mol underground facilities, with identifical heating probes but different types of thermal loadings and backfilling materials (Figure 1).

B/ WORK PROGRAM

1. CACTUS ONE : Emplacing of a prototype heater with backfilling material and heating after hydro-mechanical equilibrium. It was planned as a preliminary test.

2. CACTUS TWO : Emplacing of a heater with backfilling material and earlier heating.

C/ PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

CACTUS 1 has been installed in May 1990 and power was switched on in September at a level of 1200 watts. This first heating cycle was interrupted in November after an electrical insulation fault has been detected.
Heating started again at the same power in March 1991 and stopped in January 1992. The cooling-down phase of this second cycle is still going on before a new heating scheduled next year at higher power.

CACTUS 2 was re-designed and thoroughly tested after probe 1 problems, leading to significant increases in costs and delivery time. Therefore the second probe was installed at Mol in December 1991. Heating started in February 1992 and lasted all the year without problem.

CACTUS 1 was initially intended as a prototype. Actually this probe was successfully employed for two complete thermal cycles, a third one being still possible. In that respect, it has been decided not to implement the last experiment, i.e. CACTUS 3 probe.

Progress and results

CACTUS 1

In 1990, the first cycle of CACTUS 1 has contributed to understand the irreversible phenomena caused by the heat loading. Three phases are identified :

1/ Before heating, the peripheral instrumentation has made it possible to accurately observe the behaviour of the clay under isothermal conditions. When drilling the borehole, a drop in the pore pressures and stresses was particulary observed. i.e. hydro-mechanical expansion of the clay. After emplacement of the probe, the pore pressures and stresses re-established a new state of equilibrium as the clay closed around the probe and the backfilling.

2/ When heating started, the pore pressures immediately increased. These however began to dissipate while the temperatures continued to rise, tending towards a state of initial equilibrium. This is because the Boom clay, of which permeability is very low, first reacts under undrained conditions (Figure 2). The total stresses (radial and orthoradial) increased in correlation.

   Measures of water contents and dry specific densities indicate an initial phase in which the clay expands followed by progressive collapse which appears to correspond to the dissipation of the pore pressures. This behaviour may denote temperature consolidation, well-known in clay media.

3/ When heating stopped, it was found that the clay did not return to its initial state but remained slightly denser in the vicinity of the probe. The heating would thus have caused irreversible deformations of the clay (Figure 3).

During Cycle 2, mechanical and hydraulical behaviour are identical as during cycle 1. This is not the case of density and water content : cycle 1 evidenced irreversible effects (thermal consolidation) whereas cycle 2 deformations were reversible. These observations are consistent with the concept of thermal hardening.

CACTUS 2

At this time only one cycle has been initiated. Compared to probe 1, the only difference is that the heating has begun after a shorter waiting time after emplacement. The first results indicate that the behaviour is similar to that of CACTUS 1, i.e. irreversible deformations.

Publication

PICARD JM., BAZARGAN B., ROUSSET G. and VIGNAL B.
"Behaviour of Boom clay under thermal loading : first results from CACTUS 1 in situ test" Braunschweig workshop on pilot tests on Radioactive Waste Disposal in Underground facilities - June 19-21 1991

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PICARD JM. : Essai thermo-hydro-mécanique dans une argile profonde (essai CACTUS) - Rapport d'avancement n° 1 - Commission of the European Communities - Mars 1991

PLAS F. : Essai thermo-hydro-mécanique dans une argile profonde (essai CACTUS) - Rapport d'avancement n° 2 - Commission of the European Communities - October 1991

PICARD JM. : Rapport d'avancement n° 3 - Commission of the European Communities - Mars 1992

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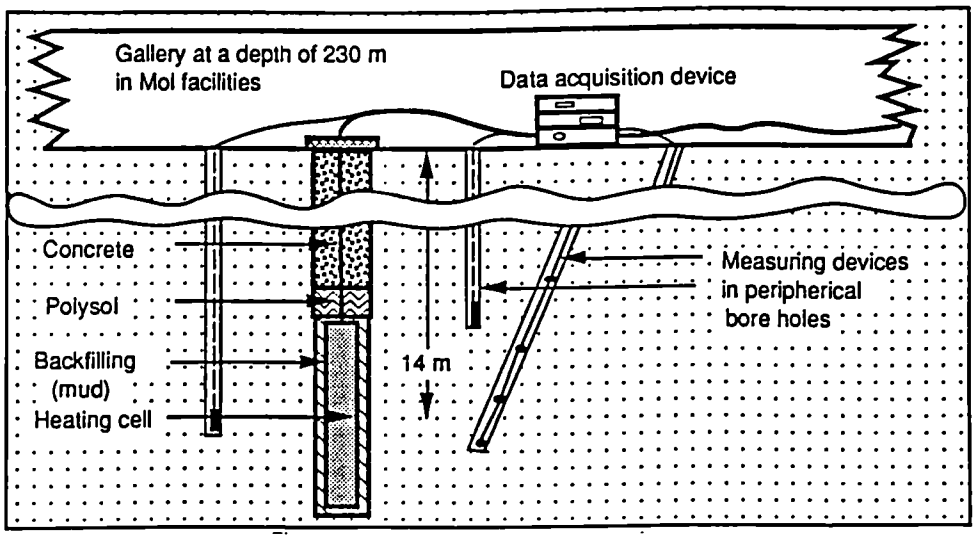

Figure 1 : Sketch map of CACTUS in situ test

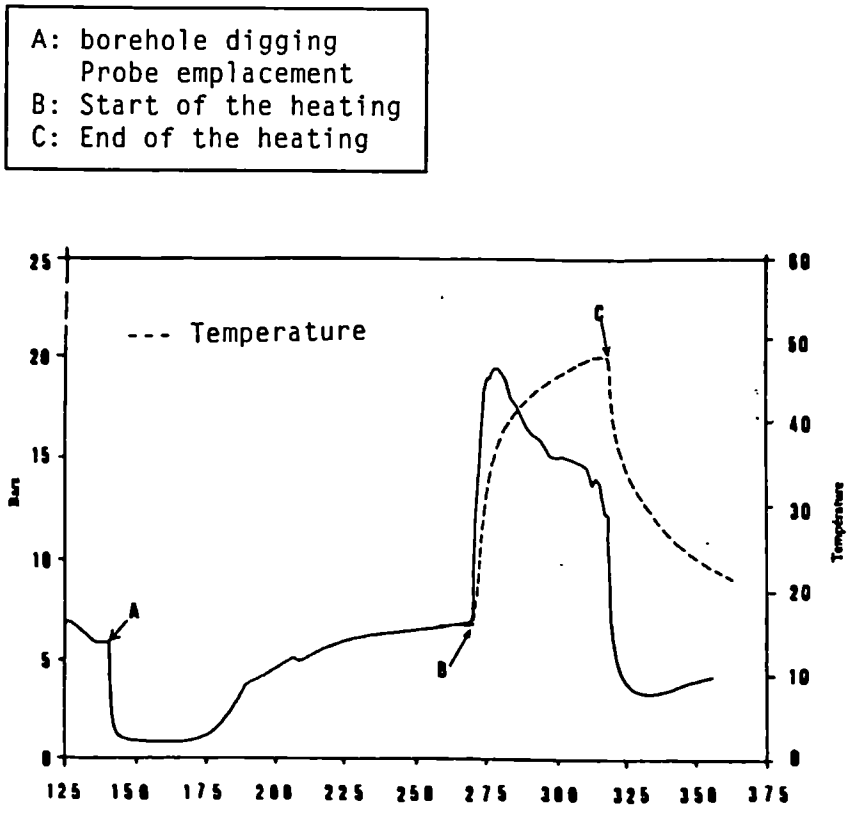

Figure 2 : CACTUS 1- Pore pressure evolution
(H = 1.6 meter and R = 0.6 meter)

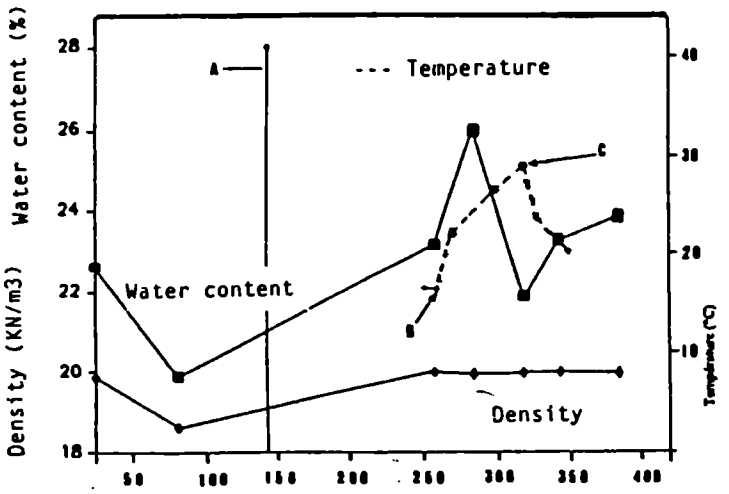

Figure 3 : CACTUS 1 - Water content and density evolution
(H = 15 meters and R = 0.9 meter)

DEMONSTRATION OF THE IN SITU APPLICATION OF AN INDUSTRIAL CLAY-BASED BACKFILL MATERIAL (BACCHUS 2)

Title :	Demonstration of the in situ application of an industrial clay-based backfill material (BACCHUS 2)
Contractors :	SCK/CEN, ANDRA, ENRESA
Contract N° :	FI2W-CT91-0098
Duration of contract :	from 01-10-1991 to 30-04-1995
Period covered :	from 01-10-1991 to 31-12-1992
Project leaders :	G. Volckaert (coordinator), C. Mayor, B. Vignal

A. OBJECTIVES AND SCOPE

The BACCHUS 2 experiment aims at the optimization and the demonstration of an installation procedure for a clay based backfill material. The installation procedure, materials and techniques have to be as close as possible to realistic industrial processes and capabilities.
The backfill material will consist of a mixture of high density pellets and powder. The experiment is developed in cooperation with ENRESA and ANDRA/CEA.

The instrumentation of the experiment will be optimized in such a way that it can be used as a validation experiment for the hydro-mechanical model developed under CEC contract FI2W-CT90-0033.

The BACCHUS 2 project also includes the characterisation of the granular backfill and the retrieval and the expertise of the BACCHUS 1 test mock up.

B. WORK PROGRAMME

1. Study and optimization of the backfill material

The sealing material will consist in a mixture of clay pellets and clay powder. The ratio powder/pellets and the density, size and water content of the pellets will be used as parameters in the optimization process.

Fundamental properties of this mixture such as the hydraulic conductivity and the swelling pressure will be measured.

2. Recuperation of the BACCHUS 1 experiment

The BACCHUS 1 mock-up installed in '88 will be retrieved by overcoring. The aspects and hydro-mechanical properties of the retrieved Boom clay seal and the FoCa-bentonite buffer will be studied.

3. In-situ demonstration of the application of the backfill material

The demonstration will consist in the sealing of the large borehole (50 cm diameter) left after the retrieval of the BACCHUS 1 mock-up. The backfill material developed under 1 will be installed around a central filter tube which will also be used as support and access tube for the instrumentation.

Probes for water content measurement, based on the experience gained by CEA in the BACCHUS 1 project, will be embedded in the backfill material. Also the instrumentation installed previously in the host clay around the BACCHUS 1 mock-up, can be further used for monitoring the host clay behaviour.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

A method for the production of high density clay pellets has been worked out and was tested using an industrial pilot facility. The method was applied to three different reference clays. Several techniques for the further densification of a mixture of clay pellets and clay powder have been tested.

The characterisation of the granular backfill has well advanced. The bulk density of the mixture was determined as function of the ratio pellets/powder.' The hydraulic conductivity and swelling pressure have been measured as function of the density. X-ray tomography has been applied successfully to measure the density distribution and the progress of a wetting front.

In cooperation with a drilling firm, a reliable technique for the retrieval of the BACCHUS 1 mock-up has been worked out in detail. The design and the technical plans for the BACCHUS 2 mock-up have been finalised. After discussion with all partners and with the modellers of contract n° FI2W-CT90-0033, the instrumentation scheme has been optimized.

Progress and results

Development of an industrial technique for the production of the granular backfill material

The technique for the production of the granular backfill material consists mainly in the following four steps :

- drying of the excavated clay;
- grinding of the dried clay;
- compaction of the clay powder to high density pellets;
- mixing of the high density pellets with clay powder and/or other additives.

Drying and grinding of the clay are very important preparation steps as the water content and the grain size distribution largely determine the dry density to which the powder can be compacted.

Industrial techniques for drying, grinding and mixing are well known and are daily applied on clays in the ceramics industry.

An essential step, whose feasibility still needed to be demonstrated on an industrial scale, is the production of high density (> 2.0 g/cm^3) clay pellets. Therefore contact was taken with the firm SAHUT-CONREUR which is specialized in the production of industrial equipment for the agglomeration, compaction and granulation of materials and which has more than 100 years of experience in this field. At their workshops in Raimes (North France) they have a pilot factory especially equipped for feasibility studies. The core of this facility is the compactor/granulator. Its principle, shown in Fig. 1, is the following :

The powder falls from the feeder in a conical screw of Archimedes which precompacts the powder and presses it between two moulding cylinders which turn in opposite directions. One of these cylinders has a fixed position while the other can be horizontally pressed towards the fixed cylinder with a maximal force of about 20 t per centimeter of width of the moulding cylinders. As these cylinders turn, the precompacted powder is dragged between the cylinders and is pressed in the savings of the moulding cylinders with a high force. This compactor type is

available in capacities from 100 kg/h to 50 t/h.

With this equipment, pellets of the Boom clay and the French FoCa and Spanish S2 bentonite have been produced and a density of about 2.1 g/cm^3 could be easily obtained.

For the further densification of a mixture of pellets and powder as well compaction as vibration techniques have been tested. In this way it was possible to reach a density of about 1.7 g/cm^3 for the mixture of pellets and powder.

Characterisation of the granular backfill

X-ray transparent oedometers have been constructed and X-ray tomography has been applied to measure the density distribution in a Boom clay and a S2 bentonite backfill sample. It was found that although the density distribution within a cross-section is wide, the mean density does not vary much from one cross-section to another one.

X-ray tomography has also been applied to follow the hydration of a Boom clay backfill sample. This test showed an initially fast water uptake and a fast reduction in the width of the density distribution in a cross-section. Swelling pressure measurements were also performed on S2 bentonite and Boom clay samples and values of respectively 0.6 to 2 MPa and 0.2 to 0.6 MPa were obtained. For Boom clay again an initial fast water uptake and fast raise in swelling pressure was found.

For Boom clay backfill samples with a dry density ranging from 1.55 to 1.7 g/cm^3 hydraulic conductivity values between 4.10^{-10} and 9.10^{-12} m/s were measured.

Retrieval of the BACCHUS 1 mock-up

The retrieval method agreed upon, consists in the following three steps :

1° 12 "small" diameter (100 mm) boreholes are drilled at the external diameter of the casing of the BACCHUS 1 mock-up;

2° a large annular drilling (ext. diameter 520 mm, int. diameter 480 mm) is performed over the lining of the BACCHUS 1 mock-up. A special drilling head and special large diameter drilling rods will be used;

3° the concrete plug is retrieved in steps of 1 m and the experimental part of the mock-up (Boom clay seal and FoCa clay buffer) is retrieved in one or two steps.

After the retrieval of the BACCHUS 1 mock-up, the remaining borehole will be cleaned and its bottom flattened in preparation of the installation of the BACCHUS 2 mock-up.

Design and instrumentation of the BACCHUS 2 experiment

The experiment consists essentially of a central filter surrounded by the clay pellets-powder mixture on a thickness of about 23 cm. At the bottom of the central filter a flange with hydrostatic and total pressure sensors will be installed. The experiment will be installed between a depth of 11 and 14 m below the gallery floor. The design is shown in Fig. 2.

The central filter allows the air to escape during the hydration of the backfill and to measure the pressure at this boundary. At the end of the test it will also allow to measure the hydraulic conductivity by water injection. The filter consists of four sections to check the homogeneity of the hydraulic conductivity. Between the sections, total pressure

transducers will be installed. The central filter will also be used as a guiding tube for a neutron/gamma source and of a heat pulse generator. Both will be used to follow the hydration of the backfill.

On the request of the modellers hydrostatic pressure sensors and total pressure sensors will be embedded in the backfill. Also at the interface with the borehole wall such sensors will be placed. In this way the evolution of the pressure field in the backfill can be measured.

Three "spider webs" with thermocouples will be installed in the backfill material. In combination with the above mentioned heat pulse generator, the radial hydration can be followed by measuring the radial changes in thermal conductivity.

For the measurement of the pressure and temperature fields in the host rock, the instrumentation installed for the BACCHUS 1 experiment will be re-used. Tests have shown that 2 piezonests, 2 tubes with Pt100's, 1 Glötzl stress monitoring station and the access tube for the neutron/gamma source are still operational.

Conclusion

A method for the production of a clay backfill composed of high density clay pellets and powder has been developed and optimized. It has been demonstrated that the method can be applied on an industrial scale using commercially available equipment.

With such a backfill material a dry density of about 1.7 g/cm^3, a swelling pressure of about 0.6 MPa and a hydraulic conductivity as low as 1.10^{-11} m/s can be obtained (Boom clay). By X-ray tomography it has been shown that the material becomes homogeneous during hydration.

A method for the retrieval of the BACCHUS 1 mock-up has been designed in detail.

In cooperation with the modellers, the design of the BACCHUS2 experiment and its instrumentation scheme has been finalized. The technical plans have been finished and are now ready for execution.

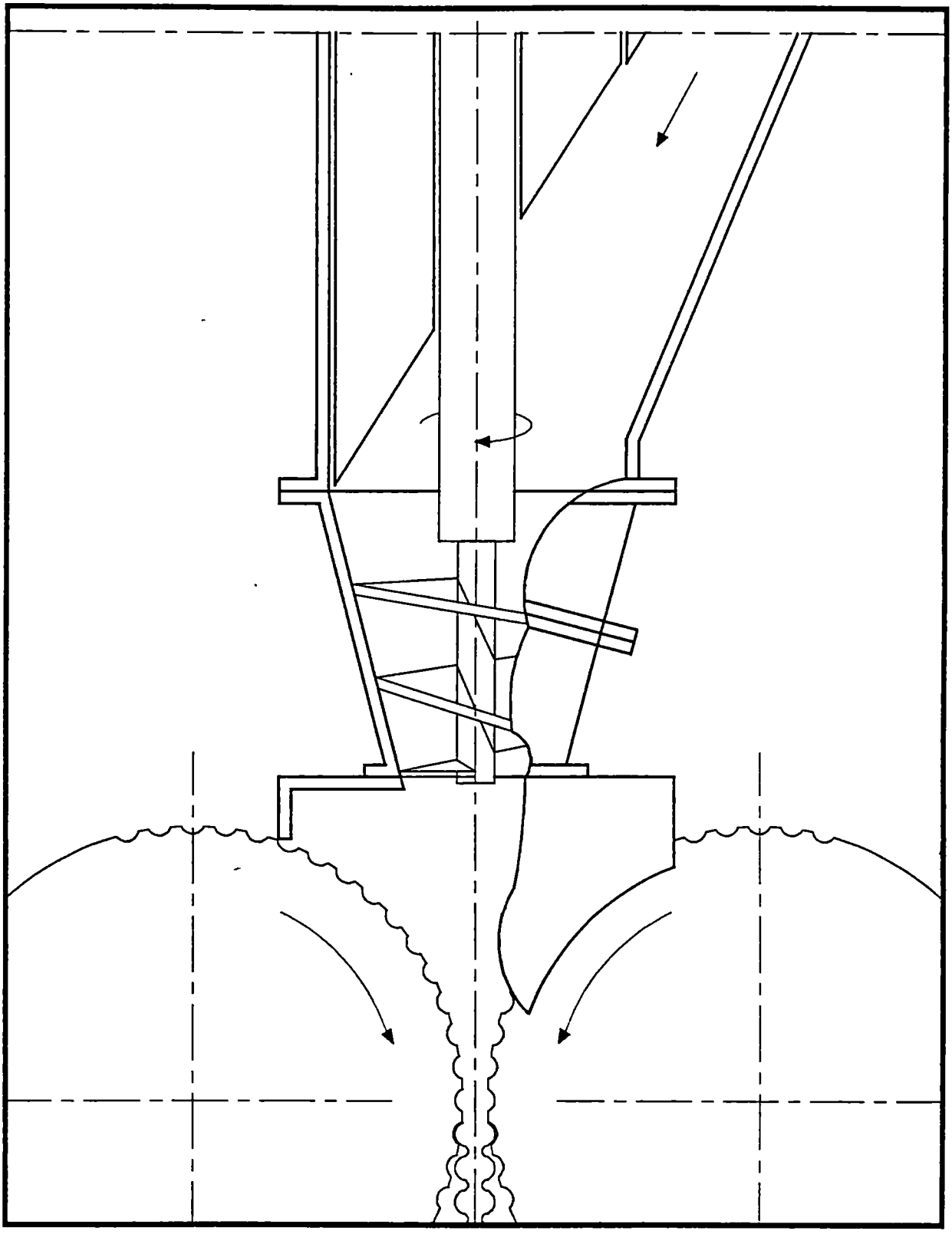

Figure 1 : Principle of the compacter/granulator

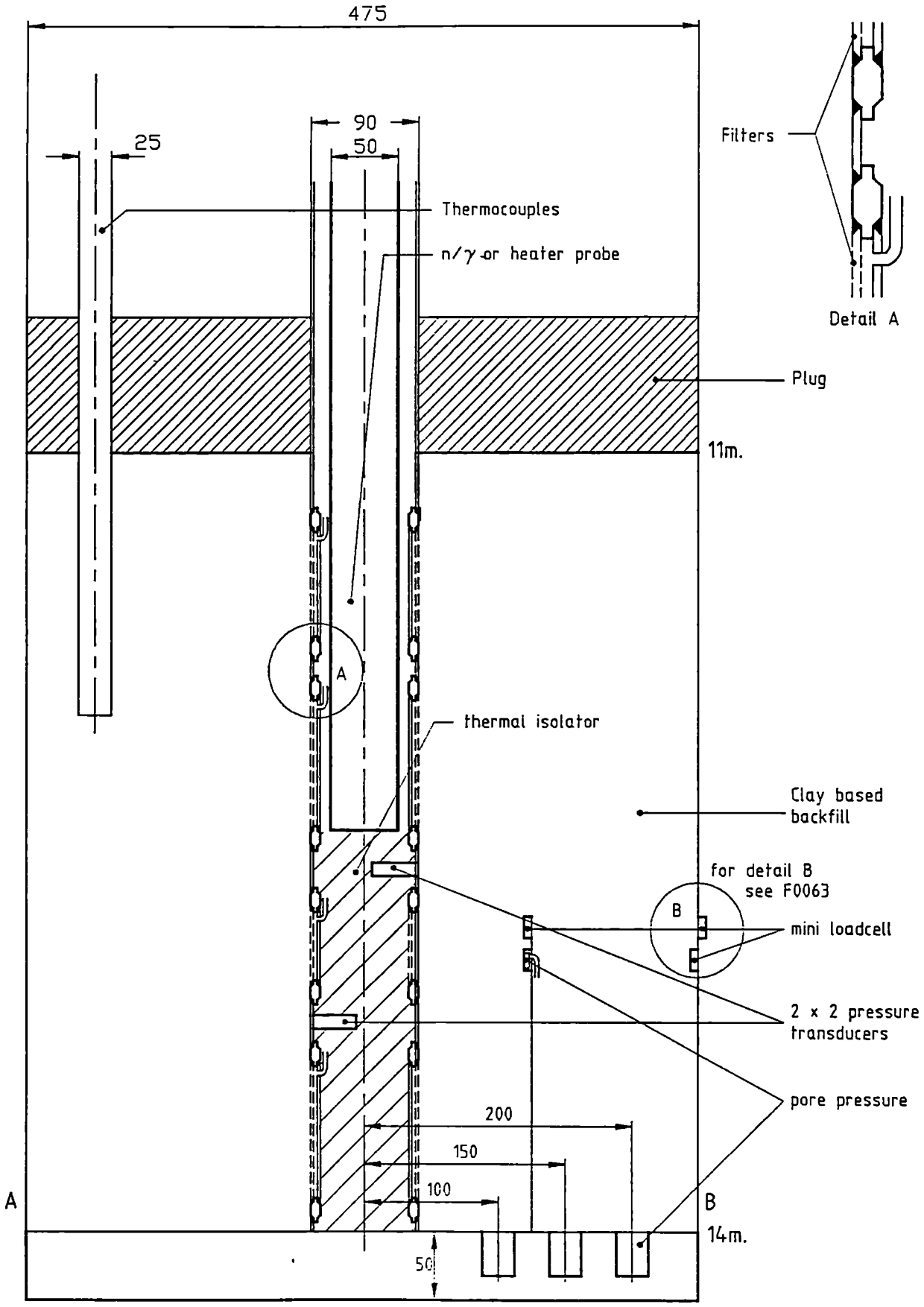

Figure 2a : BACCHUS 2 - design

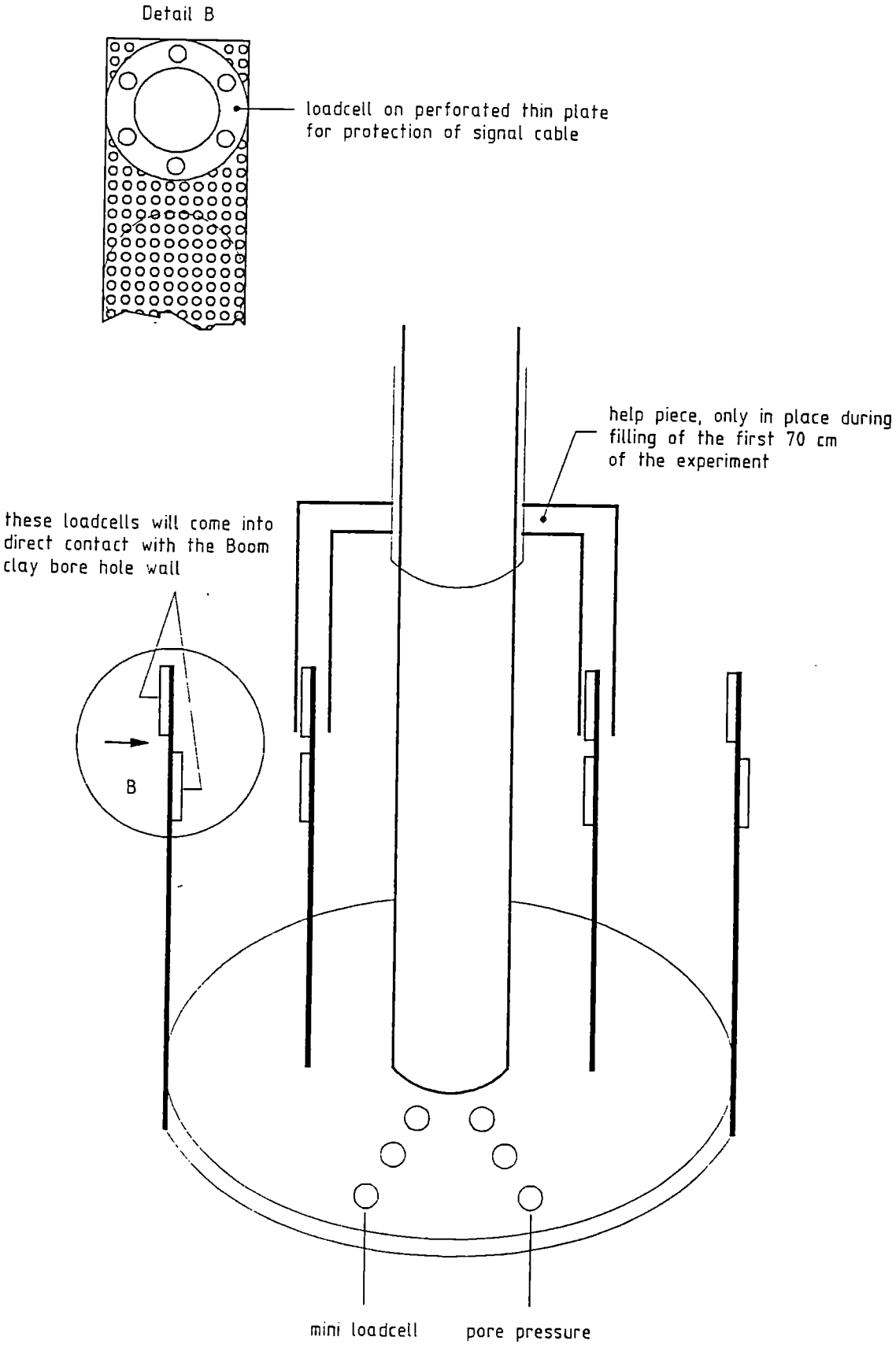

Figure 2b : BACCHUS 2 - design (detail B)

MODELLING AND TESTING OF THE HYDRATION OF BACKFILL AND SEALING MATERIALS

Title :	Modelling and Testing of the Hydration of Backfill and Sealing Materials
Contractors :	SCK/CEN, CEA, UWCC, UPC
Contract N° :	FI2W-CT91-0033
Duration of contract :	from 01-07-91 to 30-06-94
Period covered :	from 01-01-92 to 31-12-92
Project leaders :	G. Volckaert (coordinator), C. Imbert, H. Thomas, E. Alonso

A. OBJECTIVES AND SCOPE

If compacted clay-based materials will be used for the backfill and sealing of radioactive waste repositories the hydro-mechanical behaviour of unsaturated materials have to be understood. When these materials are used as a backfilling around HLW packages their behaviour during saturation is further complicated by the thermal transient due to the heat emission of the waste.

Elasto-plastic models of the Cam-Clay type are not able to describe the irreversible volumetric strain (swelling or collapse) or the evolution of the mechanical property limits due to changes in the water content. In the case of partly saturated clay materials the suction phenomena, which have a strong influence on the hydraulic, mechanical and thermal properties of the material, are to be considered.

The goal of the study is to analyze and model the behaviour of a clay based engineered barrier during its hydration phase under real repository conditions. The hydro-mechanical and thermo-hydraulical models will be coupled to describe stress/strain behaviour, moisture migration and heat transfer.

In this project the CEA and SCK/CEN are responsible for the main experimental work and the research groups at the universities of Cardiff and Catalunya are performing the modelling work.

B. WORK PROGRAMME

1. Hydration experiments

Uniaxial experiments determining the influence of the suction potential on the hydration rate, swelling or swelling pressure, will be performed. The progression of the hydration front will be followed by x-ray tomography.

2. Hydro-mechanical experiments

These experiments will determine the mechanical characteristics as a function of the water content and the suction potential of swelling clay at room temperature. Tests with imposed suction potential will be performed.

3. Modelling

The first step will be the adaptation of the existing models to dense, swelling clays. In the heat and moisture transfer model, strain and deformation effects will be included as independent variables, while in the moisture migration and stress/strain behaviour model, expansive soil effects will be included.

In the second step a coupling of the models will be done by automatic data transfer from one model to the other.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

SCK/CEN

The swelling pressure of Boom clay has been measured as a function of the initial dry density and the initial saturation.

The medical X-ray tomograph at the University of Ghent has been calibrated for variations in volumetric water content of Boom clay at a dry density of 1.7 g/cm^3. A hydration experiment in which the wetting front was followed by X-ray tomography was performed. A suction controlled oedometer has been designed and constructed. Validation test are in progress.

CEA

The CEA has performed oedometer experiments on the French reference clay FoCa-7. First experiments were performed to measure the collapse upon loading at constant water content. Then experiments were performed to determine the behaviour during mechanical loading and hydration. The experimental results have been compared qualitatively with the predictions of the model of Alonso and Gens.

UPC

The hydro-mechanical code NOSAT has been improved with regard to the representation of the boundary conditions and the solver formulation. The code has also been linked with a powerful graphical post-processor DRACVIU. With this code a preliminary analysis of the BACCHUS 2 experiment has been performed.

The new constitutive model for partially saturated soils has been implemented in a finite element code which was checked for some simple test cases.

The basic elasto-plastic model has been extended to account for phenomena such as the existence of a maximum of collapse upon wetting at a critical stress and the relevant features of truly expansive soil behaviour (active clays). The predictions of these new models have been compared to the results of relative extensive experimental programs published in literature.

Scoping tests have been performed on mixtures of Madrid clay and bentonite and on Boom clay.

UWCC

The software necessary to solve the theoretical formulation on the one hand for temperature, capillary potential and air pressure and on the other hand for soil suction, air pressure and deformation has been written and debugged. Independently from UPC, an isothermal coupled air pressure, soil suction and deformation code incorporating Alonso's et al. (1990)[1] elasto-plastic model has been written and debugged. This will allow cross verification. A first version of a coupled non-isothermal code with a linear elastic state surface approach has been developed and tested. A second version incorporating an elasto-visco-plastic constitutive relationship has been completed.

Progress and results

SCK/CEN

For the calibration of medical X-ray tomograph of the State University of Ghent six clay plugs with a dry density of 1.7 g/cm^3 and with a volumetric water content in the range from 1 to 32.4 were used. These clay plugs were made by uniaxial compaction of clay powder with a well controlled water content. Of each plug several cross-sections were scanned by the tomograph, which showed that the plugs have a homogenous density and water content. The results allow to measure a change in water content of 1 volume%.

The progress of the wetting front in a 2 cm long clay plug was followed by X-ray tomography. Dry clay powder was compacted directly in the permeater to a dry density of 1.7 g/cm^3 and was hydrated by applying a hydrostatic pressure of 1 m water column at the bottom of the plug. The evolution of the water content as function of height is given in Figure 1. Initially the clay plug takes up water very fast but once it is about 50 % saturated the process becomes very slow.

To determine the relation initial water content - dry density - swelling pressure, 31 swelling pressure measurements were performed on clay plugs with a dry density between 1.62 g/cm^3 and 2.27 g/cm^3 and an initial degree of saturation between 2 % and 80 %.

The results show that at high density; even at high initial saturation degree the small fraction of smectite in the Boom clay can still generate an important swelling pressure. This is in agreement with the model of Alonso and Gens that predicts that the swelling pressure will increase with increasing initial suction, which increases with increasing dry density and decreasing saturation.

CEA

Oedometer tests were performed on FoCa clay with a constant water content of 10 weight%. In these tests the powder was first compacted to a maximum stress of 35 Mpa. Two loading-unloading cycli were performed. The overconsolidated, unsaturated clay showed an elastic, non-linear behaviour. The width of the elastic zone depends on the maximum preconsolidation stress.

Hydro-mechanical experiments were performed in which three different paths in the stress-suction space were applied :

- hydration at low stress (0.1 Mpa) followed by a loading-unloading cycle;
- loading to maximum stress, then unloading followed by hydration and a second loading-unloading cycle;
- loading to maximum stress followed by hydration at maximum stress followed by unloading.

The results of the latter two stress-suction paths are given in Figure 2 and 3. The collapse or swelling observed during the hydration can be well explained by the model of Alonso and Gens which states that in the elastic zone the result of hydration is swelling while outside this zone it is collapse.

The next step in the experimental development will concern the direct control of the suction, in order to study the behaviour under wetting-drying cycles.

UPC

Code development

Improvements have been implemented in the NOSAT code regarding the following aspects :

- modification of the representation of boundary conditions in order to simulate correctly drains or seepage faces;
- new solver formulation to ensure convergence in long-term analysis;
- coupling of the NOSAT code with the graphical postprocessor DRACVIU to allow the representation of stresses, displacements, air and water pressures, saturation and relative permeabilities.

With the NOSAT code a 2-D model of the BACCHUS 2 experiment has been developed. The model reproduces a horizontal section, at mid level, of the backfill core of Boom clay. The model includes the representation, by means of state surfaces, of the relation between void ratio, degree of saturation, mean stress and suction. These state surfaces are mainly based on the existing experimental information. A first calculation of the progressive wetting of the backfill and it's influence on the Boom clay has been performed. Figure 4 shows the variation of the suction, at a point 5 cm away from the natural Boom clay - backfill interface, in the backfill and in the natural Boom clay.

The constitutive model for partially saturated soils defined in Alonso et al. (1990)[1] has been implemented into a finite element subroutine. The following developments were required :

- formulation of the model in a way suitable for finite element applications;
- generalisation of the model to three-dimensions;
- computation of the derivates of the yield surface with respect to the stresses and the suction;
- checking of the subroutine using "SM2D", a soil testing program for two dimensions.

This subroutine will be included in the general finite element computer program under development (see contract n° FI2W-CT91-0102).

Model development

The basic elasto-plastic model has been extended to account for phenomena such as a the existence of maximum of collapse upon wetting at some critical stress and the relevant features of truly expansive soil behaviour (active clays). The three models thus defined (Model 1 : Original elasto-plastic; Model 2 : Maximum collapse; Model 3 : Expansive) have been applied to the modelling of compacted soil behaviour. Three relatively extensive experimental programs on different types of compacted soils subjected to loading and wetting stress paths have provided a good basis to check the predictions of the models. The research carried out has shown the generally good predictions achieved with the models. In addition, conceptual explanations for observed experimental features have been provided. These include the differences between double oedometer techniques and wetting-under-load procedures, especially relevant in the swelling range of the volumetric behaviour. It has also been shown with regard to stress ratio effects on collapse that stress ratio has a very limited influence on volumetric strain.

The comparison between experimental results and model predictions has increased the insight into compacted soil behaviour and modelling capabilities. The results obtained indicate that for some types of soils a simplified framework to interpret compaction may be proposed. In this

framework the model parameters reflect changes in soil type and compaction method whereas the specific dry density and compaction water content are taken into account by means of two stress variables : the pre-consolidation total stress and the water suction. Both describe the initial state of the soil. This is equivalent to saying that microstructural differences, not accounted for by changes in void ratio, are relatively unimportant. If this is the case the models presented offer a relatively simple and powerful tool to reproduce compacted soil behaviour for a significant range of initial water content and density.

It is recognized that for some soils this simplified framework is probably insufficient and a dependence between model parameters and compaction conditions must be specified. This type of behaviour has also been explored.

Experiments

Oedometer tests of mixtures of Madrid clay and bentonite have been performed in order to improve the knowledge of expansive materials. The tests involved an initial loading step followed by wetting. The following parameters have been investigated : soil composition, initial dry density, vertical load and specimen thickness. Tests have also been performed under suction control and in a special designed oedometer cell to measure horizontal stresses.

A number of basic tests have been performed on Boom clay. Compaction characteristics and the water retention curve of the compacted material at several dry densities have been determined. The latter data are already been used in the above mentioned simulation of the BACCHUS 2 test.

UWCC

Hydro-thermal model

A new theoretical formulation describing coupled heat, moisture and air transfer in unsaturated soil was developed. Previous work based on a capillary potential/temperature formulation has been extended to include air pressure as an additional variable. The numerical solution of the formulation was developed using the finite element method to describe the spatial variations of the governing differential equations and a finite difference algorithm to describe transient behaviour. To illustrate the capabilities of the formulation the method was applied to a one-dimensional test problem. The results give a qualitatively correct representation of the physical behaviour of the test problem.

The research is now being extended to examine the interface between unsaturated and saturated behaviour. In particular the phenomenon of the dissolution of air in the pore water as the soil becomes saturated is being investigated.

Hydro-mechanical model

Software has been written and debugged to analyze this problem and a small one-dimensional test problem has been solved.

Attention has been focused on the solution of two test problems specified by UPC, so that code validation by comparison with UPC's approach could be achieved. This task has been completed and the calculation results are sent to UPC for comparison.

The next step is the application of the model for the simulation of a full scale field problem.

Development of a software framework for a coupled thermo-hydro-mechanical model

A first version of the code has been completed. The salient features of this approach are :

- the stress/strain behaviour of the soil is accommodated via a linear elastic state surface approach;
- both vapour and liquid flow are included;
- heat transfer by conduction, latent heat effect and convection are accommodated in the energy balance.

A numerical solution of the governing differential equations was achieved via the use of the finite element method as a spatial discretisation technique coupled with a finite difference recurrence relationship for the description of the transient behaviour. As an example of the application of the work, an analysis of the behaviour of a typical section of a possible underground repository was performed. The results indicated strong interactions between temperature, pore water content, suction and deformation of the soil.

A second version of the model has also been completed. The salient features of this approach are :

- an extension of the previous work to an elasto-visco-plasticity constitutive relationship;
- the numerical solution of the problem using an elasto-visco-plastic algorithm;
- the use of a Von-Mises yield surface as the representation of the soil's plastic behaviour.

Verification of this version is in progress.

References

1 Alonso E., Gens A. and Josa A., A constitutive model for partially saturated soils. Geotechnique, 40, 3, 405-430, 1990.

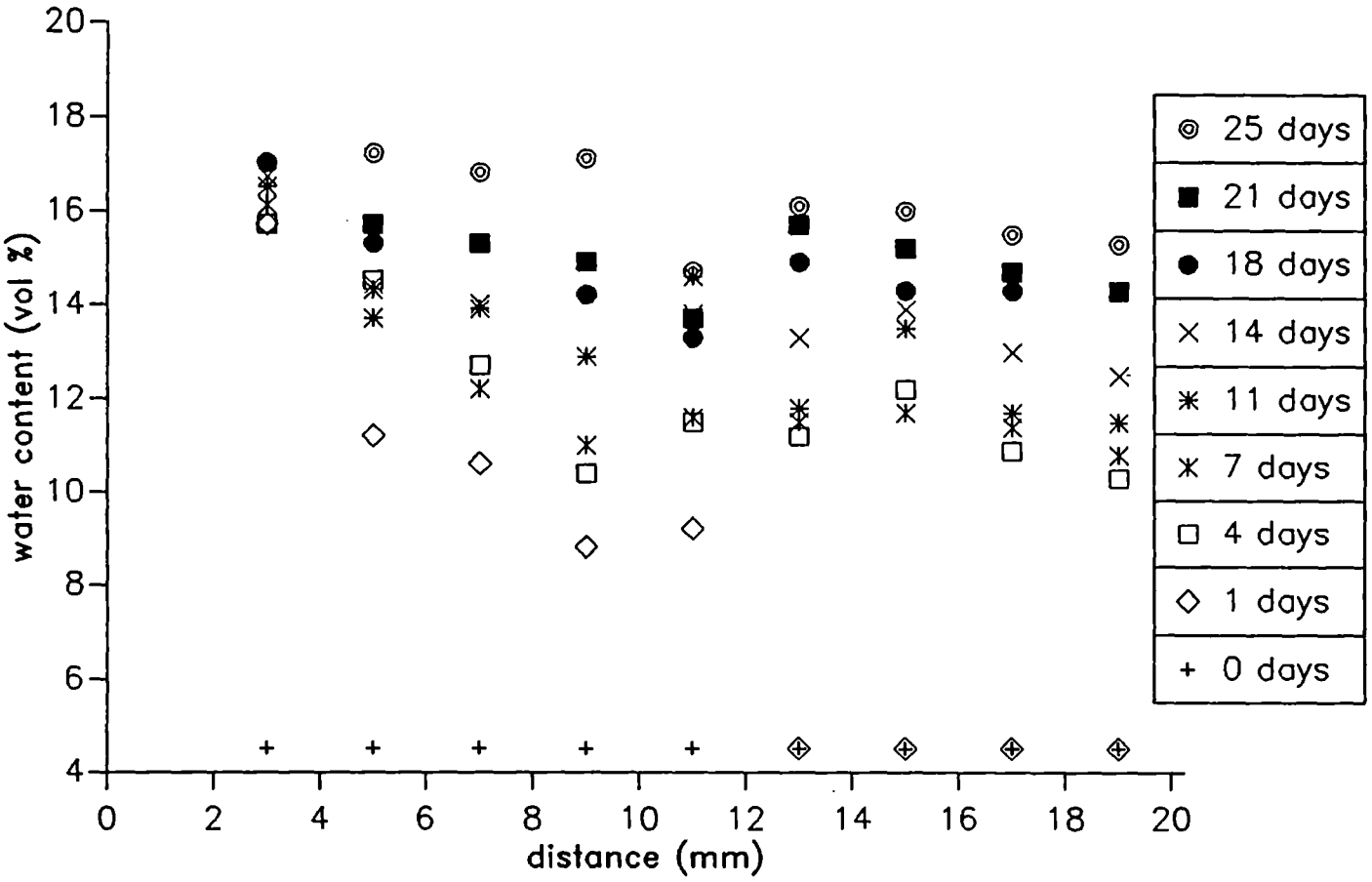

Figure 1 : Evolution of the wetting profile in a Boom clay plug with a dry density of 1.7 g/cm^3

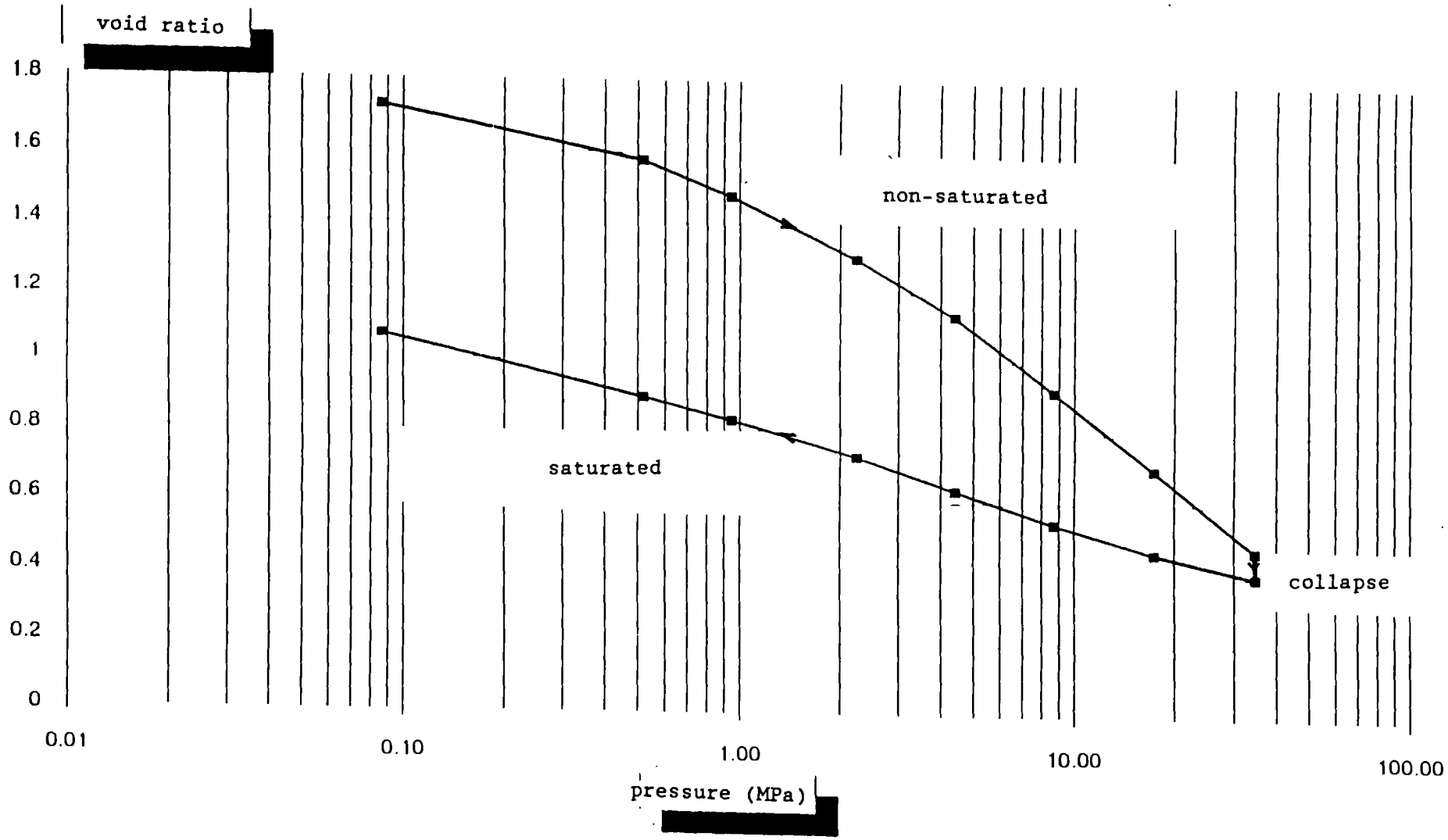

Figure 2 : Oedometer test with hydration at maximum stress

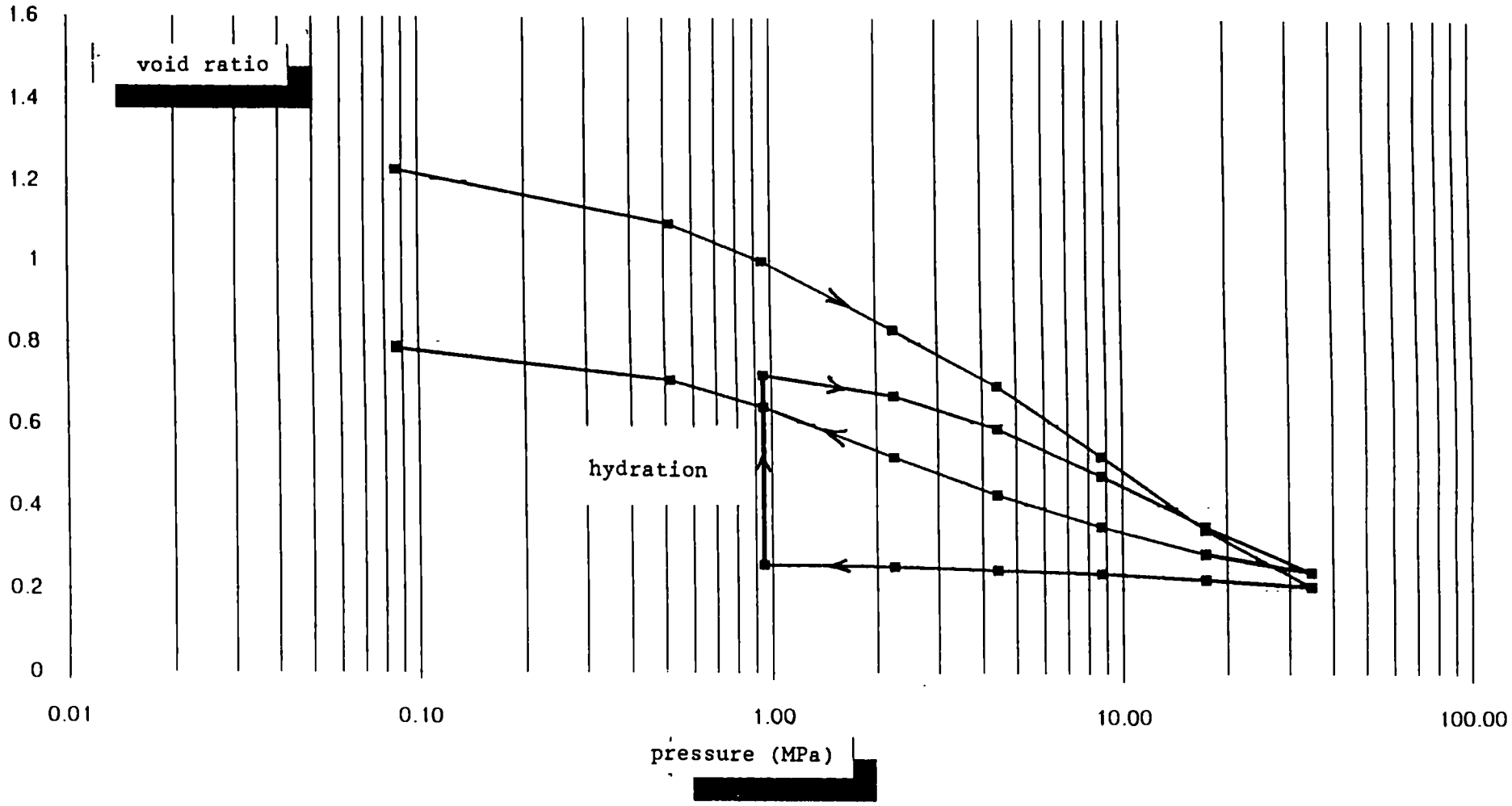

Figure 3 : Oedometer test with hydration after loading-unloading cycle

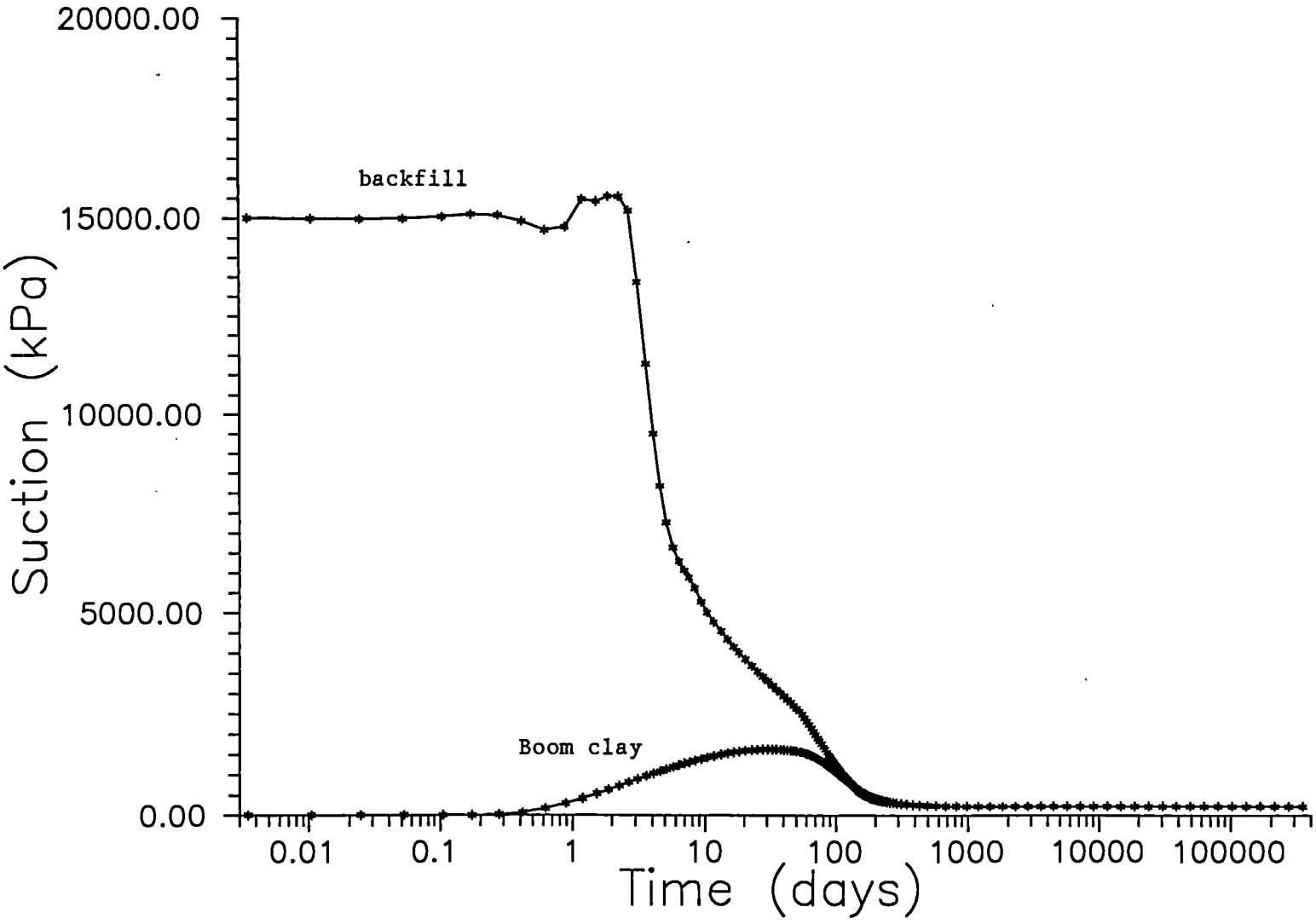

Figure 4 : Evolution of the suction in the Boom clay and in the backfill at 5 cm from the Boom clay - backfill interface

MODELLING AND VALIDATION OF THE THERMAL-HYDRAULIC-MECHANICAL AND GEOCHEMICAL BEHAVIOUR OF THE CLAY BARRIER

Title :	Modelling and validation of the thermal-hydraulic-mechanical and geochemical behaviour of the clay barrier
Contractors :	SCK•CEN, ENRESA, CIEMAT
Contract N° :	FI2W-CT91-0102
Duration of contract :	from 01-10-91 to 30-09-94
Period covered :	from 01-01-92 to 31-12-92
Project leaders :	G. Volckaert (coordinator), C. Mayor, E. Alonso, J. Samper, P. Rivas

A. OBJECTIVES AND SCOPE

When considering compacted clay-based materials as engineered barrier in the immediate environment of a HLW container, not only the hydromechanical performance needs to be studied but also thermal and hydrochemical evolution needs to be known.

The influence of temperature on the hydrological, mechanical and chemical field, has been studied for each of these fields separately. However to be able to assess the overall performance of the clay barrier, it is the objective of this project to model the combined effect of temperature on the hydromechanical and hydrochemical field.

The development of codes for the simulation of multiphase flow under nonisothermal conditions and their application to the interpretation of the experimental work will be carried out by CIMNE (UPC-DIT) under subcontract with ENRESA.

The laboratory experiments will be designed by CIEMAT in cooperation with the modellers and the SCK•CEN.

B. WORK PROGRAMME

Code development

A code to simulate multiphase flow under nonisothermal conditions will be developed and, on the one hand coupled to a chemical transport code and on the other hand to an elasto-plastic model adapted to account for expansive material effects.

Experiments

Tests will be carried out on ad hoc designed cells that will allow to determine the evolution of temperature, pressure and fluid concentration fields, produced in the clay barrier by heating of the central zone and by flow of water.

Model application

The thermo-mechanical and thermo-chemical models will be used in the interpretation of the above experiments and experiments carried out in complementary CEC programs (contracts n° FI2W-CT90-0033, FI2W-CT91-0098).

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

Experiments

A thermo-hydraulic cell has been designed and constructed. This cell allows to apply at the same time a hydraulic and a temperature gradient while measuring the temperature and stress distribution over the height of the clay sample. Oedometers with suction control have been constructed and used for the determination of the suction - water content - deformation relation. One oedometer with suction and temperature control is under development. Several triaxial tests on unsaturated clay have been performed.

Model development

Thermo-hydro-mechanical

In the constitutive model area, the framework for the mechanical behaviour of expansive materials of soil type has been completed and the development of a consistent mathematical model is in progress. Advances have also been made in the development of a complete constitutive model that includes saturation and thermal effects. With respect to the development of numerical code task the work has been focused on the discretization of the already developed field equations with a special reference to the recently introduced "mass-conservative" procedures which have some important advantages in the context of this research. Coding has also been carried out in the areas affecting the general structure of the programme.

Thermo-hydro-chemical

Most of the work on the first year of the project has been devoted to the development of a coupled solute transport chemical model. This model accounts for reactions taking place in the aqueous phase and mineral dissolution/precipitation reactions under isothermal conditions. Significant effort has been put on developing a sound geochemical model both for equilibrium and kinetic conditions. Basic subroutines have been prepared which will be utilized in later phases of the project.

Two different approaches are being considered for the solution of the coupled solute transport and chemical equations. One is based on the direct substitution of the chemical equations into the transport partial differential equations. The second approach is a sequential iteration method which solves separately the transport and the chemical equations. Both approaches have been implemented numerically for a one dimensional flow system.

Progress and results

CIEMAT

Experiments have been carried out to study the thermo-hydro-mechanical behaviour of unsaturated swelling clay. In all the experiments performed up to now a Spanish montmorillonite has been used. In the future, also Boom clay will be used.

A thermo-hydraulic cell has been developed. The center of its upper face is equipped with a heat source and its lower face is equipped with a filter through which the clay sample can be hydrated. The evolution of the

temperature and radial pressure at different heights of the sample are monitored by thermocouples and pressure transducers. First some preliminary tests to check the control and monitoring system of the cell have been performed. A three-months test with simultaneous heating and hydration has been carried out on a clay sample with dry density of 1.65 g/cm^3. The test showed that after 3 months the sample is not yet saturated. The lower part of the sample has swollen and is probably saturated. The upper halve of the sample is not saturated and near the heater it was even desicated.

The water content - suction relation, which is an important parameter in the hydro-mechanical models, have been determined for samples with different initial density and water content. For values of suction less than 160 kg/cm^2, the suction is applied by a nitrogen pressure inside a membrane cell. For a suction pressure up to 3000 kg/cm^2 the sample is introduced in a desiccator with the relative humidity controlled by the water activity of a sulfuric acid solution of a given density. A typical result is given in Figure 1. It was found that the initial dry density has a small influence : at a given water content the equilibrium suction is higher for higher densities.

Both above mentioned methods for suction control have been implemented on oedometers. With these oedometers experiments have been performed in which the relation suction pressure - vertical stress - deformation was determined. Several drying-wetting cycli have been applied on the same sample. The influence of the suction and vertical stress is shown in Figure 2.

Consolidated, drained triaxial tests have been performed on unsaturated clay samples, but without suction control as this was still too complex to implement on a triaxial cell. These tests clearly showed the increase of cohesion and friction angle with increasing suction.

These experiments will be used to calibrate/validate the UPC and UWCC models.

UPC (main sub-contractor to ENRESA) - geomechanics

Constitutive model development

Most of the work carried out in this period has been performed in relation with the further development of the existing elasto-plastic constitutive model for partially saturated soil. Two aspects of behaviour have been addressed :

- expansive soil effects;
- thermal effects.

A conceptual framework for the description of the behaviour of unsaturated expansive clays has been completed. The framework is totally compatible with the existing elasto-plastic model for unsaturated soil and is able to reproduce most of the basic features of behaviour of expansive clays. It is based on the distinction within the material of a microstructural level where the basic swelling of the active minerals take place and a macrostructural level responsible for major structural rearrangements. By adopting simple assumptions about the coupling between the two structural levels, the observed mechanical behaviour of expansive clays is recovered. In this way the basic microstructural behaviour characteristics of expansive minerals and the models already developed for unsaturated soils of low activity can be integrated in a single coherent system.

This work has been further extended by developing a mathematical formulation necessary to ensure the consistency of the framework and the

applicability of the constitutive law to the modelling of boundary value problems. During this first stage attention was focused only on the reliability of setting up a fully consistent general model by devising an adequate mathematical structure. This phase of the work has now been completed.

In the same way that the expansive clay model has been based on the existing elasto-plastic constitutive law for partially saturated soils, the approach adopted to introduce thermal effects in the constitutive law has also been based on the generalization of the elasto-plastic model in such a way that the existing model becomes a particular case of the general thermo-mechanical law for isothermal conditions. For this purpose, the saturated thermal model developed by Hueckel and co-workers has been found to be especially useful because of its structural similarity with the unsaturated plastic model. In a sense the new unsaturate thermal elasto-plastic model can be considered as the result of a merging of the two earlier models dealing respectively with unsaturation and thermal effects.

Code development

The elaborated coupled field equations have been discretized. The space discretization has been carried out conventionally using the Buvnov-Galerking finite element formulation. With respect to the time integration there is wider range of possibilities : weighted residuals and finite differences. In addition special attention has been given to the more recent "mass-conservative" approaches which appear to result in more efficient solution schemes and in smaller numerical errors. The decision has been taken to introduce all three schemes in the final code in order to have a wider range of alternative methods in case of convergence difficulties.

The finite element code is structured such that it allows for the widest possible scope. Although, initially, only a limited number of possible features will be included in the code, the approach is to adopt a structure that permits the inclusion of other features with only a minimum disruption to the existing programme.

The programme structure is based on a nested scheme in which the successive loops correspond to :

- stage (geometry changes);
- time and loading steps;
- time and loading increments.

The programme permits a geometry that changes with time, essential if construction e.g. placement of compacted material and/or excavation e.g. borehole drilling must be modelled. Each stage corresponds to a specific geometry and there will be a stage change every time there is an episode of construction or excavation. Within each stage there may be one or several steps in which a set of boundary conditions is applied over a fixed period of time.

Laboratory testing

In addition to the work performed by CIEMAT, it was considered useful to set up a limited test facility with temperature and suction control to check particular features of the thermo-plastic model.

With conventional equipment a suction controlled oedometer test at 40 °C has been performed.

Using psychrometric techniques, it was tried to determine the water content - suction relation at various temperatures. Though the scatter in

the results at 40 °C and 60 °C shows that this method, as it stands at present, is not reliable.

A new oedometer with both suction and temperature control has been designed and the prototype has been constructed so that tests can be started next year.

UPC (main sub-contractor to ENRESA) - geochemistry

Progress has been made in the three following tasks : data base compilation, development of an improved geochemical code and coupling of this code with a transport model.

Data base compilation

Geochemical data base compilation work is in progress for the updating of the hydrochemical data base. This work has been carried out in cooperation with other related EC Research Programs. It is planned to strengthen the cooperation with the CHEMVAL Project in which ENRESA is taking part.

The data bases provided by currently available chemical programs (such as EQ3/6, WATEQ, PHREEQE, ...) are being complemented with thermodynamic data published on scientific journals. This compilation also includes data on kinetic parameters.

Development of an improved geochemical code

Subroutines have been prepared for :

- standard input of minerals, species, reaction rates, ...;
- reading of thermodynamic data and computation of equilibrium constants;
- switching between sets of primary species;
- calculation of activity coefficients;
- calculation of the amount of dissolved/precipitated mineral for a selected transport model (direct coupling approach);
- calculation of the solute concentration of the amount of dissolved/precipitated mineral in equilibrium (sequential iteration approach);
- updating of the system parameters after each time step.

In addition to these subroutines, a computer program for the analysis of fluid-solid phase interactions has been developed. The program simulates solute concentrations as the amount of dissolved/precipitated minerals in a closed chemically equilibrated system that suffers an external perturbation. This program solves the transport model by assuming that at every node of the mesh there is a chemical perturbation caused by the transport. The program solves the mass balance and the chemical equilibrium equations after a linearization process. It has been verified against existing codes such as PHREEQPITZ and EQUIL. One of the applications considered so far has been the simulation of the chemical evolution of water and mineral precipitation during evaporation of various mixtures of seawater and fresh continental water. At present the program simulates the hydrochemical evolution at a temperature of 25 °C. Work is in progress to extend it to higher temperatures.

Coupling of the geochemical code with transport

An extensive literature review has been carried out to update the state-of-the-art on coupling hydrochemical reactions and solute transport. The three most representative approaches are :

(1) direct coupling;

(2) two-step coupling of a solute transport code and a chemical model;
(3) sequential iteration approach in terms of total concentrations of components.

With the current knowledge, there are no general criteria to decide which is the best approach to follow. For this reason, the UPC group has not taken yet a final decision on the choice of the approach to be pursued. Instead, it has been decided to develop simple prototype coupled solute transport hydrochemical models based on each of the three approaches which will be used to gain insight into various aspects such as :

(1) the numerical efficiency of different coupling approaches;
(2) the proper choice of primary and secondary variables;
(3) the proper choice of nonlinear numerical techniques;
(4) possible ways to handle simultaneously chemical equilibrium and kinetics;
(5) effect of varying temperatures.

At this time, prototype models are intended to simulate one dimensional transport with a small number of chemical species and minerals. For the sake of preliminary testing and validation of the models, a case study in an evaporite system has been selected. The area is located in Los Monegros, a semiarid closed-basin region located 200 km east of Barcelona, Spain. The UPC has been studying the hydrogeology and hydrochemistry of the area during the past five years. The high solubility of the geological materials allows a strong water-rock interaction. This hydrogeological system is probably one of the most adequate examples for validating a coupled hydrochemical solute transport model.

SCK/CEN

In order to coordinate this project with the related projects "BACCHUS 2" (contract n° FI2W-CT91)0098) and the project on modelling and testing of the hydration of clay backfilling and sealing materials (contract n° FI2W-CT90-0033) two meetings with the partners of the three contracts have been organised. It was decided that Boom clay would be used by all partners for some intercalibration tests. Therefore the SCK/CEN did sent samples of the same batch of Boom clay powder to all partners.

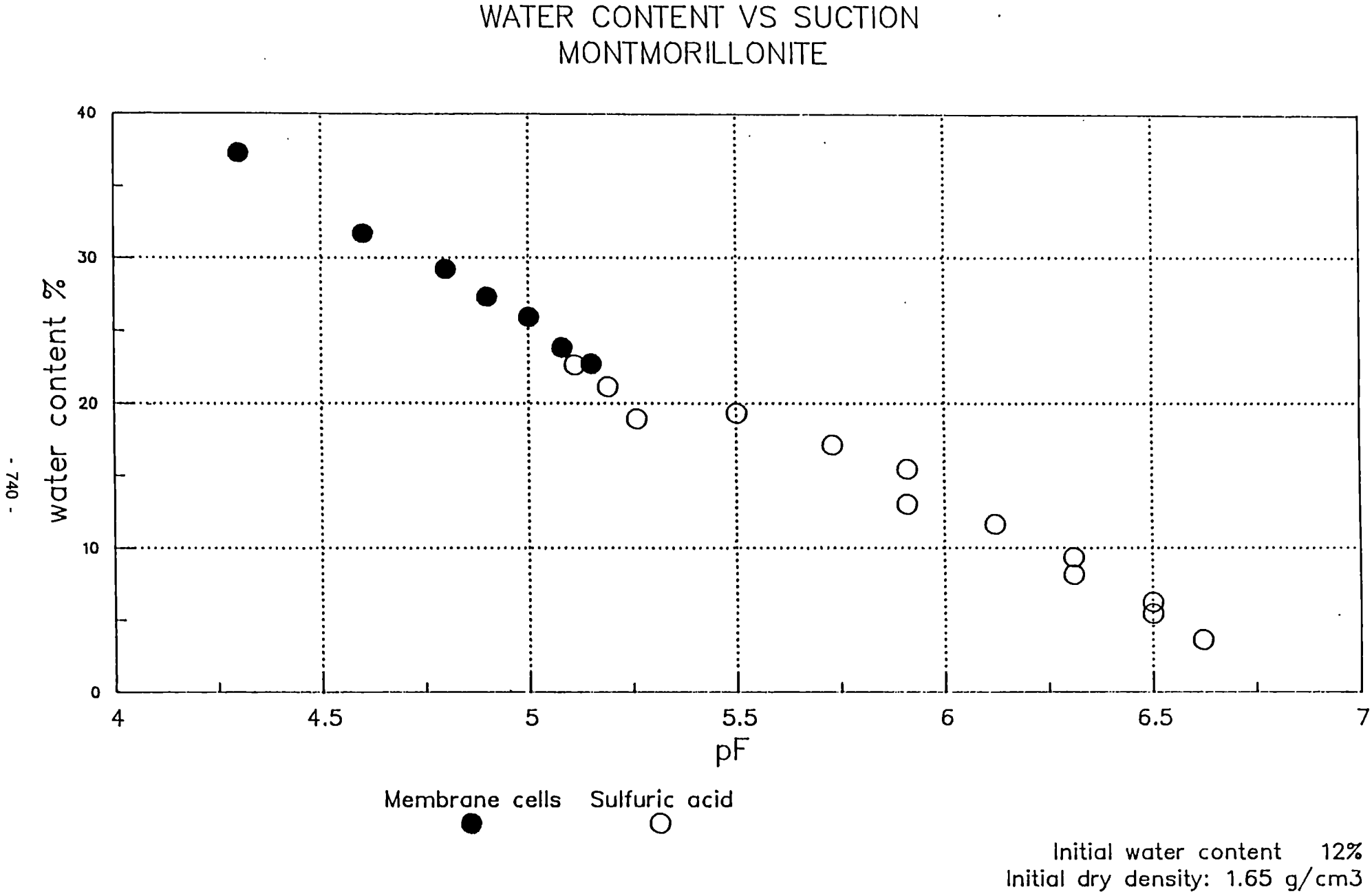

Figure 1 : Water content vs suction curve for montmorillonite. Points obtained in nitrogen cells and sulfuric acid solution deseccators

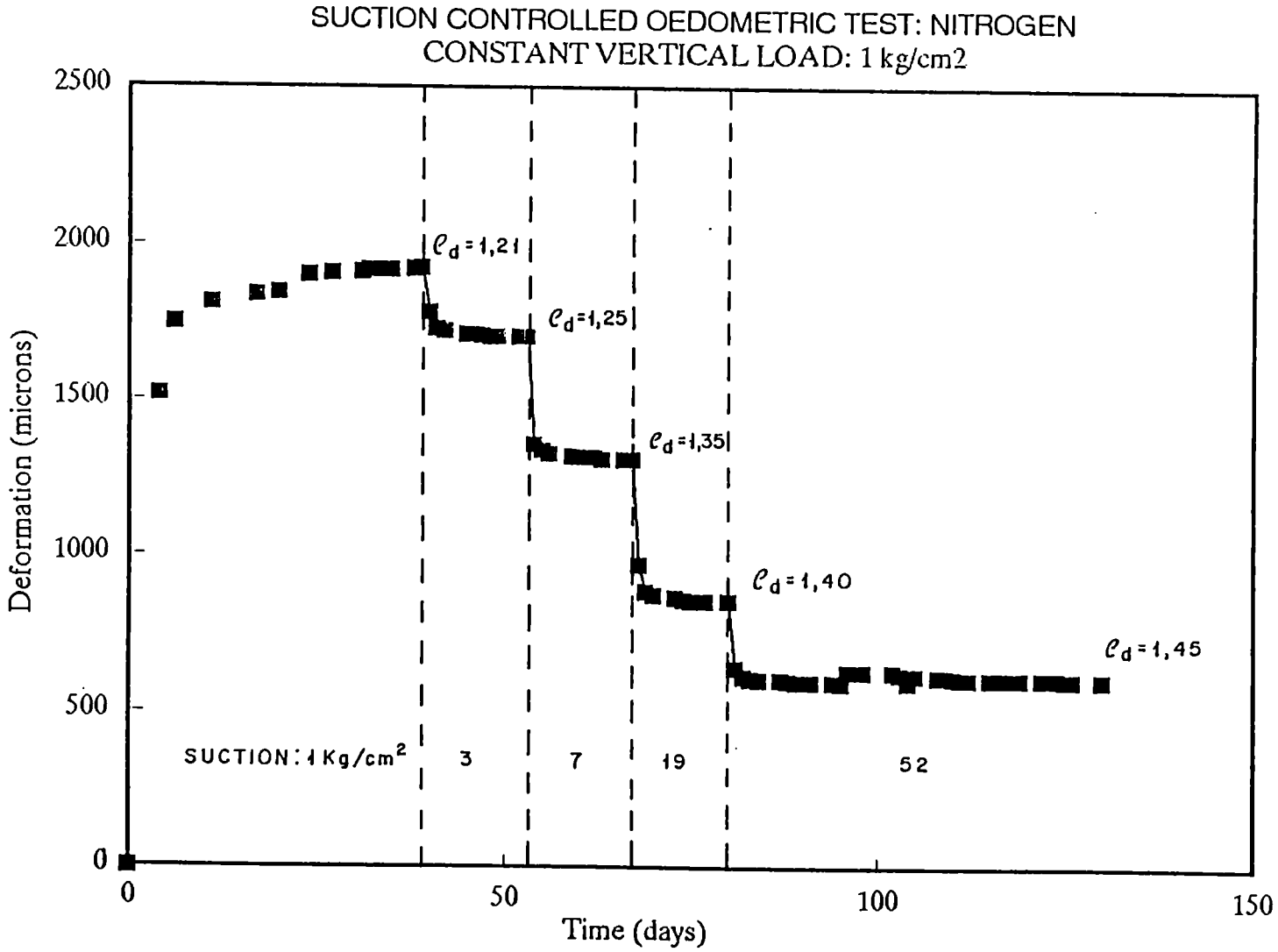

Figure 2 : Consolidation curves of an oedometric test in a nitrogen cell. Increasing suction steps. Montmorillonite

Processus d'acquisition et de régulation de la chimie des eaux en milieu argileux (ARCHIMEDE).

Contractor :	ANDRA / DESI
Contract N° :	F12W/0117
Duration of contract :	from January 1st 1992to December 31st 1994
Period covered :	1992 (12 months)
Project leader :	T. MERCERON, ANDRA

A) Objectives and scope.

Clay is a candidate environment to host high radioactive waste disposal. The radionuclides can progressively arise from the waste into the host geological formation over a long period of time. The understanding of the behaviour of natural elements in clay formations is an unavoidable step towards the understanding of the fate of such radionuclides. Further laboratory studies are also needed to help forecast, by analogy the behaviour of radioelements released from deep radioactive repositories.

The ARCHIMEDE project aims at three major goals

1.- understanding the mechanisms of acquisition and regulation of formation water chemistry in clay environment, as a result of water rock interactions ;
2.- testing and validating the physico-chemical parameters that describe the clay formation and its properties and that feed geochemical models ;
3.- applying these results to model a real clay environment : the Boom Clay formation.

Rock sample characterization is generally realized in the laboratory after sampling. Sampling techniques usually applied can sometimes significantly disturb the original geochemical and microbial state of the sediment. In this study special attention is paid to prevent such a drawback : the Boom clay formation (solid, fluid and gaseous phases) is sampled from the Underground Research Laboratory facility in Mol (Belgium) under anaerobic and aseptic conditions, and experimental works are designed in order to measure non conservative (pH, Eh) or potentially versatile parameters (interstitial fluids, trapped gases, cation exchange capacity) directly in the formation. Microbiological techniques will be developped for natural sample bacteriological characterization, in conjunction with conventional bacteriological investigations.

Four scientific teams are in charge of the animation of the different phases of the project, under the coordination of ANDRA, Division d'Etude des Sites (France) : SCK/CEN (Belgium), BRGM (France), CEA-DSD (France), GRAM SA, with the collaboration of CNRS (France). The ARCHIMEDE project will be achieved within three years (1992 - 1994).

B) Work programme.

The four main topics of the project are as follows

1. fluid and solid sampling, in situ measurements : all teams are involved in this topic which is planned over 1992 ;
2. fluid (CEA-DSD) and solid (BRGM) characterization. This step of the project is planned over the second year (1993) ;
3. microbial investigations (GRAM SA), that will extend over three years (1992- 1994) ;
4. fluid-rock equilibria modelling (CEA - DSD and BRGM) will intergrate the results obtained after the characterization step (1994).

C) Progress of work and obtained results

The main topic of the ARCHIMEDE project in 1992 was collecting samples as much representative as possible of the actual state of the Boom Clay Formation, and setting up in situ experiments in order to better characterize the geochemical environment..

To achieve this, seven drill works in the HADES Underground Research Facility at Mol were planned. They have all been completed in 1992, apart from one which encountered technical problems and which will be done again in 1993
1.- solid and fluid sampling a 20 m long horizontal core was drilled in the URF for solid and fluid sample collection. The work was performed under sterile and anaerobic conditions ;
2.- fluid sampling two 15 m long horizontal piezometres were drill on both sides of the previous work in order to collect large amounts of interstitial fluid. As previously they were completed under sterile and anaerobic conditions. One of them is equipped to house an optic fiber dedicated to in situ pH determination ;
3.- experimental work achieved is in situ deep freezing and coring (2 cores 2 m long), active geochemistry piezometre setting, and pH/Eh probe setting for in situ measurment. The experiments themselves will be carried out in 1993.

The analytical step of the project has also started in 1992. The first results obtained so far do not allow characterization of the sediment yet. The detailed analytical work planned in 1993 will however benefit from the general features which appear from the preliminary results.

Participant nº 1 (SCK/CEN, Belgium).

The ARCHIMEDE project aims at modelling pore water chemistry acquisition in clays. To achieve this, the Boom Clay Formation at Mol was retained to be sampled from within the Underground Research Facility.

Classical methods of rock and fluid sampling by coring usually lead to significant disturbance of the initial state of the formation to be studied. Some parameters such as gas content, temperature, pressure, pH, redox potential and microbial characteristics can only be correctly evaluated on undisturbed sediments. The same applies, to a lesser extent, to such parameters as moisture and interstitial fluid composition which are sensitive to sample handling and storage conditions.

The ARCHIMEDE project requires undisturbed samples and aims at estimating critical parameters variability with time and/or sampling conditions.
After each team has defined its needs, SCK/CEN was in charge of realizing the work on site, according to the requirement of the user of the samples (Figure1) :

1.- one 20 m long corehole, which was needed to collect samples for solid phase and microbial characterization, and for interstitial fluid extraction. This required realizing an horizontal corehole in both aseptic and anaerobic conditions. Asepsis was guaranteed by sterilising tools and hands in contact with the sediment, and minimizing contact with ambient air. Anaerobic conditions were required because of the strong reducing properties of the Boom Clay. This was ensured by avoiding contact with air in handling the samples in sterilized pouches and/or glove bags filled with sterilised nitrogen. In order to minimize physical damage to the samples, coring has been realized using preliminarily sterilized 4 inches in diameter cutting edge tools. Thirty half metre long cores were collected along the 20 metre long horizontal work by pushing the cutting edges using an hydraulic piston. Twenty five centimetre of clay were bored between each cores in order to make sure that the next core is taken from an undisturbed part of the formation. The work was completed by the sterile setting of a piezometric nest to collect interstitial fluids far from the gallery for the purpose of microbial studies ;
2.- two piezometric nests (15 m long each) were also needed for interstitial fluid collection. As previously, they were sited in sterile conditions. The piezometres are made up of five independent filters that allow collection at various distances from the wall of the gallery.

In addition to ensuring sample collection, SCK/CEN took also part in designing and realizing experimental work from within the Underground Research Facility :

1.- in situ deep-freezing of the clay was realised to collect frozen samples. The aims of this experiment are twofold : i) to check the alteration interstitial fluid characterisation induced by in situ freezing, and ii) to immobilize the porewater before sample collection and recover it by freeze-drying for isotopic (D/H, $^{16}O/^{18}O$) determinations ;
2.- in situ pH and Eh measurements ;
3.- active geochemistry experiments which aims at evaluating how a property of the clay that is measured in the lab (*viz* cation exchange capacity) expresses on site ;
4.- pore fluid characterization by in situ dialysis. This experiments aims in particular at sampling dissolved metallic species, and requires specific design of the dialysis cell port. Reinforced rubber tubing proved unsuitable to resist to the formation stress. New design of the cell port is currently on and the experiment will be carried out in 1993.

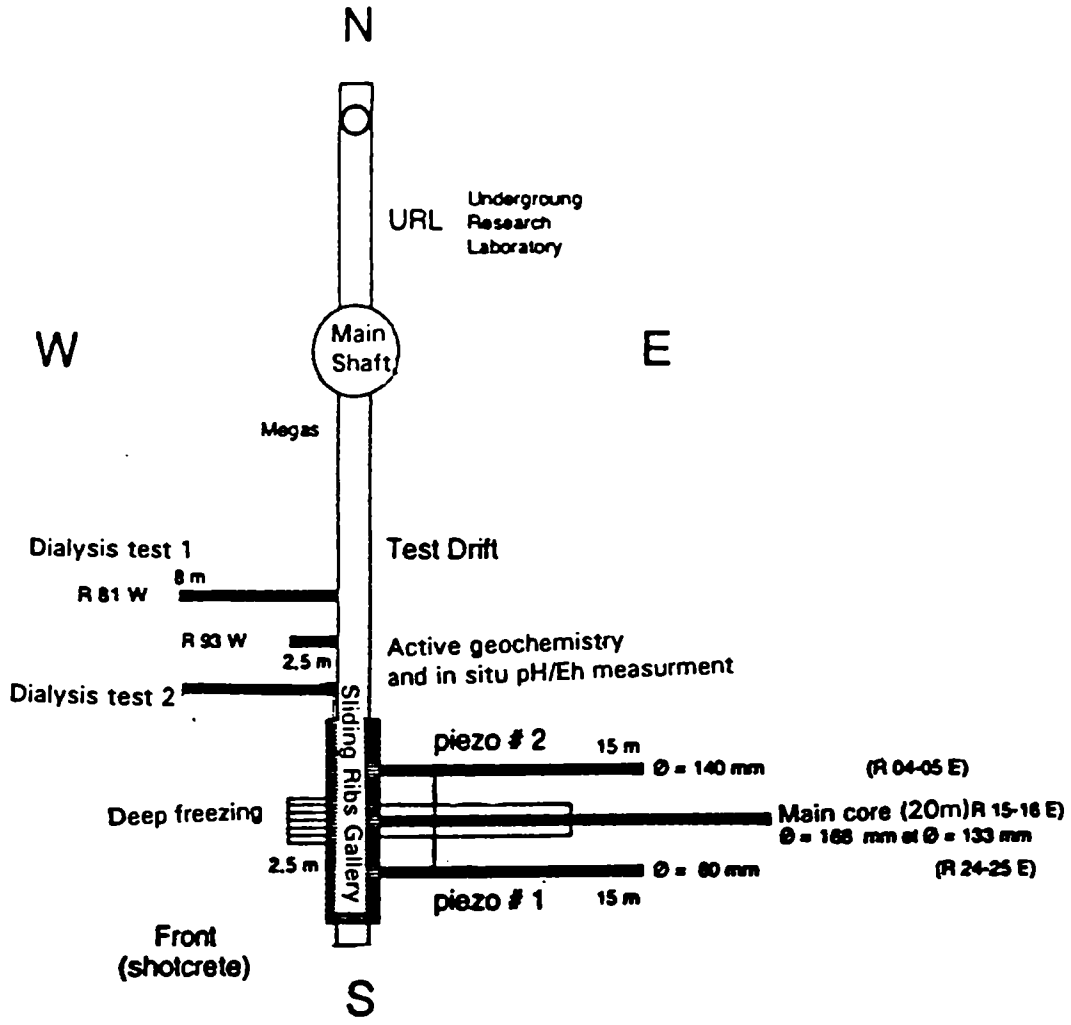

Figure 1 Location sketch of the drilling works of the ARCHIMEDE project in the Underground Research Laboratory at Mol.

Participant nº 2 (CEA-DSD, France)

Fluid chemistry acquisition and regulation in rocks results from water/minerals interactions. In the case of granite, the chemistry of fluids shows correlations between the elements, that indicate that the fate of a given element strongly related to that of its neighbour. The aim of CEA is to determine to which extent this approach can be applied to pore waters in sediments, in order to model the processes of fluid evolution in clay.

Fluid collection in clays requires specific means in order to get samples as much representative of their actual state as it is possible. Piezometric nests can be used for recovering fluids by natural drainage of the formation. These fluids, which can be considered as free porewaters may differ from those obtained using other techniques. In the ARCHIMEDE project, leaching as well as squeezing of fresh samples were also applied to collect interstitial fluids. The preliminary results show some differences in the detail of the chemistry of these fluids. In a second step, we must determine to which extent these differences are a consequence of the technique itself and which other phenomena can be evidenced. In addition, dialysis cells will be used to capture the pore fluid chemistry by ion transfer through semi permeable membranes.
In situ pH determinations will be carried out using a dedicated optic fiber which will be pushed into the chamber of one of the piezometers. The optic fiber technique for measuring pH has already been tested before by CEA using short fibres. Here, a 15 metre long optic fiber will be used in order to measure pH far enough from any possible disturbed zone within the Boom Clay Formation.
In purpose of fluid collection, two 15 m long horizontal piezometres have been placed on both sides of the 20 m long core (Figure 1). As fluid samples are also needed for microbial investigations, work has been carried out in sterile conditions.
The water samples gathered in 1992 were first reserved for bacterial and microbial sampling, in order to avoid any contamintion of the water sampling system. Meanwhile, sample collection from the underlying Rupelian aquifer was carried out in purpose of regional characterisation (Figure 2). The chemistry of this aquifer shows some analogies with the known chemistry of the Boom Clay, and the first results obtained on this aquifer allow to draw correlations between elements for those samples that are collected the deepest (Figure 2).
After the sterile sampling has finished, geochemical sampling of the Boom Clay pore water will begin to precisely characterize it.

In situ pH measurment will be carried out in 1993. A 20 m long optic fiber has been tested in the laboratory and will be pushed into the deepest piezometric nest as soon as the sterile sampling has finished.

Participant nº 3 (BRGM France)

Solid phase of the clay sediment is made up of the constitutive minerals and organic matter. Fluid geochemistry when it turns out to modelling is generally considered mainly as the consequence of the interaction between interstitial water and minerals, whereas the role of organic matter is not always taken into full account. The aim of the approach here is to try and evaluate the importance of the different elements that constitute the solid phase in the processes of fluid chemistry acquisition and regulation.

Solid samples were collected from the 20 m long core. Associated porewater was extracted on site in order to determine the geochemistry of the fluids directly related with the studied mineral phase. Along with interstitial fluid extraction, moisture content determinations, trapped gases extraction, and cation exchange capacity measurement were also performed on site. Those parameters are directly dependent on the state of the samples.

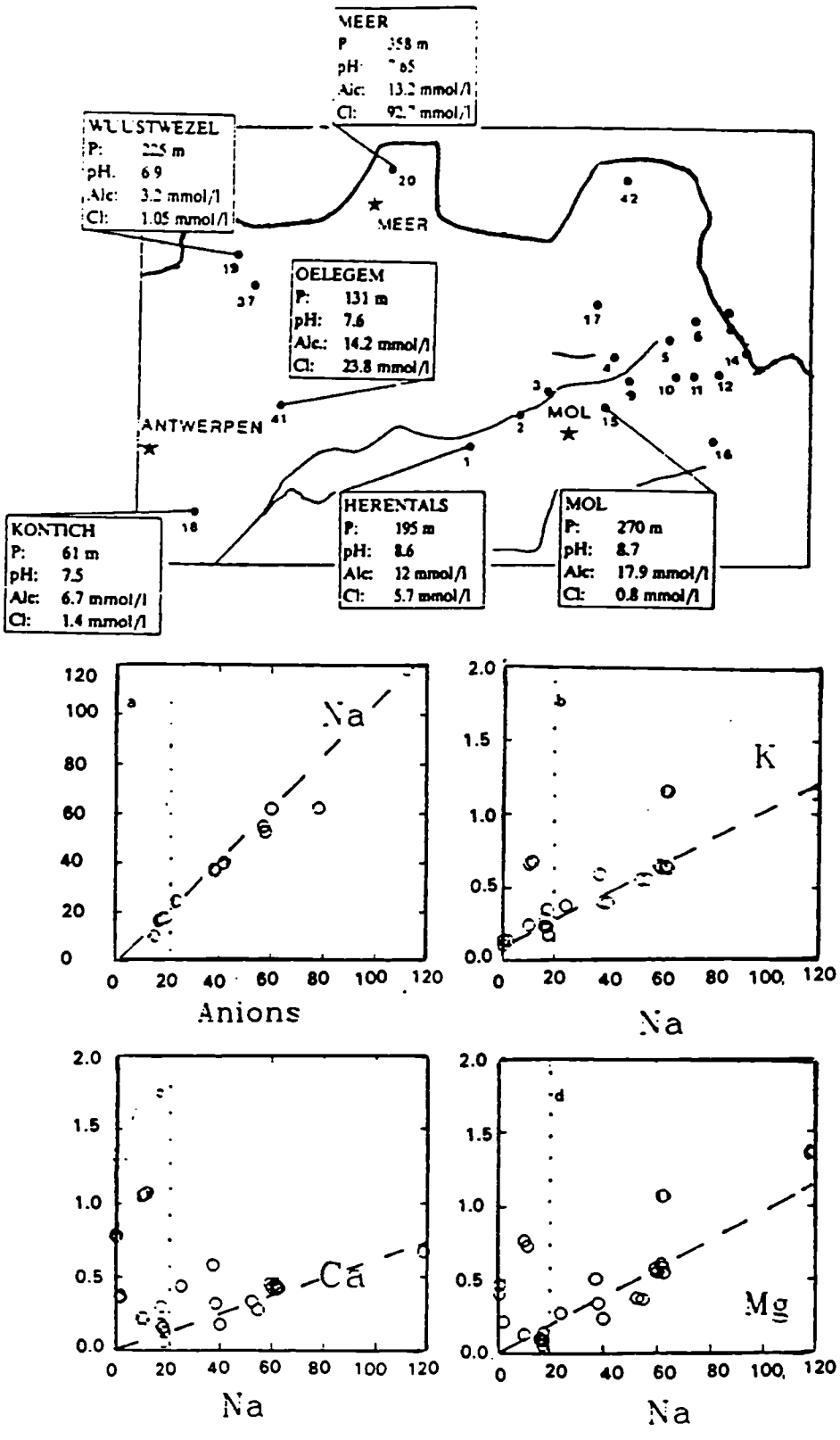

Figure 2 Location map of Rupelian aquifer sampling, and elemental correlations yielded by water analysis.

In order to verify to which extent storage and sample handling can affect them, the samples have also been stored under different conditions : in anaerobic pouches in the refrigerator, deep frozen or in confining cells. The variations in the results obtained on fresh samples on site or in the lab after some time storage can help determine those geochemical subsystems that are the most reactive and to which extent they take part to the fluid geochemistry regulation processes.

In 1992 efforts have focussed on sample collection and versatile parameter determination. In particular, cation exchange capacity was important to determine, because this property is to be tested in situ by active geochemistry experiment. The cation exchange capacity of a rock is not an absolute property because it is partly dependant of the conditions of measurment : exchange cation used, whether it is measured on fresh samples or on preliminary dried samples. In particular, cation exchange capacity can be determined by colorimetry using trivalent cobalt as exchange cation. By circulating such a solution in a loop at the end of which it can be in contact with the clay, it is envisaged to follow the variation of trivalent cobalt concentration with time without need of collecting series of subsamples. Unfortunately, this method is particularly sensitive to the redox conditions of the formation. That the reason why different experiments of cation exchange capacity were carried out in various conditions using trivalent cobalt (fresh reducing to oxydized dried sediment) to be compared with experiments utilizing elements non sensitive to redox conditions such as cesium (Table 1).

In situ pH and Eh measurment experiment is currently on using a probe placed in the clay formation.

Solid phase characterization has just begun, showing remarquable homogeneity of the sediment. Detailed investigations on the clay minerals and the organic matter properties are necessary, and will be achieved in 1993. Meanwhile, some particular geochemical subsystems such as the system pyrite-carbonate-sulphate, which are quantitatively not important, seem to play a key role in the chemistry of the interstitial fluids. They will be investigated more in detail in 1993.

Isotopic studies are also envisaged. Deep frozen clay were collected and kept frozen. The water extracted by freeze-drying them can be condensed and analysed for D and ^{18}O.
Similarly, previous experiments run on the Boom Clay in 1992 have shown that by treating fresh samples in a microwave, it was possible to extract water along with carbon and sulfur dioxide. Sulfur originates from pyrite decomposition, whereas carbon probably originates mainly from organic matter. If this is the case, S and C stable isotopes will give an insight into two important phases of the sediments.

Exchange cation is Cobalt meq/100g	On site measurement fresh	On site measurement dried	After 6 months storage fresh	After 6 months storage dried
apparent CEC	30 +/- 6	24 +/- 4	26 +/- 2	23 +/- 1
Na	9.0+/- 1.0	6.0 +/- 1.0	6.0+/- 1.0	8.0 +/- 1.0
K	2.3 +/- 0.4	2.6 +/- 0.5	2.5 +/- 0.2	2.5 +/- 0.2
Mg	3.8 +/- 0.8	5.5 +/- 1.0	6.7 +/- 0.7	7.6 +/- 0.7
Ca	3.7+/- 0.8	5.5 +/- 1.0	7.0 +/- 1.0	8.0 +/- 1.0
Sum of exchanged cations	19 +/-2	22 +/-4	24 +/-3	25 +/-2

Table 1 Evolution of the apparent CEC and exchangeable cations with time and analysis conditions : example with cobalt.

Participant nº 4 (GRAM SA, with collaboration of CNRS, France)

Clay is a particularly complex geochemical environment, partly because of its mineralogical features. But interactions between organic and inorganic constituents of the sediment are rarely taken into account. Yet microbial activity certainly plays a key role in the chemical evolution of the sediments. In addition, the evolution of the microbial population present in the sediment can tell about the evolution of the sediments itself.
The principal difficulty when it turns out to bacterial study, is to access uncontaminated sediments. In the case of the Underground Research Facility, no particular precaution was taken when it was digged : digging has braught underground allochthonous microbes from the surface, and human activity since has added to the contamination.
The aims of the microbial investigations in the ARCHIMEDE project are first to estimate the extent of human microbial contamination in the underground laboratory and its possible consequences now and in the future on the clay geochemical environment. A second aspect is to try and collect microbes in uncontaminated zones of the formation, that is far enough, in order to investigate which microbial populations were present at time of deposition, how they evolved since and what impact they can have on the global geochemical properties of the sediment.

In order to collect uncontaminated sediments, it was necessary to sample far from the wall of the gallery. To achieve this, it was of primordial importance not to carry allochtonous microbes with the tools or hands during coring or sample handling. For this reason asepsis was required : everything in contact with the sediment was thouroughly washed with alcoholic (50/50 vol) solution. The samples were treated within 24 hours after collection in order to minimize bacterial proliferation. Meanwhile, they were kept in refrigerated boxes (+4º C) and were shipped by air to the laboratory.

Conventional techniques of bacterial determinations rely on growing of the microbial populations in controlled conditions.
This technique which is currently applied to the Boom Clay samples, minimises the real microbial state of the sediment, because only living organisms can be evidenced, and those for which the growing conditions are the most suited will be favoured over those for which the conditions are less favorable. It results a distorted picture of the reality of the microbial characteristic of the sediment. It is usually considered that conventional techniques allow to identify only about 1% of the real microbial population in such deep geological environments.
Microbiology techniques will be used to overcome this drawback . These techniques, still not applied for natural samples are the same as those applied for human or animal microbiology. A living organism is characterized by its genetic signature which is beared in the nucleus. If it is present in the sediment, it can be identified by its genetic signature which is unic, and quantified.
Microbiology allows to investigate the genetic patrimony of living organisms. Duplication and/or replication of part of the genes is made possible using specific enzymes (Figure 3). In this study, RNA 16S is the gene considered. The structure of the RNA molecule is then compared to that of the known species, held in an international database continuously updated.
Both fluids and solids will be investigated. Preliminary results with conventional techniques have shown bacterial contamination and activity up to about 80 cm within the clay from the walls of the gallery. No activity or occurence of living organisms could be evidenced above the detection limit of the method in the samples collected deeper in the formation. This results do not mean actually that there are no living organisms, but at least that they could not be grown using the classical techniques. This shows also that apparently no external contamination has taken place and that the precautions taken for realizing a sterile corehole proved successful.

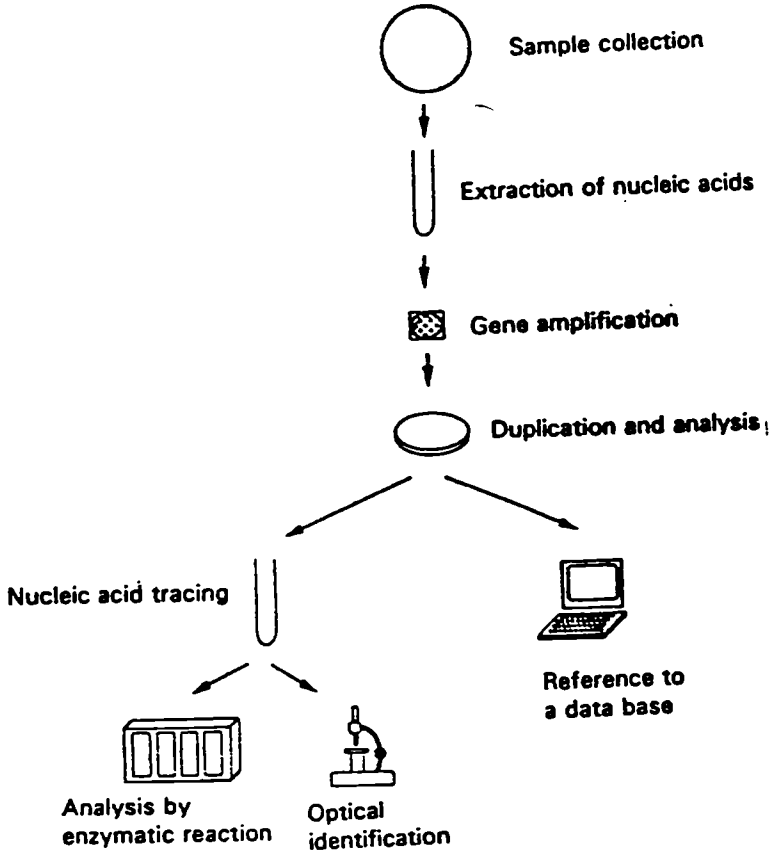

Figure 3 Schematic flow chart of microbiological processes for microbial characterisation of the samples.

Title: Phenomenology of Hydrical Exchanges Between Underground atmosphere and Storage host-rock

Contractors : Agence Nationale pour le gestion des Déchets RAdioactifs (ANDRA) - France -

Contract n°: FI2W-CT-91-0116

Duration of contract: January 1992 to December 1994

Project leader: M. RAYNAL

A/ OBJECTIVE AND SCOPE

The aim of the PHEBUS project concerns the study of the hydrous behaviour of a clay formation around ventilated excavations. It consists of a modelling, a laboratory mock-up and an in-situ test carried out at Mol facility in Belgium.

In a first phase, this consists in developping methodological tests not on core samples but on remoulded highly compacted clays. This procedure provides an appropriate control of the hydrical and mechanical history of the sample, making possible to understand the real hydrous phenomena.

In a second phase, an in-situ test will be carried out to validate the mock-up results. Using an accurate apparatus, this phase allows to reach some parameters and their time-dependence that can't be measured on a mock-up. With this short scale, it will be possible to evaluate the usefullness of a gallery ventilation test and to assess its technical feasibility : air conditioning system, porous lining conception and planning.

B/ WORK PROGRAM

B1. MODELLING

This initial phase consists in developing a simplified model of the hydrical transfer, in isothermal condition and without mechanical coupling (constant volume and porosity). This allows to study the parameters sensibility and to propose a first evaluation of the hydrical behaviour of the clay medium under a ventilation effect (orders of magnitude of water fluxes, desaturation area and phenomenon duration) on the basis of the present datas.

B2. MOCK-UP TESTS

The mock-up tests aim to well understand the phenomenology of hydrical exchanges between a controlled humidity air and the initially saturated clay, and to validate the model. It consists to conceive and manufacture an apparatus to test under high stress a clay with a cylindrical opening in the centre that simulates the ventilated gallery. At the end of each test, the mock-up is dismantled in order to measure the hydrical state around the opening.

B3. IN-SITU TEST

This phase will be carried out at Mol underground facility. It will consist in drilling an horizontal

borehole with a porous lining and an adequate peripheral instrumentation. The ventilation of this borehole will be controlled (dry temperature and relative humidity) and the amount of extracted water measured. Simultaneously the measurement of the clay hydrical state around the borehole will allow to evaluate the desaturation line. The experimental results will be compared to the model predictions.

C/ PROGRESS WORK AND RESULTS

State of advancement

The modelling (B1 phase) is now achieved. The main parameters are the relative humidity of the air and the saturated clay permeability. It shows that the desaturation effect will concern a few meters area around the openings, sufficiently to affect the clay mechanical parameters and so the mechanical interaction between the clay and the lining. Under repository conditions the desaturated area should be independent of the radius of the gallery.

The modelling was used to dimension the mock-up apparatus. The design is achieved. The specifications have been defined according to the safety regulations. The apparatus mainly consists in an oedometer and a controlled ventilation system. Both are achieved. They are under test before starting the experimental phase.

The in-situ test has been roughly defined. The emplacement, the drilling mode and the peripherical instrumentation have been defined in close coopreration with the CEN/SCK.

Progress and Results

B.1 MODELLING

The model is based on the different types of clay interstitial water (free water, capillary water and adsorbed water). In deep clay most of the water is in adsorbed state. The model takes into account the specific transfer mechanisms of each type of water. It has been shown that, when the gas phase is under constant pressure, the total water transfer could be addressed with one parameter : the saturated clay permeability. On this basis it has been dimensioned the mock-up and the in-situ test (cf. Figures 1, 2 and 3).

With a permeability of 10^{-12} m/s and for three relative humidities, we calculate the water flux per surface unit, the total water volume and the desaturation line. One can see that the water flux decreases rapidly and reaches after two months a pseudo-permanent state independent of the relative humidity. For our experiments that means that it wouldn't be significant to continue after two months.

B.2 MOCK-UP TESTS

The mock-up apparatus is based on an classical oedometer for high stress (0-40 MPa) which includes an additional cylindrical hole in the centre. An air flux will circulate through this opening to desaturate the compacted clay and to simulate the ventilation in an underground gallery (cf. Figure 4). Two clays will be tested : Boom clay and Parisian basin clay. The diameters and the air flux have been calculated and optimized according to the model to simulate repository conditions. Each test will include a consolidation phase (#1 month) to obtain the highly remoulded compacted clay from natural clay, and the ventilation phase in order to desaturate (#2months).

B.3 IN-SITU TEST

The principle of this in-situ test is to blow a dry air flux in a borehole in order to desaturate the surrounding clay through a porous lining (without hydrical effect). The water is extracted from the air at the output of the test chamber and measured as well as the clay parameters vs the distance from this chamber (dry density, water content).

The general emplacement and dimensions of the test have been already defined according to the model calculations (cf. Figure 5). The test zone will be far enough from the present excavations in order to minimize their mechanical or hydrical effects. The borehole will be 14 meters long and 300 mm diameter. The test chamber is limited at three meters. The controlled ventilation and water extraction system is under definition.

The CEN/SCK has proposed a peripheral instrumentation based on piezometer nests and a gamma-neutron probe already used in Mol facility.

<u>Reference</u>

[1] Rapport 621 RP GEO 91.002
"Modélisation des transferts de masse entre un massif argileux et l'atmosphère d e s ouvrages souterrains profonds - Première approche'
EUROGEOMAT

[2] Rapport 621 RP 92.003
"Evaluation sur modèle réduit des transferts hydriques entre un massif argileux et l'atmosphère d'une galerie - PHEBUS"
EUROGEOMAT

[3] Rapport 621 RP GEO 92.004
"Etude paramétrique des transferts hydriques entre un massif argileux et l'atmosphère d'un ouvrage profond - Application aux argiles de l'Aisne et de Boom"
EUROGEOMAT

[4] Note SIMECSOL NT 01-09470 01 B
"ANDRA - Consolidomètre PHEBUS - Projet final - Dossier de consultation"
SIMECSOL

[5] Rapport 621 RP BRG 91.023
"Laboratoire souterrain en site argile - Projet PHEBUS -
Réflexions pour la préparation du test in situ" BRGM

[6] Rapport 621 RP BRG 92.002
"PHEBUS - Etude du revêtement poreux de l'essai in situ"
Edition en cours BRGM

[7] Rapport 621 NT CEN 92.001
"The PHEBUS test - (06/91 - 03/92)"
SCK/CEN

[8] Document de travail SCK/CEN : "PHEBUS : mesures neutroniques"

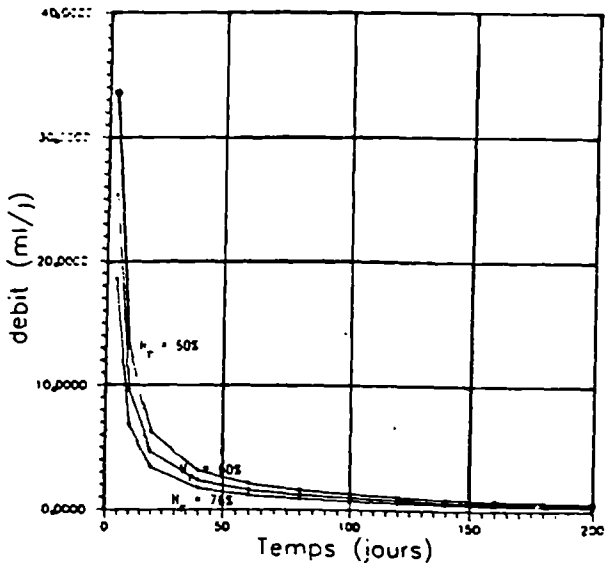

Fig. 1 WATER FLUX PER SURFACE UNIT

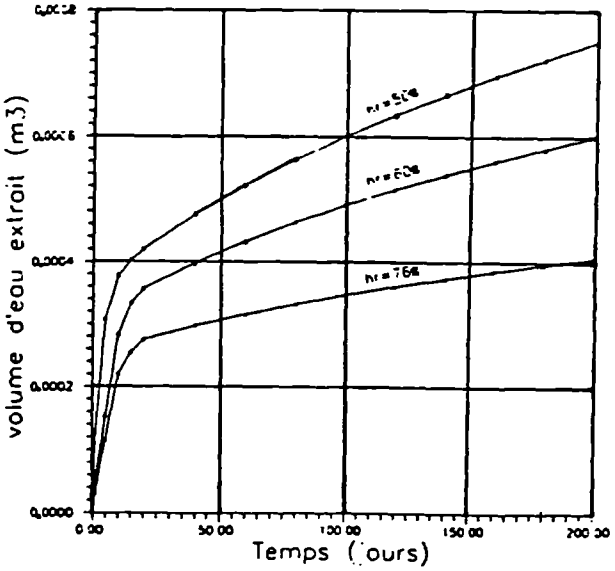

Fig. 2 WATER VOLUME PRODUCED PER SURFACE UNIT

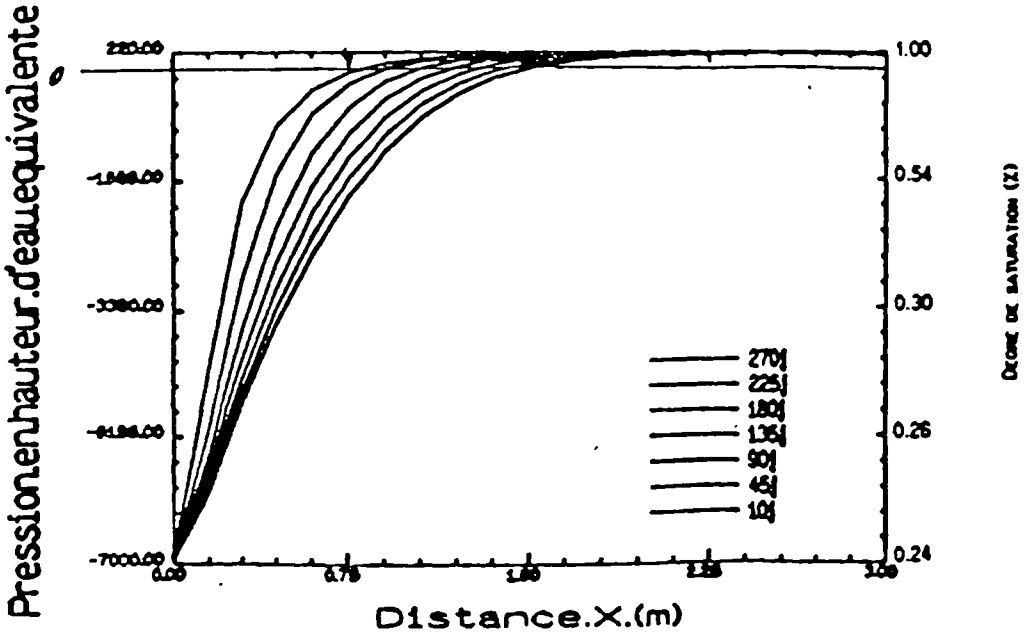

Fig.3 DESATURATION LINE VS TIME FOR HUMIDITY = 60 %

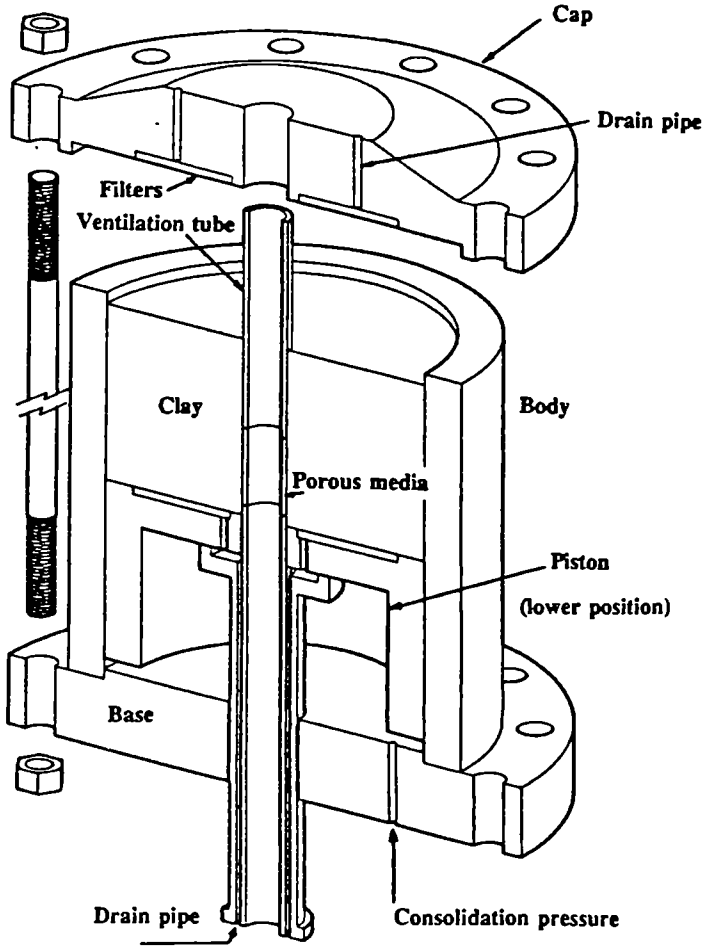

Fig.4 MOCK-UP TEST : PHEBUS OEDOMETER

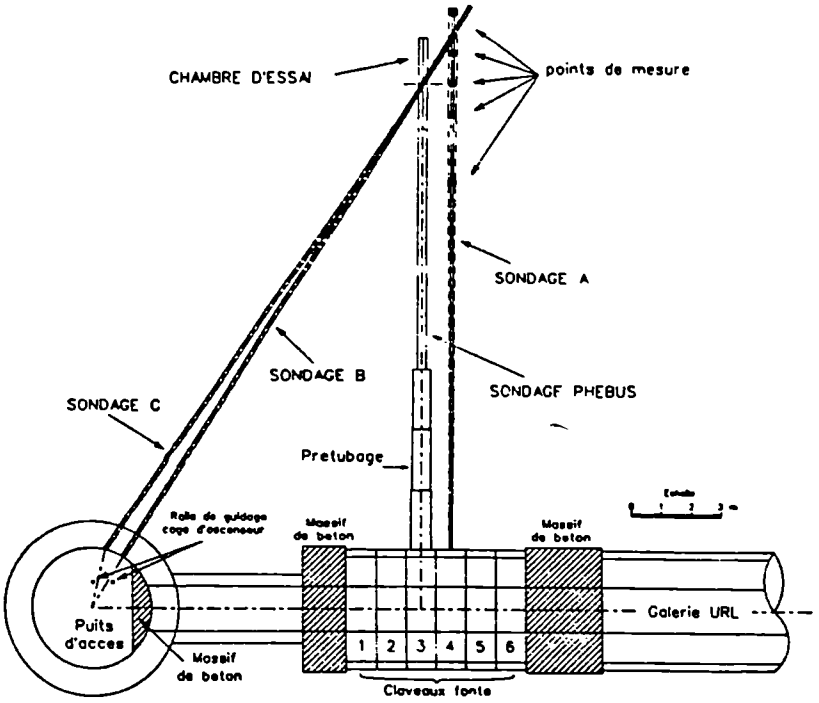

Fig. 5 a IN-SITU TEST SITE : HORIZONTAL CROSS SECTION

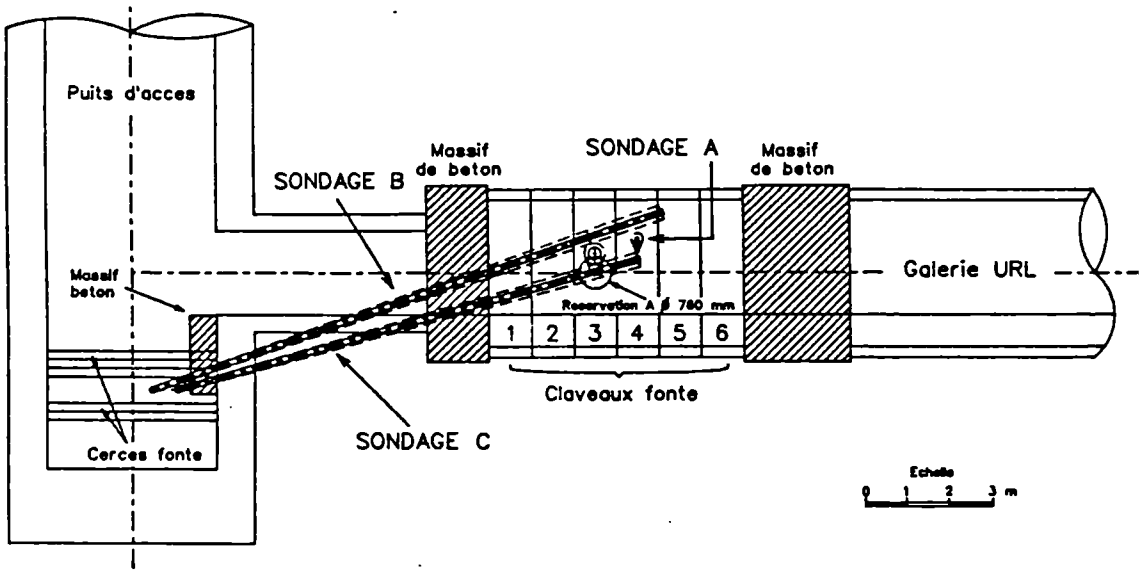

Fig. 5 b IN-SITU TEST SITE : VERTICAL CROSS SECTION

Title: HYDROLOGICAL CHARACTERISATION OF FRACTURED ROCK (SELLAFIELD)

Contractor:	**UK Nirex LTD**
Contract No:	**F12W/0114**
Duration of Contract:	**from 1st April 1992 to 31st March 1994.**
Period Covered:	**1st April 1992 to 31st January 1993.**
Project Leader:	**Dr A J Hooper**

A. OBJECTIVE AND SCOPE

The overall objective of the project is to decrease uncertainties in the hydrogeological and structural characterisation of a volume of rock at Sellafield in Cumbria. This rock is currently being considered as a potential host for a low and intermediate level solid radioactive waste repository in the United Kingdom.

The specific aims of the work are to perform geophysical and hydrogeological tests in and between two boreholes in a fractured and layered volcanic rock sequence, the Borrowdale Volcanic Group. Geophysical data will be integrated into a model of the rock volume. The results of single and crosshole hydrogeological testing will be used to clarify the lithological and structural features or combinations which control groundwater flow in the Borrowdale Volcanic Group.
This model will be applied to develop and validate concepts of groundwater flow in the immediate vicinity of the proposed repository.

The work is being performed in conjunction with Sir Alexander Gibb and Partners, acting as Geological Consultant. In addition, the following contractors have been defined: Schlumberger, SKB (with ABEM), Golder Associates UK Ltd.

B. WORK PROGRAMME

1. Review methodologies and prepare Design Intent Memorandum.
2. Geophysical testing in Sellafield borehole no 4.
3. Cross-borehole geophysical testing.
4. Single borehole hydraulic measurements in borehole 4.
5. Design of cross-borehole interference testing.
6. Cross-borehole interference testing.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

During the year, two separate Design Intent Memoranda for borehole radar and crosshole seismics have been produced. A third Design Intent Memorandum for the crosshole interference testing will be developed under Task 5. With these changes to the original Work Programme, Task 1 is now complete. Wireline logs have been run in borehole 4 and borehole 2. Task 2 is thus complete. Additionally, single borehole hydraulic testing has been completed in borehole 2, not borehole 4 as originally programmed. Borehole 4 was monitored during this testing. Task 4 is thus complete, which represents a change to the original sequence of programmed items. This change was necessary to meet the overall site investigation programme of UK Nirex Ltd. A trial of borehole radar has been attempted and cross-borehole seismics are due to commence in February 1993. Task 3 is thus partially accomplished.

Progress and Results

1. Preparation of Design Intent Memoranda.

Methodologies for cross-borehole geophysical testing and their applications at Sellafield have been reviewed. Separate Design Intent Memoranda for borehole radar and cross-borehole seismics have been produced. Based on this work it was concluded that cross-borehole radar would not be feasible at Sellafield, and that due to the saline groundwaters in the BVG the anticipated penetration of single borehole radar was uncertain.

2. Geophysical testing in boreholes 4 and 2.

Wireline logs and VSP have been run in both boreholes 4 and 2 as a standard element of the sequence of drilling and logging exploratory boreholes at Sellafield. The suite includes: Caliper log, Dual Lateralog, Dipole Shear Sonic Imager, Litho Density log, Natural Gamma Ray Spectroscopy log, Compensated Neutron log, Formation MicroImager, Acoustic Borehole televiewer, Geochemical Logging Tool, Vertical Seismic Profiling.

Of these logs, appropriate data providing information on the variation in lithological and structural properties down the borehole, and correlations between boreholes 2 and 4 at Sellafield will be collated. Currently an appraisal of the logs is underway. There is significant variability in the logs, representing the significant heterogeneity inherent in the Borrowdale Volcanic Group. It is anticipated that detailed and systematic cross-correlation of the logs and other data will be required to identify any significant heterogeneities which correlate with groundwater flows.

3. Cross-borehole geophysical testing.

3.1 Borehole radar.

Due to the high salinity of groundwaters within the BVG at Sellafield, there was uncertainty over the likely success of a borehole radar survey. Therefore, a trial of omnidirectional single borehole radar and directional single borehole radar has been carried out in borehole 7A at Sellafield.

The aims of this trial were to establish the range (penetration and resolution) of radar in the Borrowdale Volcanic Group and to provide information regarding the contrast in electrical properties of the rock mass at a distance from the borehole. The ABEM RAMAC Borehole Radar System was used. The performance of the radar trial in the BVG was poor. The performance of the radar was compared with a resistivity profile of the borehole obtained from the Dual Lateralog (DLL). At resistivity levels of less than 100Ω, no direct radar signal was detected by the downhole receiver. Evidence from the Formation MicroImager, Sonic Televiewer, core logs and single borehole packer tests confirm that these areas of low resistivity correspond to areas of major faulting, zones of fracturing and regions of "high" hydraulic conductivity.

Based on this trial and the correlations of radar range with the DLL, predictions of radar range for boreholes 2 and 4 were made. Resistivity profiles for the boreholes were derived from the DLL and confirmed by fluid conductivity data. The predicted ranges are given in Figures 1 and 2.

Predicted ranges for boreholes 2 and 4 are better than those encountered in the trial. This was not unexpected as the groundwater is less saline in the location of boreholes 2 and 4. However, the maximum predicted range was 35m in an unfractured zone between 620 and 800 m depth in borehole 4. In the fractured zones, range fell to less than 10 m. It is concluded that continued radar reflection surveys in the BVG at Sellafield will not significantly enhance the data obtainable from the dual-lateralogs and anticipated from the cross-hole seismics.

3.2 Cross-hole seismics

The Cross-hole Seismic Survey will start in early February 1993. A modelling study has been performed to maximise the achievable resolution of the field survey and to optimise the source/receiver couple configurations. As a result, a fan survey design will be adopted.

4. Hydraulic Testing in borehole 2, monitoring in borehole 4.

Profiles of hydraulic conductivity and points of inflow into borehole 2 are given in Figure 3. There is no immediate apparent correlation between structure and the location of inflows into the borehole.
A limited additional programme of longer term straddle packer tests (Post Drilling Tests) using variable drawdowns increasing in five steps to 150 m drawdown were carried out, focusing on zones of inflow into borehole 2. The results of these tests are given in Table 1, together with the value of hydraulic conductivity derived from the initial test sequence.

Table 1. Hydraulic conductivities from initial EPMs/hydrotests and post-drilling tests.

	Depth	Freshwater Hydraulic Conductivity from Post Drilling Tests	Freshwater Hydraulic Conductivity from initial hydrotests
PDDET 1	1587-1602m	$5x10^{-9}$ - $7x10^{-9}$ m/s	$4x10^{-9}$ m/s
PDDET 2	1006-1020m	$7x10^{-9}$ - $9x10^{-9}$ m/s	$2x10^{-9}$ - $4x10^{-8}$ m/s
PDDET 3	706- 716m	$1x10^{-8}$ -$1.2x10^{-8}$ m/s	$6x10^{-9}$ - $1x10^{-8}$ m/s
PDDET 4	542- 552m	$2.0x10^{-9}$ - $2.7x10^{-9}$ m/s	$2.6x10^{-9}$ - $1.2x10^{-8}$m/s
PDDET 5	1419-1469	$4x10^{-10}$ - $6x10^{-10}$ m/s	$3x10^{-10}$ m/s

These tests have been focused on the more permeable zones encountered in the boreholes. In general, the distribution of hydraulic conductivities for bulk flow in the BVG centres in the range 10^{-11} to 10^{-9} m/s.

During the post-drilling tests in borehole 2, the pressure in the full open hole section of borehole 4 was monitored. There was no evidence of hydraulic interference at the low applied drawdowns between boreholes 2 and 4. Variations in the pressure monitored in borehole 4 were seen on a 12 and 24 hour basis, probably related to tidal effects. However, the amplitude of these cycles was close to the resolution of the gauges.

In conclusion, interference tests between the two boreholes will need to be of significantly greater drawdown than that applied for the post-drilling tests.

5. Design of cross-hole interference testing.

No progress on the design of the cross-hole interference testing has been made. This task will draw on data available from the previous tasks.

6. Performance of cross-hole interference testing.

This task is still programmed to commence in mid 1993, following completion of Task 5.

List of Publications

No publications of this work have been made during the reporting period

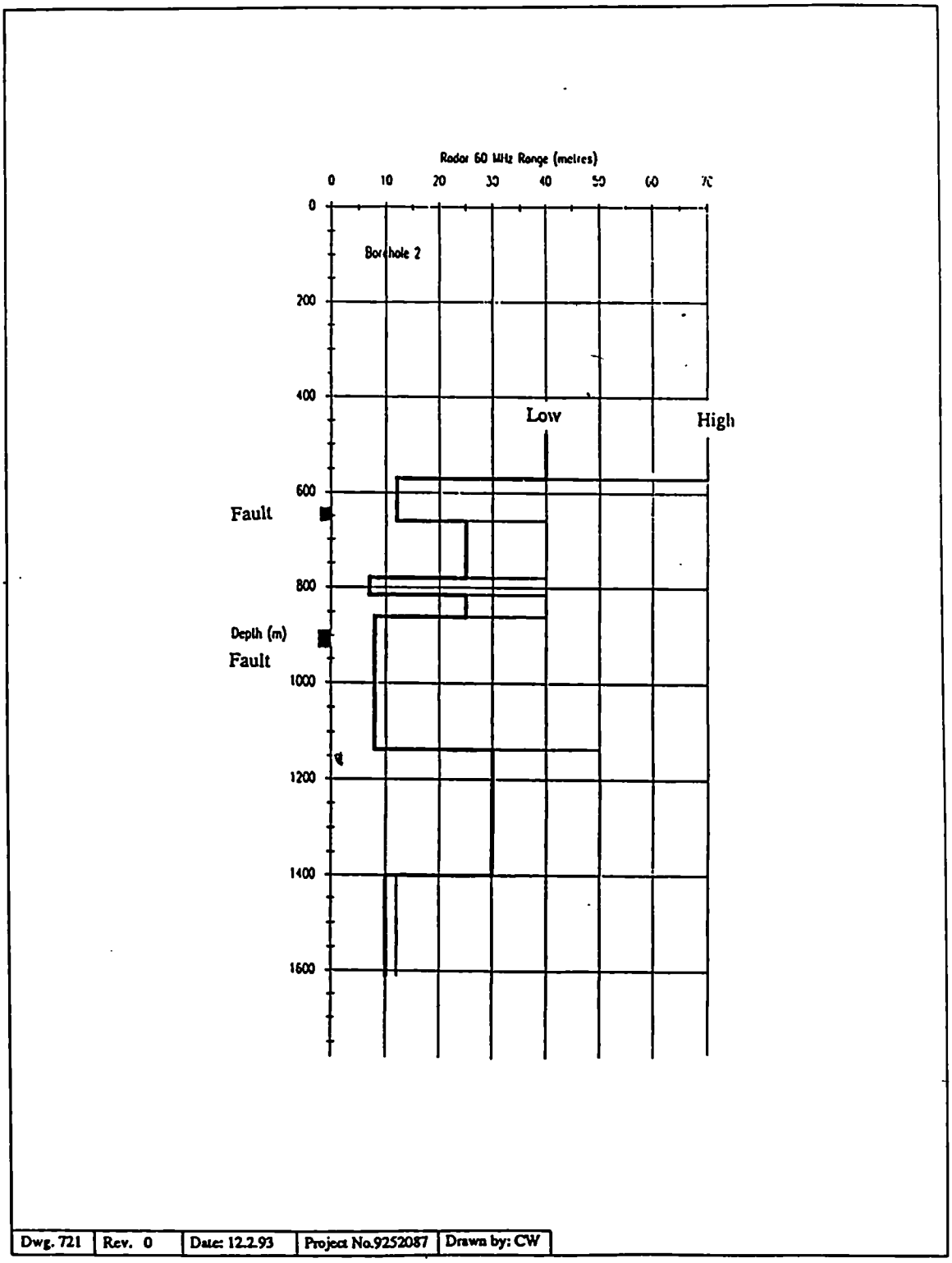

Figure 1 : Estimated radar range (60 MHz) in Borehole 2

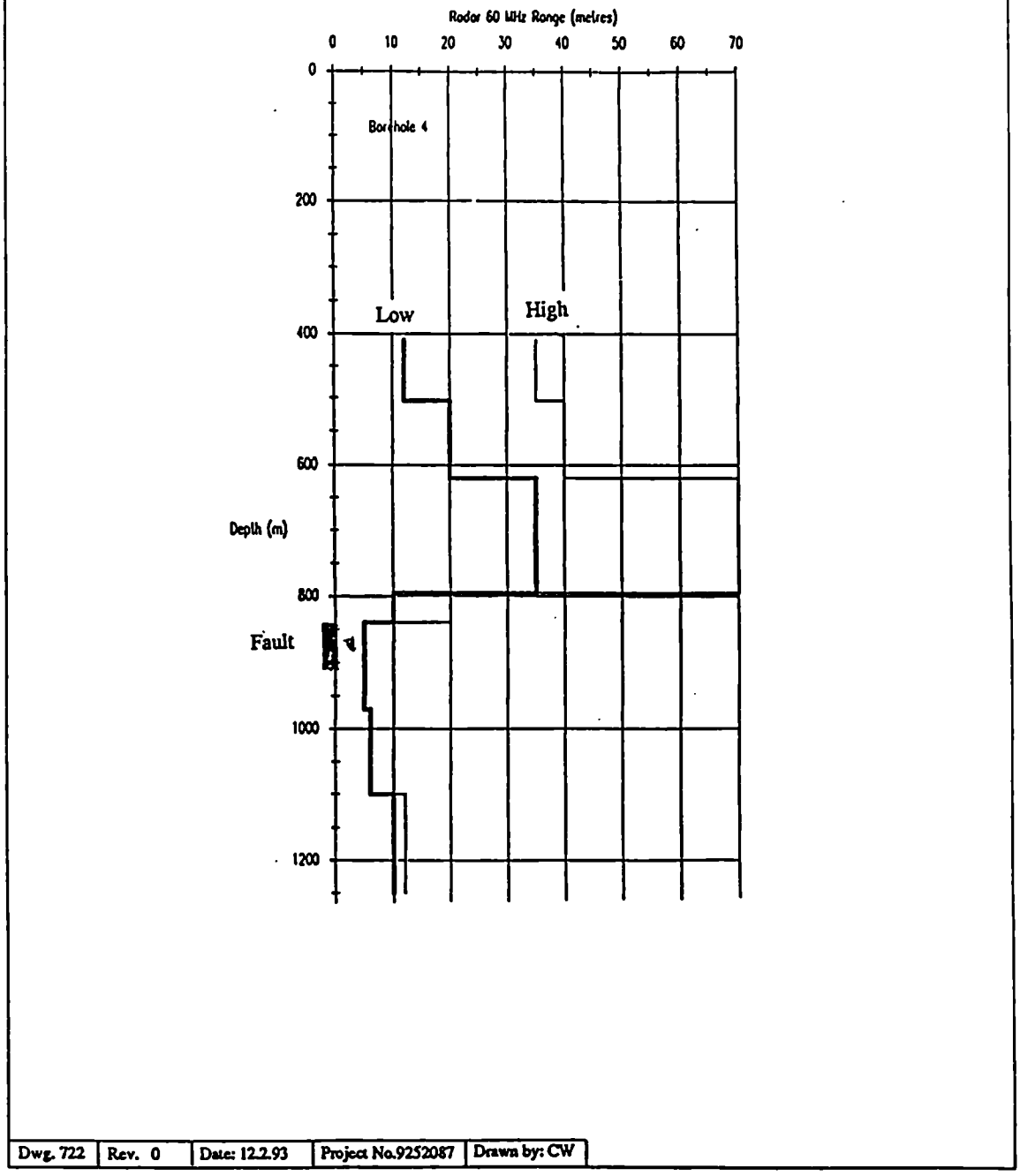

Figure2: Estimated radar range (60 MHz) in Borehole 4

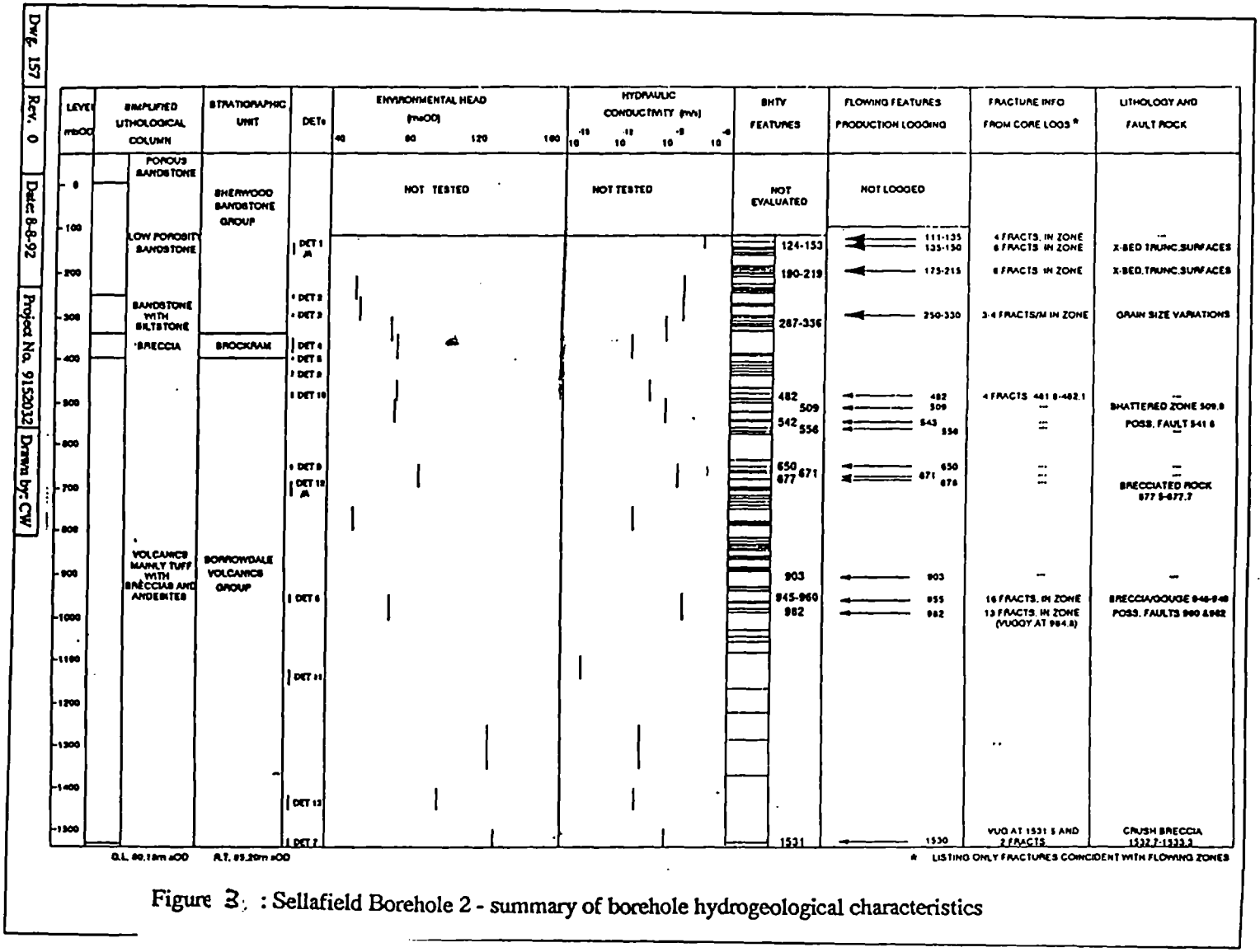

Figure 3 : Sellafield Borehole 2 - summary of borehole hydrogeological characteristics

ANNEX : List of organisms and companies participating in the programme during 1992

AEA(UKAEA)-Dounreay	AEA (UKAEA) Dounreay Nuclear Power UK-THURSO, CAITHNESS KW14 7TZ
AEA(UKAEA) Harwell	AEA (UKAEA) Harwell Laboratory Didcot UK-OXFORDSHIRE OX11 ORA
AEA(UKAEA)-Winfrith	UKAEA-AEA Technology Winfrith Techn. Centre, B44 Dorchester UK-DORSET DT2 8DH
ANDRA	Agence Nationale pour la Gestion des Déchets Radioactifs Route du Panorama Robert Schuman B.P. 38 F-92266 FONTENAY-AUX-ROSES
ARMINES	Association pour la Recherche et le Développement de Méthodes et Processus Industriels Ecole Nationale Supérieure des Mines de Paris Rue Saint Honoré 35 F-77305 FONTAINEBLEAU
ATKINS	WS Atkins International Limited Woodcote Grove, Ashley Road UK-EPSOM, Surrey KT18 5BW
BAeSEMA	BAeSEMA Systems Division 20/26 Lambs Conduit Street UK-LONDON WC1N 3LF
BAM	Bundesanstalt für Materialforschung-u-Prüfung Unter den Eichen 87 D-W1000 BERLIN 45
BATTELLE	BATTELLE Institut e.V. Am Römerhof 35 D-6000 FRANKFURT-am-MAIN
BERTIN & CIE	Bertin & Cie Centre de Bayonne Z.I. F-40220 TARNOS
BGS (NERC)	British Geological Survey Natural Environment Research Council Kingsley Dunham Centre UK-KEYWORTH, NOTTINGHAM NG12 5GG

BNFL	British Nuclear Fuel Plc Risley UK-Warrington, Cheshire WA3 6AS
BRGM	Bureau de Recherches Géologiques et Minières Service Géologique National B.P. 6009 F-45060 ORLEANS Cédex 2
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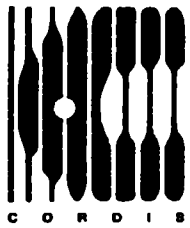

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