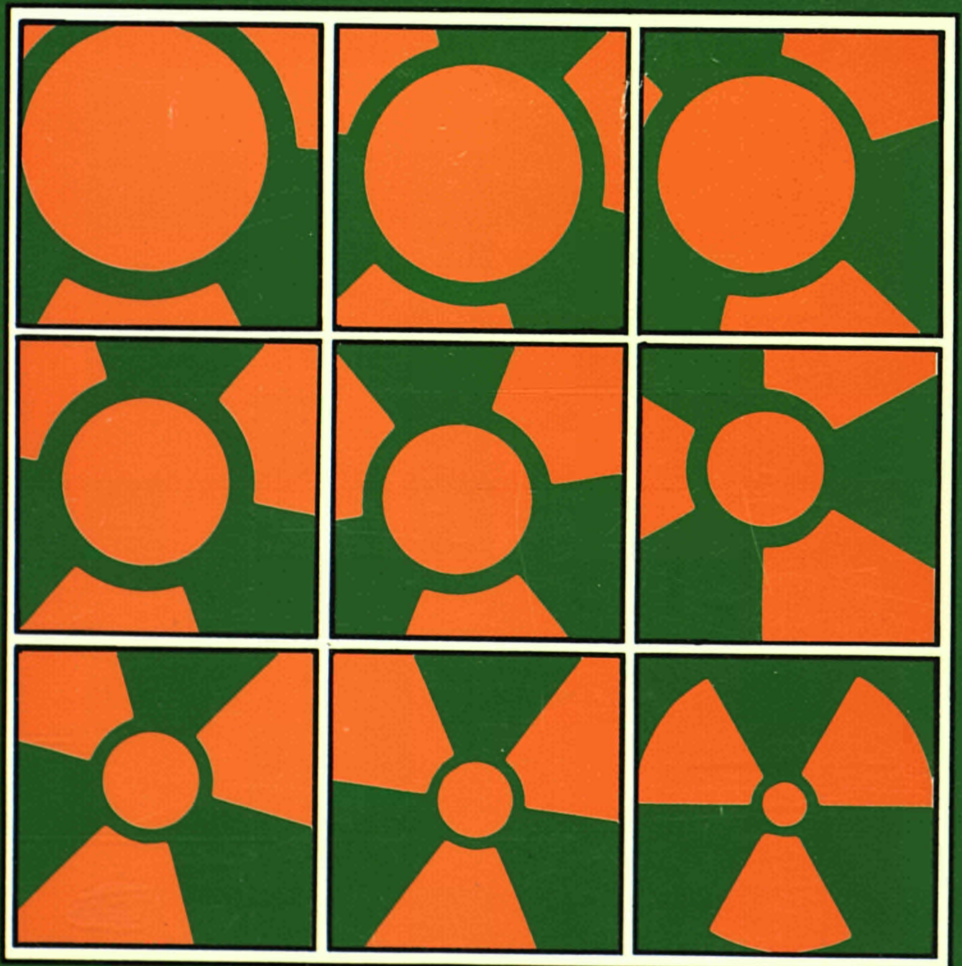
Commission of the European Communities

nuclear science
and technology

The Community's research and development programme on radioactive waste management and storage

Shared cost action

Annual progress report 1986



Report

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Commission of the European Communities

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Shared cost action

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FOREWORD

This is the first Annual Progress Report of the European Community's 1985-1989 programme of research on radioactive waste management and disposal, carried out by public organisations and private firms in the community under cost-sharing contracts with the Commission of the European Communities.

The Council of the Ministers of the European Communities adopted the programme in March 1985 (1), considering : "The use of nuclear energy inevitably involves the production of radioactive waste; it is therefore essential to implement effective solutions to guarantee the safety and protection of man and the environment against the potential risks associated with the management of such waste".

The Council also recognised that the 1980-1984 programme of research on radioactive waste management and disposal, which was the second of its kind, "has enabled a large amount of information to be obtained which it is advisable to complete and validate by the implementation of research, development and demonstration actions representing the real waste management and disposal conditions which can be expected in the future". The main publications relating to the results of this second programme are listed in reference (2), and the main results in reference (3).

The 1985-1989 programme is therefore aiming at perfecting and demonstrating a system for managing the radioactive waste produced by the nuclear industry, ensuring, at the various stages, the best possible protection of man and the environment; its contents are as follows :

A. WASTE MANAGEMENT STUDIES AND ASSOCIATED R & D ACTIONS

TASK 1 : SYSTEMS STUDIES

TASK 2 : IMPROVEMENT OF RADIOACTIVE WASTE TREATMENT AND CONDITIONING TECHNOLOGIES

TASK 3 : EVALUATION OF CONDITIONED WASTE AND QUALIFICATION OF ENGINEERED BARRIERS

TASK 4 : RESEARCH IN SUPPORT OF THE DEVELOPMENT OF DISPOSAL FACILITIES; SHALLOW BURIAL AND GEOLOGICAL DISPOSAL STUDIES

TASK 5 : SAFETY OF GEOLOGICAL DISPOSAL

TASK 6 : JOINT ELABORATION OF RADIOACTIVE WASTE MANAGEMENT POLICIES

B. CONSTRUCTION AND/OR OPERATION OF UNDERGROUND FACILITIES OPEN TO COMMUNITY JOINT ACTIVITIES (INITIALLY FOR THE THREE PROJECTS LISTED BELOW, BUT TAKING INTO ACCOUNT THAT ADDITIONAL PROPOSALS ARE LIKELY)

PROJECT 1 : PILOT UNDERGROUND FACILITY IN THE ASSE SALT MINE (FEDERAL REPUBLIC OF GERMANY)

PROJECT 2 : PILOT UNDERGROUND FACILITY IN THE ARGILLACEOUS LAYER LOCATED UNDER THE MOL NUCLEAR SITE (BELGIUM)

PROJECT 3 : EXPERIMENTAL UNDERGROUND FACILITY IN FRANCE IN A GEOLOGICAL MEDIUM OF COMPLEMENTARY NATURE

The Commission's participation to the cost of the programme amounts to 62 Million ECU for its five years duration.

The Commission is reponsible for managing the programme.

In this task, the Commission is being assisted by the Management and Co-ordination Advisory Committee "Nuclear Fission Energy - Fuel Cycle/Waste Processing and Disposal" (see annex I).

At the beginning of the 1985-1989 programme, the Commission issued a first call for research proposals dealing with tasks 2, 3, 4 and 5. Over 250 research proposals have been received at the closing date (15th June, 1985), trespassing in total several times the available budget, and only a fraction thereof could be accepted for negotiation. A second call for research proposals has been issued in 1986 with 31st October, 1986 as a closing date.

This first report, covering the period of putting the programme into action, describes the work to be carried out under the research contracts already concluded before end of 1986, as well as the initial work performed and the first results obtained.

For each contract, the Paragraph C "Progress of work and obtained results" has been prepared by the contractor, under the responsibility of the project leader. The Commission wished to express its gratitude to all scientists who have contributed to this report.

S. ORLOWSKI
Head, Nuclear Fuel Cycle Division

References

(1) Council decision of 12th March, 1985 adopting a research and development programme on the management and storage of radioactive waste (1985 to 1989)
O.J. No. L 83, 25.03.1985, p. 16

(2) Community R & D programme on radioactive waste management and storage - scientific reports - 2nd edition - report EUR 10745 EN

(3) Radioactive waste management and disposal, proceedings of the 2nd European Community Conference, Luxembourg, April 22-26, 1985
R. SIMON od. Cambridge University Press, 1986 - EUR 10163

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PART A

WASTE MANAGEMENT STUDIES AND ASSOCIATED R & D ACTIONS

CHAPTER 1

TASK No. 1 : SYSTEMS STUDIES

CHAPTER 1

TASK No. 1 : SYSTEMS STUDIES

A. Objective

To characterize the various overall management schemes for some waste categories with a view to evaluating their feasibility and availability and optimizing their radiological and economic features.

B. Research topics dealt with under the 1980-1984 programme

Studies on the evaluation and comparison of various management modes for two well defined categories of waste have been performed during the last programme :

- Solid Plutonium contaminated waste

- Alkaline liquid wash waste, arising during spent fuel reprocessing operations.

C. 1985-1989 programme

The systems studies to be carried out are related to three subjects :

- Assessment of management alternatives for reactor waste

- Assessment of management alternatives for hulls

- Comparison of waste management implications of spent fuel disposal and reprocessing.

Additionally, in order to allow comparison of management options with large differences in cost and radiation exposure, procedures are to be developed to provide a rational base for comparative evaluations. In particular, two subjects are to treated :

- Comparative weightings for cost and radiological parameters in the assessment of radioactive waste management options

- Accounting method of radiation doses due to long-lived natural radionuclides and daughters.

D. Programme implementation

The three subjects mentioned above under C were selected during the first half of 1986 with the support of an ad hoc group of national experts nominated by the competent Management and Co-ordination Advisory Committee.

At the end of 1986, several contractors have been selected on the basis of the proposal received following to the second call for research proposals issued by the Commission in August 1986.

CHAPTER 2

TASK No. 2 : IMPROVEMENT OF RADIOACTIVE WASTE TREATMENT AND CONDITIONING TECHNOLOGIES

CHAPTER 2

TASK No. 2 : IMPROVEMENT OF RADIOACTIVE WASTE TREATMENT AND CONDITIONING TECHNOLOGIES

A. Objective

To optimize waste management by minimization of the volume, reduction of discharges and promotion of new conditioning processes for some types of wastes.

B. Research topics dealt with under the 1980-1984 programme

Research on the treatment and conditioning of low- and medium-activity wastes mainly concerned :

- Denitration of highly acid waste, chemical precipitation, whether or not combined with ultrafiltration, and electrochemical reactions with a view to reducing the volume of low- and medium-activity wastes

- Mineral ion exchangers, solvent extraction and the selective precipitation of actinide and rare-earth oxalates for the separation of long-lived radionuclides from low- and medium-activity wastes.

Research on the treatment of solid waste contaminated with plutonium concerned the study and development of an incineration process making use of pyrolysis and the construction and acceptance of the following installations for experimental operation with radioactive materials :

- The ALONA pilot plant, which makes use of an acid-digestion treatment process

- A prototype high-temperature incinerator and incombustible waste can be decontaminated by special washing operations.

As regards high-activity waste (fuel claddings and dissolver residues), research was conducted on :

- The characterization of the properties of irradiated fuel claddings and dissolver residues in the case of both light water reactors and fast breeder reactors

- The conditioning of fuel claddings by a method involving embedding in matrices made of lead alloys, high-density graphite or aluminium, ceramics and improved cement

- The immobilization of the claddings by melting, chemical conversion processes or embedding in glass

- The immobilization of dissolver residues in ceramic matrices with an aluminosilicate base.

C. 1985-1989 programme

The research and other work to be carried out will cover :

a) Waste from light water reactors

- Reduction at source of radioactive waste and of discharges of radioactivity into the environment by better management of effluents and the possible use of alternative treatment processes
- Development of new waste/matrix formulae in order to keep in step with safety regulations
- Analysis of the industrial operating conditions of waste conditioning installations with a view to setting up or improving quality assurance
- Development of new methods of conditioning incineration ashes.

b) Waste from reprocessing plants, plutonium fuel fabrication plants and research centres

- Decontamination of low- and medium-activity liquid waste by means of chemical precipitation with new, highly selective precipitants (for example, organic compounds). This activity will have to include active tests on real waste
- Development of processes alternative to those already developed under the 1980-1984 programme for the decontamination of reprocessing concentrates
- Conditioning of residues or concentrates rich in actinides (and possibly in fission products) in matrices of long-term stability
- Operation of pilot installations, functioning under active conditions, for the treatment of low- and medium-activity liquid waste by means of advanced processes (membrane and electrochemical processes, etc ...)
- Operation of pilot installations, functioning under active conditions, for the decontamination of solid waste and the recovery of plutonium
- Pilot-scale application of processes, under active conditions, for the conditioning of claddings.

c) Optimization of waste management at source

Improvement of management methods based on "de minimis" criteria (segregation at source, separation, monitoring).

D. Programme implementation

20 contracts have been signed and the available information is listed thereafter.

a) Waste from light water reactor

Immobilisation in Cement of Ion Exchange Resins arising from the Purification of Reagents Used for Decontamination of Reactor Circuits

Contractor: AEE Winfrith
Contract N^{o}: F1.1W.0006.UK(H)
Work Period: July 1986 - December 1986
Project Leader: D J Lee/C G Howard

A. Objectives and Scope

The overall objective of the programme is to identify a suitable cement matrix to dispose of Organic Ion Exchange resins contaminated with decontaminating agents.

For the last five years, Low Oxidation state Metal Ion reagents (LOMI) have been used to decontaminate the 100 MW(e) Steam Generating Heavy Water Reactor at Winfrith. The use of these reagents has resulted in a dilute ionic solution containing activation products which are produced by corrosion of metallic components in the reactor. It has already been demonstrated that the amount of activity in solution can be reduced using organic ion exchangers, for example Duolite C225, a crosslinked polystyrene with sulphonic acid functional groups.

The aim of the programme at present is to show that ion exchange resins used to remove activity from decontaminating agents can be successfully immobilised in cement. To achieve this, blends of Ordinary Portland Cement (OPC) and ground granulated Blast Furnace Slag (BFS) will initially be used.

B. Work Programme

B.1. Identify suitable simulant ion exchange resin waste.
B.2. Development of formulation using a range of waste simulant to cement ratios at Laboratory scale.
B.3. Demonstrate formulation is still acceptable after scaling up to 200 litres. If necessary the formulation will be adjusted.
B.4. Establish waste volume reduction factors.
B.5. Compare and contrast methods used by other LWR Operators in Europe for decontamination of their reactor circuits and disposal of the solutions generated.
B.6. Establish a satisfactory process flow sheet for encapsulating ion exchange resins in cement.

C. Summary

Duolite C225 ion exchange resin (a crosslinked polystyrene with sulphonic acid functional groups) in the sodium form can be successfully immobilised in blended cement systems. The formulation which appears acceptable is manufactured from a 9 to 1 blend of Blast Furnace Slag and Ordinary Portland Cement containing 40% ion exchange resin by weight in the form of a slurry. The product has adequate strength for handling and shows little dimensional change with time.

Experiments show that above 50% waste loading the product becomes unstable and its strength is unacceptably low.

Changes in the metal cation have shown little effect on the properties of the product. Increasing the waste loading appears to have little effect on the hydration rate of the product.

Preliminary calculations show that a volume reduction factor of 4 is obtained by taking the active LOMI effluent, removing the activity onto the Duolite C225 and then immobilising in cement.

Introduction

In 1980 a pilot plant was constructed at Winfrith to demonstrate that organic ion exchange resins could be used to remove radioactive nuclides from the Decontaminating agent LOMI. Using a strong Cation exchange resin like Duolite C225, most of the activation products eg Fe^{59} Cr^{51}, Mn^{54}, Zn^{65} and Co^{60} plus the Vanadium from the LOMI and some of the fission products Cs^{137} and Sr^{90} can be removed from solution. Results also showed that some of the picolinate and formate from LOMI were also trapped in the resin.

Formulation Development

When developing a formulation for immobilising materials in cement a number of factors have to be considered including

1 The product in the mixing stage must be fluid enough to give a homogenised product.

2 The product must not have free water on the surface of the product (bleed) at 24 hours.

3 The product must have undergone initial hydration within 24 hours.

4 The product must have adequate strength for handling.

5 The product must be sufficiently dimensionally stable to ensure durability with time.

For any formulation a compromise of the ideal values for each parameter must be achieved. To investigate the properties of the cemented ion exchange resin a number of well established tests were used including

(i) Dimensional stability
(ii) Compressive strength
(iii) Pulse Velocity (Non-destructive determination of Compressive Strength)
(iv) Conduction Calorimetry (heat output at constant temperature)
(v) Viscometry

Small Scale Trials

A number of experiments were undertaken to determine the effects of Duolite C225 resin on the properties of cemented matrices. Most of the experiments were undertaken using the sodium form of the resin in a damp state. The slurry of the resin contained 30% water. To ensure the results produced for various BFS/OPC systems were comparable a water cement ratio of 0.33 was chosen. This was based on experience with BFS/OPC grouts that above 0.35 free water will segregate from the cement ("bleed") and below 0.30 the product becomes so viscous that it becomes unmixable in a simple mixer. For the resin based system the water cement ratios are total water including the amount included in the damp resin.

Small scale experiments using pure OPC as the matrix to immobilise the resin caused swelling at a very early stage. The effect of this swelling was that the waste form distintegrated after about a week. This occurred using a 20% loading of damp Duolite resin.

To improve on the product's properties and the waste loading, BFS was blended with OPC. BFS hydrates very slowly, however, when blended with OPC it acts as a latent hydraulic binder. Using a blend ratio of 3:1 (BFS/OPC) an improvement in waste load from 20% to 30% loading was obtained; however, at 30% the product was very fragile. If a blend ratio of 9:1 (BFS:OPC) is used a further improvement is achieved. At this blend ratio at least 50% resin can be incorporated in cement without incurring expansion which causes the product to crumble.

Scale up experiment

A 20 litre mix was undertaken to confirm that the product properties were acceptable based on the small scale formulation studies. Using a 40% waste loading and a blend ratio of 9:1 (BFS:OPC) a number of samples were manufactured for testing. At 90 days the compressive strength of 1 litre cubes was around 10 Nmm^{-2} and the prisms (286 mm x 25 mm x 25 mm) showed no dimensional change after 90 days.

A small sample of the mix was used to determine that the viscosity of the product was within an acceptable limit. The product underwent hydration within 10 hours.

Further Small Scale Work

Small scale experiments also showed that increasing the resin loading increased the viscosity of the product measured after mixing. Resin loading had little effect on the hydration rate of the product.

Experiments were undertaken to determine the effect of changing the cation in the resin. Very little effect was observed on the hydration properties or the dimensional stability of the product, if the sodium was replaced with Cs^+ or Ca^{2+} prior to mixing with cement blends. If however the H^+ form of the resin was used, rapid hydration occurred due to an exothermic reaction betweeen the resin and the cement blend. Hydrogen sulphide was also generated from the reaction between the acidic proton from the resin and the Sulphides in BFS.

Volume Reduction Factor

At present each decontamination operation at the Winfrith reactor requires $4M^3$ of LOMI. Most of the activity can be removed if the liquor is passed through a total of approximately 600 litres of resin. If this material was immobilised in cement it would take up a volume of 1,000 litres and weigh approximately 1,500 Kg. This gives a volume reduction factor of 4 assuming the effluent from the ion exchange resin column is considered non-radioactive.

Modified Sulfur Cement: a low porosity encapsulating material for LLW, MLW and alpha Wastes

Contractor: ECN, Petten, The Netherlands
Contract N°: FI1W/0008
Duration of Contract: June 1986-July 1988
Project Leader: A. van Dalen

A. Objectives and Scope

Modified sulfur cement is a material comparable in strength and hardness to concrete products with a low porosity and resistant to attack by salts and acids. The handling of modified sulfur cement is comparable with bitumen: melting, and solidifying by cooling. This material has promising features regarding better retention of mobile radionuclides compared with ordinary concrete products by low porosity. High strength should prevent swelling of encapsulated salt wastes as in the case of bitumen. The restrictions on the use are about the same as for bitumen: heat producing waste is to be avoided; it is burnable but does not sustain fire.

Modified sulfur cement is in use in plants as floors and ponds to replace or protect concrete against attack by salts and acids. It has been proposed as a backfill material in shallow land burial but it has never been realized.

B. WORK PROGRAMME

For a critical judgement of modified sulfur cement as encapsulating material data are lacking for:

B.1. Radiation resistance.
B.2. Maximum loading capacity of modified sulfur cement with ashes, sludges, spent ion-exchangers regarding strength and leachability.
B.3. Porosity regarding tritiated water.
B.4. Reactions with metal components of discarded equipment to be encasulated.

C. Progress of Work and obtained results

This year report covers the investigations carried out from the start of the contract on June 1st, 1986 till December 31, 1986 and was devoted to the items given in the time schedule of the contract for 1986: sample preparation and gamma irradiations for compressive strength.

Modified Sulfur Cement is a product developed by the US Bureau of Mines. The existence of the two allotropic forms of elemental sulfur is a drawback for the use of sulfur as a construction material. Below the temperature of 96 °C the rhombic form is stable, and between 96 °C and the melting point the monoclinic form. The higher density of the rhombic form results in disintegration of a sulfur ingot by recrystallization of the monoclinic form. The product Modified Sulfur (MS) cement is manufactured by reacting sulfur with cyclopentadien.

According to the description a cyclopentadien molecule is added to S_8 molecule in the liquid phase in the temperature range of 120-150 °C. On cooling the MS cement forms an amorphous product at 120 °C. The solid material is stable and no allotropic forms are known. This material in the form of chips obtained from Chemical Enterprises, Inc. Houston, Texas U.S.A. is used in our experiments.

Modified sulfur in liquid form resembles elemental sulfur: the viscosity is lowest just above the melting temperature of 120 °C. Beyond 150 °C the viscosity increases rapidly. At temperatures above 220 °C the molten mass ignites in air. The rate of burning is slow with small blue flames and the fire can be extinguished very easily by adding cold material, even MS, or by closing the vessel to cut off the air.

This behaviour has consequences for the preparation of simulated waste materials on laboratory scale: the workability of mixtures of salts, ashes with MS is best at temperatures between 120 and 140 °C. The solidifying temperature of the mixtures is 120 °C so the temperature difference between the molten preparation and the solid material is very small. For the small ingot to be used on laboratory scale the rate of solidification is too fast when the liquid is poured in a cold form even in the case of a wooden form with low heat transfer. The cooling starts very quick at the walls resulting in a depression in the middle of the ingot, and small air bubbles are trapped in the material. A better way of preparation is to pour the molten material in a prewarmed mould of glass tubes and to cool slowly in an oven preheated to 130 °C. The smooth cylinders can be pushed out off the glass cylinders. The cylinders have a diameter of 2 cm and a height of 5 cm. This procedure of slow cooling of the samples has been chosen to simulate the much slower cooling rates of large ingots.

Good preparations were obtained of MS with chalk (calciumcarbonate), silicates (dune sand, diatomite), pulverized fly ash, borate salts and lead iodide. The incorporation of ion-exchange resins is less easy: during the preparation the ion-exchange beads are heated and lose the main part of their adsorbed water. During a few days in humid air or a few hours in water the cylinders disintegrate completely. Ion-exchange beads on the outside of the cylinder take up again water, swell,and crack the outer layer and so on. This is in accordance with the findings at Brookhaven National Laboratory /1/. By covering the cylinder with a layer of 2-3 mm of MS this destructive action is avoided, but breaking or cracks in the cylinder will reactivate the disintegration. Another way of incorporating ion-exchangers has been discovered: prolonged heating of the mixture results in the development of hydrogensulfide; the ion-exchange beads darken and loose their property of water uptake and swelling. Both cation and anion exchangers react in the same way. A cation exchanger loaded with Co was treated and a qualitative leaching experiment indicated the formation of CoS an insoluble compound. A sample of simulated borate waste in MS cement was placed in water and the pH was recorded. The qualitative interpretation was that only a few microns of the cylinder surface gave off the soluble compound and the cylindric form does not show traces of attack.

Samples of MS cement with fly ash and sand in a ratio of 3:2:4 have been prepared for the measurement of radiation stability of the MS cement with inert components. The compressive strength was measured to have an indication of the radiation effect. The results were 0 MGy - 43 MPa; 2.6 MGy - 41 MPa; 6.1 MGy - 50 MPa; 16 MGy - 55 MPa. The doserate was 30 kGy/h.• It was noted that the unirradiated samples reacted in a slightly more plastic way during the compression test. The irradiated samples were harder and scattered into pieces at the breaking point. These results indicate that MS cement is sufficient radiation resistant to be used as encapsulating material for non-heat producing radioactive waste.

The water uptake of the same type of samples has been measured now for 100 days and amounts to 0.3 % of the sample weight.

Reference

/1/ ARNOLD, George, et al. Brookhaven National Laboratory Report BNL-51923(1985), Modified Sulfur Cement Solidification of low-level Wastes.

The treatment of radioactive effluents of PWR - nuclear power plants by centrifugation

Contractor : Laborelec (Belgium)

Contract N° : FI 1 W - 0007 - B (GDF)

Duration of contract : 18 months

Project leader : R. Roofthooft

A. Objectives and scope

The objective of this study is to develop a treatment system for the radioactive waste solutions which are not recovered of the Tihange nuclear power plant. The activity should be absorbed on a solid phase which will be separated from the liquid by centrifugation. The procedure should be applied to all types of liquid wastes except the primary effluents from which boric acid is recovered and which is treated by evaporation.

This program can be seen as the continuation of a previous study on a continuous floculation and settling system in the nuclear station of Chooz.

The centrifugation should lead to a more compact system. Before the centrifugation a batch type floculator will be used. This system seems to be more flexible and adaptable to different waste types. It could also decrease the amount of reagents and hence the amount of sludge.

B. Work program

B.1 Systematic analysis of the effluents in unit 2 of Tihange.
B.2 Study of a procedure to precipitate Co-58 and Co-60.
B.3 Caracterisation of the flocs.
B.4 Influence of chemical composition on the floculation.
B.5 Centrifugation tests.
B.6 Determination of the optimal conditions for a continuous centrifugation system.
B.7 Control of the grain size of particles to be eliminated.
B.8 Pilot plant tests on several effluents.

C. Progress of work and obtained results

Summary

The composition of the effluents of Tihange 2 has been examined from a chemical and radiochemical point of view. Two types of effluents are taken into account : drains and service waters. This examination shows a wide variety in chemical pollution and radioactive contamination although generally fission products are absent.

The initial procedure for the precipitation of Co-isotopes has been simplified and recirculation of the precipitate can be realized several times.

The pilot plant centrifugation tests will be delayed due to installation problems.

Progress and results

Composition of the effluents

The chemical composition and the γ-activity of drains and service waters are given in Table I.
The γ-spectrometry shows that generally fission products are absent. The main isotopes are always corrosion products, particulary ^{58}Co, ^{60}Co, ^{54}Mn and ^{124}Sb. This is due to the good behaviour of the nuclear fuel elements and the efficiency of the primary clean-up.

Treatment of the effluents

This study is a continuation of the study performed on a floculation-settling plant in Chooz. In the present case however the use of double ferrocyanides is not necessary as there are no fission products such as Cs to eliminate.

It is also an aim to reduce the surface requirements for the treatment and for this reason a compact vertical centrifugal machine with plates has been chosen. The proposed flow sheet is shown in figure 1.

In order to reduce the volume of waste the sludge will be recycled.

The tests were started in the laboratory with the following procedure :

- acidification of the effluent to solubilise Co-isotopes which can be present as colloids (pH $\simeq$ 2)
- addition of Co-carrier
- addition of Fe^{+++}
- increase pH to 9,3
- addition of a floculant.

This procedure has given excellent results on several effluents in the beginning of September '86.

However during the decennial revision of Tihange 1 more than 1000 persons have been working in the controlled area. This has given rise to a huge production of laundry waste water, which was sent to the tanks of Tihange 2 for treatment. On some occasions this laundry waste has been mixed with residual drains and service waters and this has given some problems in our tests. With a concentration of 4,2 ppm PO_4 and a "milky" colour the decontamination factor for Co decreases to a value of about 4.

Afterwards came a period of high activity due to effluents from the primary circuit (activity up to 17.200 MBq/m^3). The procedure described before gave only a DF of 5,4. Good results (a significant DF) have been achieved by using $KMnO_4$ at pH 4 as can be seen from Table II.

It should be noted however that the discharge limit to the river is 18,5 MBq/m^3 (total γ-activity).

The same type of treatment on an effluent containing important activities of ^{124}Sb gave insufficient results due to a poor DF for ^{124}Sb (DF < 2).

This pollution however is exceptional.

Tests have continued on service waters with lower activity (about 100 MBq/m^3) and replacing Fe^{+++} by Fe^{++} added before the Co-carrier. In this case a DF of 250 has been obtained for ^{58}Co and 5,6 for ^{124}Sb (DF ~ 20 for total γ-activity). In order to examine the influence of laundry waste on the treatment of drains a series of tests has been realized. In these tests the influence of different parameters has been measured :

- use of Fe^{++} or Fe^{+++}
- doses of Fe^{++} and Fe^{+++}
- necessity of using Co^{++} as a carrier
- dose of detergents
- re-use of flocs.

The results of these tests are :

- Co-carrier is not necessary
- Fe^{+++} gives better results than Fe^{++}
- a dose of 50 ppm of Fe^{+++} is sufficient
- floc can be re-used several times if the solution is acidified first
- the DF decreases when the ratio service water/drains increases.

As a result of these tests a new simplified procedure is adopted :

- acidification to pH 2,2
- addition of Fe^{+++} 50 ppm
- increase of pH to 8,5
- floc re-used with acidification (with or without addition of another 10 ppm of Fe^{+++}).

The addition of another 10 ppm of Fe^{+++} at each re-use of floc has already allowed 9 recyclings. The activity of the effluent remains below the limit of discharge.

Without the addition of 10 ppm of Fe^{+++} at each recycling of the floc, 6 treatments have been realized with an effluent activity below the discharge limit if the overflow is treated by centrifugation.

Program

The program for the next future is to decrease the amount of Fe^{+++} and to identify the agents thare are responsible for the poor decontamination in some cases (complexing agents ?).

The adsorption capacity of activated coal for detergents will be measured.

Table I

Chemical composition and γ-activity of drains and service waters in Tihange 2 (year 1986)

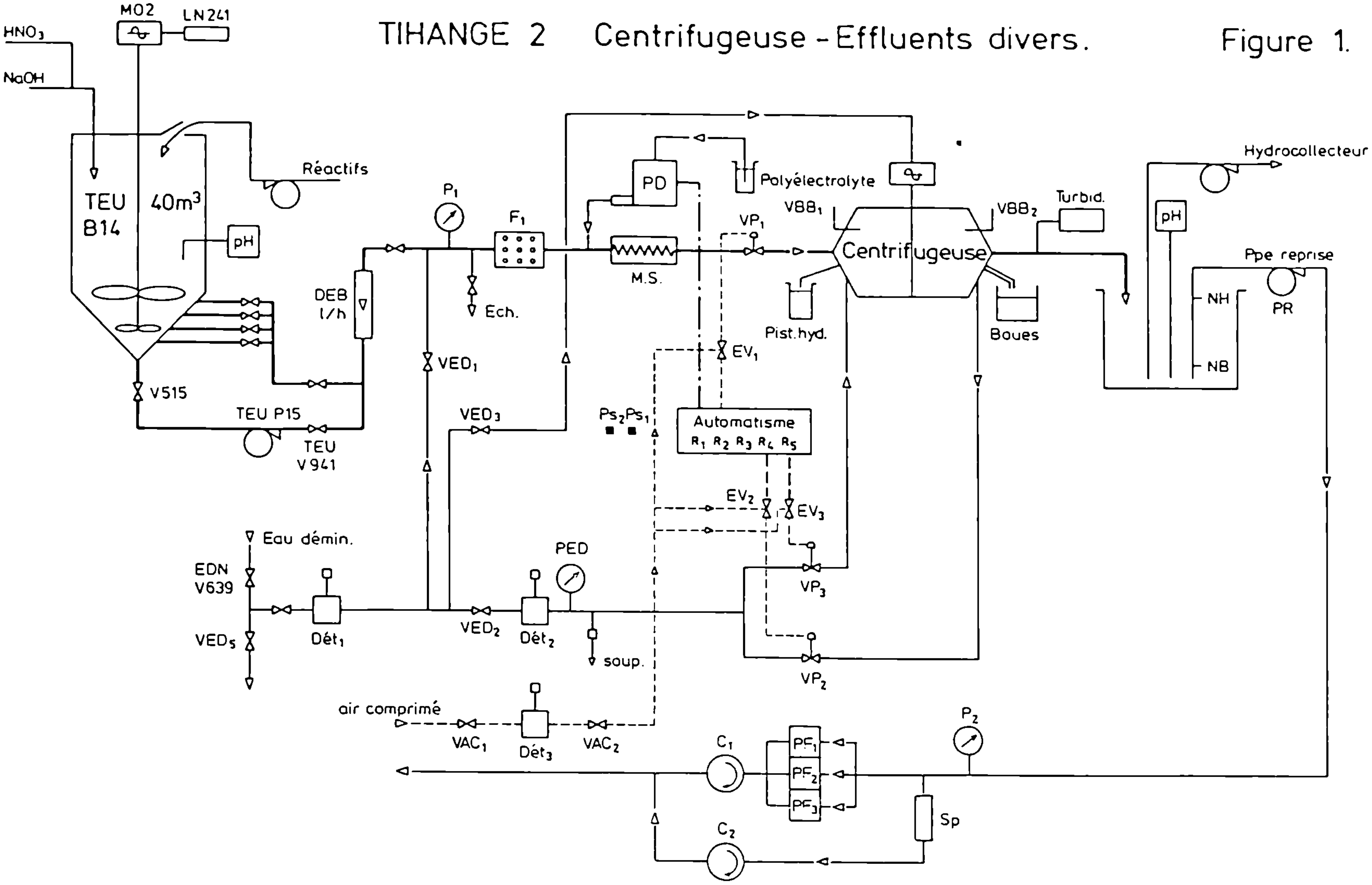
	Drains	Service waters
pH	6,25 - 9,35	2,5 - 10,5 (mostly 6,5 - 9)
B ppm	20 - 1760	5 - 2000 (mostly 5 - 100)
≡		
PO_4 ppm	< 0,1 - 3,2	0,2 - 45
Cl^- ppm	0,08 - 80	1 - 100
total γ-act. MBq/m^3	50 - 18500	Bg - 30.000 (mostly BG - 20)

Table II

Decontamination achieved by using $KMnO_4$ on highly active effluents (all activities in MBq/m^3)

Initial activity		Final activity		DF	
Total γ	^{58}Co	Total γ	^{58}Co	Total γ	^{58}Co
2322	1469	35	12	66	122
17159	8510	66	13	260	654

TIHANGE 2 Centrifugeuse - Effluents divers. Figure 1.



Study of the industrial operation of plants for the solidification of radioactive waste with regard to quality assurance

Contractor : NUKEM GmbH, D-6450 Hanau 11, Fed. Rep. of. Germany

Contract No : FI-1-W-0009-D (B)

Working period : 01.01.-31.12.1986

Project leader : Dr. H. Brunner

A. Objectives and Scope

According to German proposals, which have been developed by the Physikalisch Technische Bundesanstalt, quality control of radioactive waste - to be deposited in the KONRAD-mine - shall be provided by qualification of waste treatment systems and process control.

Purpose of the R+D-programme is the investigation of the industrial operation of four different waste treatment plants with regard to quality control: compactor, evaporator/dryer, mobile cementation unit (MOWA) and stationary cementation system (continuous process). Within the programme the application of proposed controls at start up and active operation shall be systematically investigated. Expected results are the realisation of the proposed quality assurance procedures, which cover the commonly used waste treatment systems, and technical improvements of process control.

B. Work programme

B.1. Process qualification and product control

- Establishment of the actual status
- Development of qualification concepts

B.2. Conditioning of radioactive wastes

- Participation at cold/hot function tests and operation
- Data collection and comparison with process parameters

B.3. Additional investigations

- Cold test operations with laboratory/pilot plants with not standardized wastes
- Waste characterization
- Adjustment of process

B.4. Comparison of data and establishment

C. Prorgress of work and obtained results

State of advancement

According to german proposals, developed by the Physikalisch-Technische Bundesanstalt (PTB), the quality control of wastes to be disposed in the KONRAD mine shall be provided by qualification of waste treatment systems and quality control. Content of the reported R+D-program is the investigation of four different waste treatment plants with regard to the quality control. In the reported period, we performed the work for a high force compactor (HFC). The HFC was constructed by NUKEM. We developed and performed a program for the inactive testing.

Progress and results (B.1.)

The waste produced by the HFC (fig. 1) belongs to the KONRAD waste product group 06 "Compacted waste". This wastes have to fulfill the acceptance criteria listed in tab. 1. Essential for the HFC is a miniumum pressure of 30 MPa.

The HFC was constructed for the compaction of 180-l-drums. The resulting pellets can be stored in 200-l-drums. The automatic routine operation is drum charging, compaction and drum discharging. The instrumentation consists of manometer, stamp distance measurement, balance and pellet height measurement. Integrated in the standard software are programs for misoperations like unexact drum positioning or sticking of pellets in the lower die.

The experiments for the inactive testing have been performed with the most common compactable waste simulates.

- metals (cuttings, trash)
- glass (glass wool, bottles)
- wood (bars, facings)
- plastics (glove box waste)
- paper (paper box waste, packagings)
- ash, slag
- Kieselgur

All simulates have been controlled on their humidity, the weight and the bulk densities. During each compaction the pressure, pressure time, released material (dust, water, gas) have been controlled. For each drum a pressure/stamp-distance diagram was plotted. The weight and height of each produced pellet was measured within 1 h and after 7 days after the compaction.

The results are summarized in tab. 2. The maximum pressure of the HFC was 1500 t resp. 73 Mpa. For each drum a pressure time of 5 - 10 s was sufficient to reach the maximum volume reduction. All pellets were size stable. The volume reduction factors are depending on the waste material and were between 1.5 (slag) - 16 (glass wool). The final densities of the pellets were only depending on the material, not on the type of the raw waste, and reached about 60 % of the theoretical material density:

- metals	3.7 - 3.9 g/cm^3
- glass, slag	2.0 - 2.1 g/cm^3
- ash, Kieselgur	1.2 - 1.6 g/cm^3
- wood	0.9 - 1.1 g/cm^3

In some cases, a release of liquids was detected (wood bars: 4.5 kg H_2O; paper: 0,8 kg H_2O; metal cuttings: 1.7 kg oil).

The results show a sufficient quality of the final product. According to the high pressure of 73 Mpa, a release of liquids under final storage conditions (30 Mpa) can be excluded.

Table 1

Results from the inactive testing of the high force compactor

- Pressure time : 5 - 10 sec
- all pellets had some cm backspring
- all pellets are size-stable
- volume reduction factors and final densities (g/cm^3)

. metal cuttings	: 12	3.7
. metal trash	: 4.7 - 6.6	3.9
. glass bottles	: 5.0	2.1
. glass wool	: 14 - 16	2.0
. wood bars	: 2.5	1.1
. wood facings	: 2.6	0.9
. plastics	: 2.5	1.1
. paper	: 10 - 12	1.8
. ash	: 2.2	1.6
. slag	: 1.5	2.0
. Kieselgur	: 3.7	1.2
. empty drum	: 32	2.8

- release of liquids
  - wood bars (H_2O, 4.5 kg)
  - paper (H_2O, 0.8 kg)
  - metal cuttings (oil, 1.7 kg)

1	compactor case
2	lid
3	control stamp
4	compactor stamp
5	cover
6	cover lift cylinder
7	door
8	door
9	lower die
10	stamp plate
11	compaction plate
12	drum charge
13	drum discharge
14	positioning

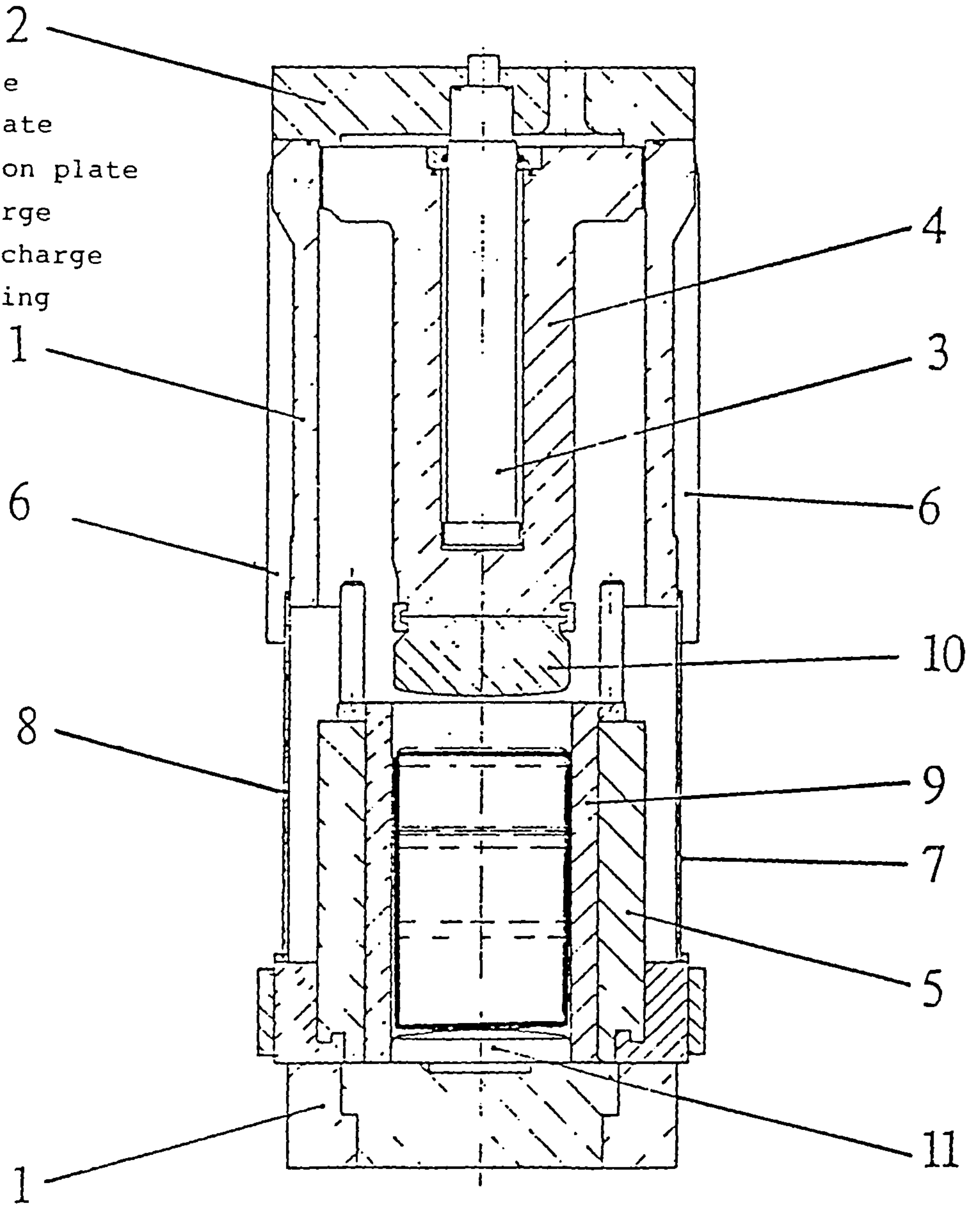


Fig. 1: High Force Compactor (HIFOC)

Conditioning of ashes from combustion plants in special melting furnaces

Contractor : NUKEM GmbH, D-6450 Hanau 11, Fed. Rep. of Germany

Contract No: : FI-1-W-0010-D (B)

Working Period : 01.01.-31.12.1986

Project leader : Dr. G. Klein

A. Objectives and Scope

Ashes from nuclear combustion plants are actually treated by cementation or they are shipped directly to intermediate storage without conditioning. For melting or slaging of these ashes R+D-programmes were performed, but nevertheless up to now doesn't exist an unexpensive simple process.

Scope of our work is the qualification of a simple and unexpensive melting furnace in order to get products of high quality for final disposal. Special item will be the quality assurance.

B. Work programme

B.1. Aquisition of basis data

- Composition of expected ashes
- Suitability and need of additives
- Conventional process experience
- Suitability of conventional furnaces
- Extent of changes in construction
- Cost analysis

B.2. Construction of a pilot plant

B.3. Laboratory experiments

- Testing of process parameters
- Characterisation of final products

C. Progress of work and obtained results

State of advancement

During the reported period the work started with a literature survey and contacts to furnace manufacturers in order to get basis data. We used the literature data systems DATA-STAR, STN and INKA to get information about the raw wastes and the composition of the resulting ashes, also about the types of furnaces used in conventional and radioactive waste combustion. Our own experiments started with melting tests of selected simulated ashes in a laboratory oven.

Progress and results

C. 1. Aquisition of basis data (B. 1.)

C.1.1. Type of raw waste

In nuclear facilities solid and liquid wastes are given to combustion. The solid wastes are wood, paper and polymer materials (PVC, rubber, resins etc.) the liquids in general organic solvents (TBP) and contaminated oils. The not burnable content with < 5 % is comparable low because of waste selection.

C.1.2. Composition of ashes

In the literature we detected totally the analytical data of 6 different ashes (see tab. 1 and 2). Depending on the different raw wastes, especially the content of TiO_2 and MgO (filler materials of paper or filters) is higher compared with domestic ashes, the Fe_2O_3 content is lower. The composition of TBP-ash is naturally different, and consists mainly of Phosphate salts. The chemical character of the ashes is acid, therefore the careful selection of oven materials is important.

C.1.3. Types of processes and furnaces

In the conventional industrie similar processes are used in the glass and ceramic production and in the domestic waste combustion. The furnaces used are e.g. tank furnaces or tunnel kilns, the processes are continuous. The heating at glass/ceramic production is done in general by direct current resistance, sometimes like at domestic waste combustion by support flames. The throughputs are some tons per day, which is not comparable to nuclear waste generation. For the nuclear use two parameters are important:

- offgas treatment
- volume reduction

Therefore the selection of furnaces resp. melting processes has to be performed in order to avoid large off gas volumes (connection with combustion off gas line) and secondary wastes like melting containers or furnace wall materials. Two types are common in nuclear use:

- In-can-melting
- Melting/Filling.

The In-can-melting takes place directly in a possible storage container. To avoid off gas problems, the electrical heating is effective (inductive or direct resistance). Because of the metal containers the maximum temp. is limited to 1050 °C. The Melting/Filling is independent from the storage container and can work at higher temperatures, but with the same type of heating the melting containment has to consist of graphite ceramic. This creates a significant corrosion.

C.2. Construction of a pilot plant (B. 2.)

The decision for a prototype process resp. furnace is depending on the actual german situation and on competing ash treatment processes like the high force compaction. It will be part of the next report.

C. 3. Lab experiments (B. 3.)

According to table 1 we simulated this 6 types of ashes by grinded oxydes or salts. Actually we detected the melting temperatures and we started with addition of compounds like glass formers resp. network transformers (Si^{4+}, B^{3+}, P^{5+}, Al^{3+}), to reduce the melting temperature.

All simulated ashes had melting points < 1300 °C. After addition of maximum 20 weight % of Sodium borates the melting points dropped below 1100 °C. The work is actually going on. The first results can be reported in the next period.

TABLE 1

Selected ash simulates (literature)

1. Battelle PNL	Glove box wastes
2. CEA Marcoule	PVC, rubber; low SiO_2 content
3. Rocky Flats	average waste; high TiO_2 content
4. Rocky Flats	combustion of average waste simulate, low SiO_2 content
5. Rocky Flats	HEPA-filter ash, high MgO content
6. KFA Jülich	average waste

TABLE 2

Composition of ashes of silid burnable radioactive waste

COMPONENT	CONTENT	REMARK
SiO_2	12 - 40	
Al_2O_3	12 - 35	
CaO	0 - 30	also as $CaCl_2$, $CaSO_4$
Fe_2O_3	0 - 8	
TiO_2	0 - 25	
MgO	0 - 34	
Na_2O	1 - 16	also as NaCl, Na_2CO_3, Na_2SO_4
K_2O	0 - 1	
C	0 - 12	
P_2O_5	0 - 5	also as Na_3PO_4
Cl	0 - 12	
SO_3	0 - 1.5	
others		ZnO_2, BaO, B_2O_3, Cr_2O_3 u.a.

2 b) Waste from reprocessing plants, Plutonium fuel fabrication plants, and research centres

TREATMENT OF RADIOACTIVE WASTES BY A COMBINATION OF PRECIPITATION AND CROSSFLOW MEMBRANE FILTRATION

Contactor: UKAEA, AERE Harwell; UK.
Contract No: FI. 1W.0017 UK(H)
Duration of contract: July 1986 - December 1989.
Project Leaders: R G Gutman/I W Cumming/A D Turner.

A. OBJECTIVES AND SCOPE

The overall objective of this programme is to improve the design and operation of membrane plant for radioactive waste treatment by the incorporation of new process developments into an existing active ultrafiltration pilot plant facility, and by evaluation of performance during processing of a real radwaste.

B. WORK PROGRAMME

B1. Tests with new precipitation agents.
B2. Tests with alternative membranes.
B3. Tests with electrically assisted process.
B4. Tests with ancillary equipment items.
B5. Design of advanced prototype unit.
B6. Operation of advanced prototype unit.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Summary

During the first six months of this new R&D programme, two new types of inorganic microfiltration membrane have been examined in a pilot plant facility processing Harwell site radioactive waste. The new membranes were shown to give enhanced flux compared to ultrafiltration membranes and similar α removal efficiency to the ultrafilters. The effect on β/γ removal efficiency from Harwell site waste of the addition of different compounds prior to ultrafiltration has also been assessed in small scale experiments. Activated carbon was able to remove Co^{60}, but only at high dosages; copper ferrocyanide enhanced both Co^{60} and Cs^{137} removal at low dosages. Laboratory experiments have also been carried out in which electrical fields were applied in order to enhance membrane performance. In these experiments tubular and planar membranes were used in combination with either continuous or pulsed electrical fields.

Progress and Results

1. Introduction

During the first 5 months of the programme, new process developments have been assessed both through extensive initial laboratory scale tests and also by short-term tests in the pilot plant facility.

2. Small Scale Ultrafiltration Experiments (B1)

Small scale experiments using a single Carbosep tubular membrane have been performed with Harwell site low level radioactive waste, in order to examine the effect of effluent chemical pretreatment, by pH adjustment and addition of various precipitates, on β/γ removal efficiency. The removal of Cs^{137} and Co^{60} was found to be enhanced at high pH, and could be further increased by the addition of a copper ferrocyanide precipitate, at dosages equivalent to $24 g/m^3$ of ferrocyanide ions. Activated carbon appeared much less attractive as a selective activity absorbing material, since a dosage of $40 kg/m^3$ was required to achieve 99% removal of Co^{60}.

Although Cs^{137} removal efficiencies of up to 90% were achieved by the addition of copper ferrocyanide to the waste, these values were much less than those achieved previously during pilot scale tests with the site low level waste, and further experiments are under way to determine whether this difference is related to the different volume reduction factor during the two processes.

Overall β removal efficiency during ultrafiltration of the low level waste has generally been found to be lower than the overall γ removal efficiency. The difference may be due to the presence of Sr^{90} in the waste, and its relatively poor removal during the existing ultra- filtration decontamination process.

3. Pilot Plant Experiments (B2)

The original ultrafiltration pilot plant(1), which started operation on Harwell low level waste in 1984 during the previous CEC radwaste R&D programme, has now been modified so that it can be used as a test bed to examine the performance of a variety of alternatives to the Carbosep 20,000 molecular weight cut-off M4 ultrafiltration membrane studied previously. The changes to the plant have meant that higher processing rates, higher crossflow rates and a wider range of operating pressures can now be studied in the plant.

So far two alternative types of membrane have been examined. A more "open" Carbosep microfiltration membrane, which has a pore size rating of about 0.08μm and about twice the water permeability of the M4 membranes, fouled rapidly on Harwell low level waste. As a result enhanced processing rates could only be sustained for a few hours. In contrast, for a Ceraflo alumina 0.2μm membrane, fluxes of over 7m/d could be maintained for at least 90 hours as shown in Figure 1. There was some indication that fouling of the Ceraflo membrane was reduced by the formation of a ferric hydroxide precipitate in the waste, and also by operation of the Ceraflo membrane at low transmembrane pressure.

4. Electrically Enhanced Membrane Processes (B3)

The electrical enhancement of crossflow micro and ultrafiltration systems has already been demonstrated at a bench top scale to increase permeation rate and solid/liquid separation factors.

In electrokinetic dewatering, an electric field is applied across a non-conducting membrane. Not only does this induce an increased permeation rate by electro-osmosis, but at the same time an electrophoretic effect helps to reduce membrane fouling and increases permeate clarity. This has been demonstrated during the dewatering to 20-40% of Harwell low level gravity settled slurries at planar 100cm^2 cotton, fibre glass and zirconia microfiltration membranes.

A ten-fold scaled-up rig (planar membrane area 0.1m^2) has been constructed and is currently being commissioned. Process rates of slurry feed up to 1.3m^3 per day should be achieved for thickening at a permeate rate of 0.1mh^{-1}. A recycle flow up to 100L/min^{-1} (corresponding to a slurry velocity of approximately 5ms^{-1} through the cell) is provided by a Monopump SAE12. Automatic control by a microprocessor is achieved by valve and auxiliary pump operation triggered by sensors in the system.

Some parameters affecting the electrokinetic dewatering of ferric hydroxide slurries at Ceraver tubular alumina membranes with porosities of 0.2, 1.2 and 5μm have also been investigated. The electric field was applied across the tube wall between an axial rod and an outer cylindrical electrode. Using a transmembrane pressure of 1 bar, the 0.2µm porosity gave the highest permeation rate, with a further enhancement from $0.5mh^{-1}$ bar^{-1} to $0.7mh^{-1}$ bar^{-1} in the presence of an electric field. At lower pressures, the electric field improved the permeation rate for all porosities. Experiments on the 0.2µm porosity membrane indicated that this increase in performance is dependent on the current and voltage applied.

Pulsed field electro-osmosis has also shown promise - further improving permeation rates at thin membranes (e.g. cotton). Experiments conducted using 1% $Fe(OH)_3$ showed that the improvement increased with minute period square wave), an additional improvement of 30% was obtained compared with the equivalent constant current process. Other membranes may have an even better response.

At electrically conducting membranes, the electrolytic generation of microscopic gas bubbles at the filter surface can be used to remove fouling layers. As only short current pulses (< 15 seconds) are required periodically (> 5 minutes) to maintain an increased permeate flux, minimal gas volumes are produced. The process has been demonstrated successfully at microporous stainless steel during the dewatering of TiO_2 suspensions and $Fe(OH)_3$ slurries using planar and annular configurations. It has also been shown on a bench top scale to be effective in cleaning the microporous graphite based 'Carbosep' tubular ultrafiltration membranes of the type presently undergoing pilot plant tests. A design for the modific-modification of a full scale ultrafiltration unit for pulsed electrical membrane cleaning is currently being drawn up.

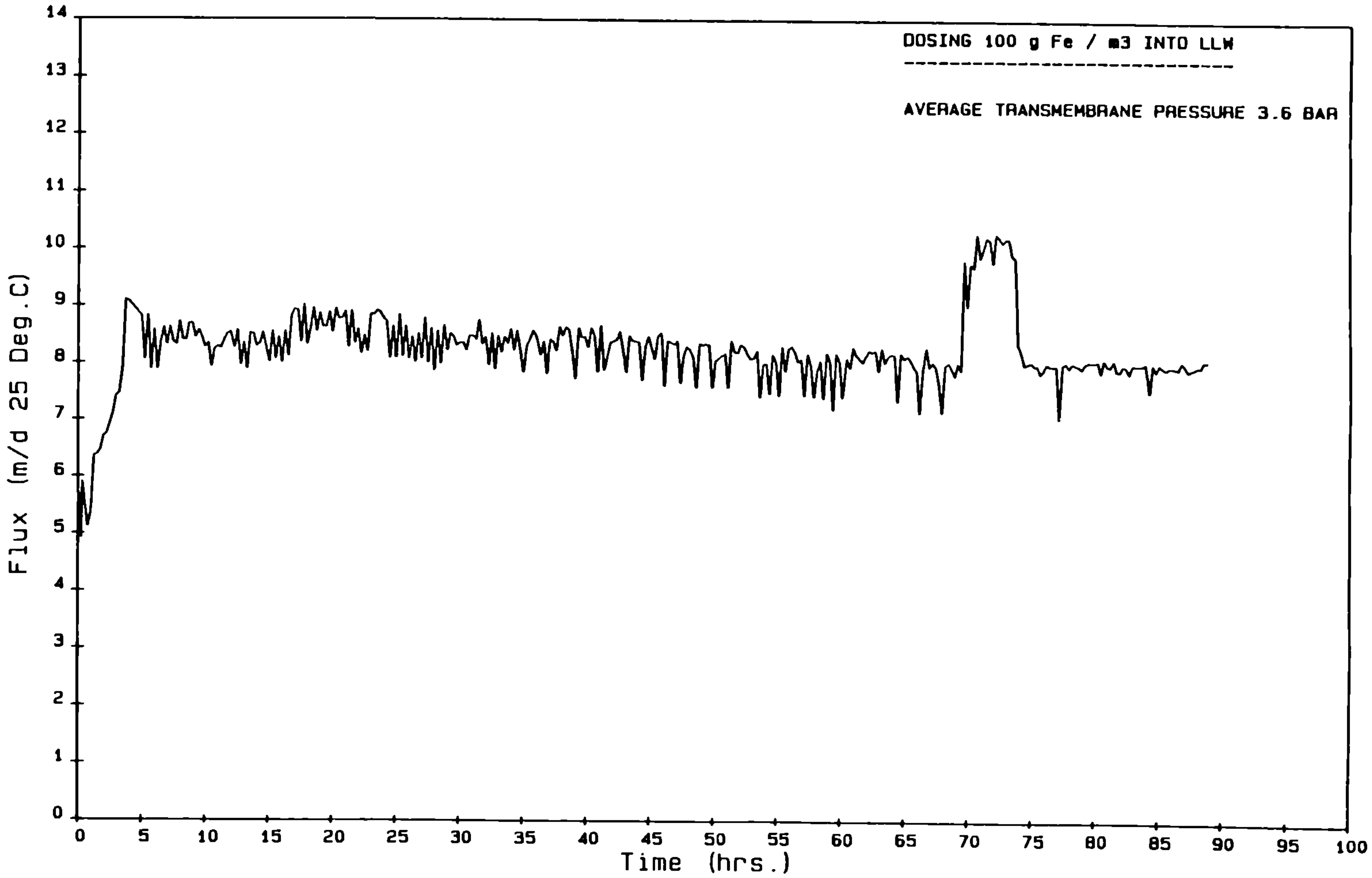


FIG. 1 VARIATION IN FLUX WITH TIME IN PILOT PLANT USING A CERAFLO MEMBRANE

Conditionning of alpha and béta-gamma ashes from incineration into different matrices.

Contractor : Commissariat à l'Energie Atomique, **CEN** -Cadarache, France
Contract n° : FI1W-0005-F
Duration of contract : June 1986 - December **1989**
Project leader : F. Josso

A. Objectives and scope

Ashes embedding takes a greater interest for storage of these radioactive products due to the volume reduction factor which can be obtained and due to the safety aspect of this kind of storage.

The different matrices usable are more or less adapted for a kind of ashes and laboratory studies are necessary to check their capacities.

The first tests are based on the research of the physico-chemical and mechanical properties of the matrix, then leaching test and radiolysis measurement are carried on. The next stage of the research is the study of full scale ashes embedding (100 or 200 liters cylinder).

These tests are useful to prove the feasibility of embedding (including the thermal's problems of polymerisation). A full scale pilot unit adapted for different types of products (cement, polymer, mixed cement-polymer) has been studied. This pilot unit will be realised in 1988.

B. Work programme

B.1. Formulations studies. Tests are performed with various embedding systems : cement, polymer and mixed cement-polymer to optimise their composition.

B.2. Selective pre-characterization. Tests are performed with a given radioactive ash to select the best matrix (using samples of 0.1 liter)

B.3. Final pre-characterization. The leaching and radiolysis measurements are performed with the matrix finally chosen on bigger samples (0.4 liter)

B.4. Pilot scale tests. Full scale tests will be made (100 or 200 liters cylinder), using a pilot unit adapted for the different types of matrices.

C. Progress of work and obtained results

Summary

Laboratory studies for determining the best formulation of ashes embedding have been done during the first period devoted to this program. The main physico-chemical and mechanical properties have been checked for ashes embedding made with cement, polymer and mixed cement-polymer formulations.

The selective pre-characterization phase is now to be done. During the last year the full scale pilot unit project has been studied, the pilot will be realised during the year 1987 and it will be operational in 1988.

Progress and results

Ashes used during phase 1 are non radioactive ones. They were obtained from incineration of wastes composed of cotton (5 %), kleneex (5 %), latex gloves (35 %) PVC (55 %).

The results of formulation studies for the three matrixes are summarized in the Table 1 (0.1 liter samples).

The results show that the formulations proposed comply with the "Basic Safety Regulations" currently recommended by the Ministry of French Industry. Polymer and mixed embedded products have the advantage of incorporating 40 % of ashes in weight with better mechanical properties than the cement embedded products which only incorporate 20 % in weight of ashes.

Initial mixing tests carried out on a semi-industrial scale on 10 liters, 50 liters and 100 liters drums have shown that certain precautions must be taken when embedding ashes :

- in the case of the polymer matrix embedded products, the core temperature of the capsule may reach 150°C during polymerization. The CIBA resin has been chosen in preference to the CDF resin as it is easier to work and improves the properties of the resulting embedded products.
- the core temperature of the mixed matrix embedded products remains below 100°C.
- the ashes in cement and mixed matrix embedded products should not contain too much non-oxidized metal fines (Al, Mg, Zn etc) as there is a risk of a reaction between the cement and the metals during setting causing the embedded product to swell as a result of the release of hydrogen. This effect is less marked in the case of the mixed matrix capsule which contains only 30 % in weight of cement and water.

These tests also showed that there is no increase in volume during embedding operations. Volumes remain equal in the case of cementing with 20 % of ash. Polymer and mixed embedded products enable an additional volume reduction gain of an order of 2.

These results are particularly important. They show that the embedding techniques chosen will enable the volume reduction factor of the incinerator to be maintained and even improved.

A full-scale pilot unit capable of producing the three types of embedded products, cement, resin and mixed, is under construction in the CEA. It is shown in Fig.1 and includes essentially :

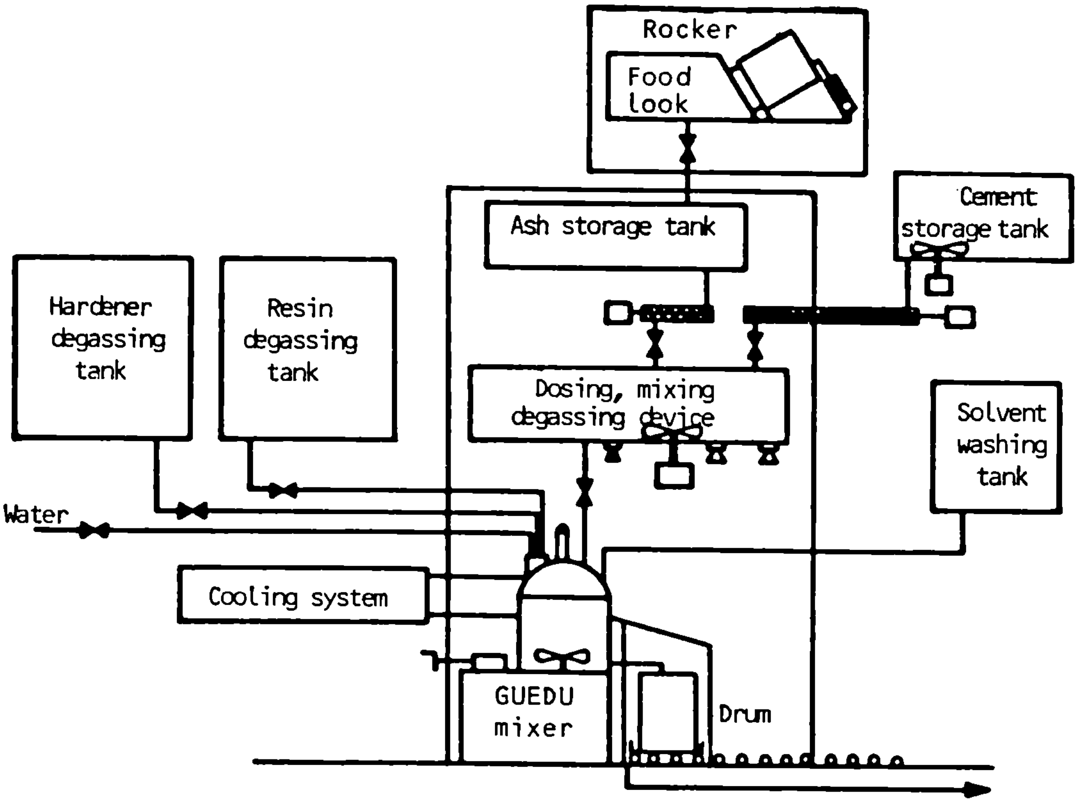
- an ashes or dry residue feed systems,
- tanks for mixes (cement, ash, water, resin, hardener, etc),
- a blade mixer with cooled walls operating under partial vacuum,
- a 200 liters drum filling system.

TABLE 1 : RESULTS OF THE ASH EMBEDDING FORMULATION STUDIES

Matrix	Formulation (% in weight)	Density kg.m^{-3} x 10^3	Hardness (shore)	Compressive strength (MPa)	Setting time (h)
CLC cement [a]	(Cement + water)80% Ashes 20% water/cement ratio 0.63	1.73	-	23	5 to 7
Epoxy [b] thermosetting resin	(CIBA resin + hardener) 60% Ashes 40% hardener/resin ratio 0.6	1.65	82	125	48
Mixed cement / resin [b]	(CDF resin + hardener) 30% (CLC cement + water) 30% Ashes 40% water/cement ratio 0.36 hardener/resin ratio 0.6	1.9	85	65	24.

[a] CLC = Pozzolanic cement

[b] vacuum-produced embedded products



PILOT PLANT FOR INCINERATION ASH EMBEDDING

Figure 1

SOLIDIFICATION OF TRU-WASTE BY EMBEDDING IN A CERAMIC MATRIX

Contractor : KfK, Karlsruhe, Federal Republic of Germany
Contract No. : FI 1W-0021-D (B)
Duration of contract : July 01, 1986 - December 31, 1988
Project Leader : A. Loida

A. OBJECTIVES AND SCOPE

Ceramic materials are evaluated as a matrix for TRU-wastes, i.e. dissolver residues from reprocessing, liquid α-concentrates from fuel element fabrication, residues from the dry incineration and from the acid digestion of TRU-wastes, as well as actinide sludges precipitated from MAW-solutions. Clay minerals (bentonite and kaolinite) and reactive corundum are preferentially selected as raw materials for the solidification of these wastes. The main process steps are (i) pretreatment of the waste, (ii) mixing with ceramic raw materials, (iii) forming by extrusion, (iiii) drying and sintering with $T_{max} = 1300^{\circ}C$ for about 10 minutes.

This way of TRU-waste immobilization has been demonstrated using all kinds of original TRU-waste known until now on lab-scale. The leach rate for actinides is less than 10^{-8} g/cm^{2}d in water and salt brines at room temperature, the average open porosity < 5 vol%, the compressive strength > 50 N/mm^2.

Aim of the current programme is to achieve a significant volume reduction of the final product by applying the potential of the ceramic matrix, e.g. by (i) increasing the waste loading (20 wt.-%) and (ii) by simultaneous ceramization of several waste streams.

B. WORK PROGRAMME

B.1 : Determination of the maximum waste loading for the alumosilicate ceramic matrix with dissolver residues; characterization of the final products.

B.2 : Determination of the maximum waste loading for the alumosilicate ceramic matrix; characterization of the final products with TRU-ashes.

B.3 : Determination of the maximum waste loading for the alumosilicate ceramic matrix with sludges, precipitated from acid digestion solutions; characterization of the final products.

B.4 : Determination of the maximum waste loading for the alumosilicate ceramic matrix with sludges, precipitated from TRU-solutions of the fuel element fabrication; characterization of the final product.

B.5 : Ceramization of TRU-waste-mixtures, according 1-4; characterization of the final products.

B.6 : Development of a technical process for the ceramization of TRU-waste. Construction of a pilot plant.

C. PROGRESS OF WORK AND RESULTS OBTAINED

The feasibility of conditioning dissolver residues by embedding them in an alumosilicate-based ceramic matrix having waste loadings up to 20 wt.-% has been demonstrated during earlier R&D-programmes supported by the CEC. In order to achieve a significant volume reduction of the final waste product, experiments have been performed to determine the maximum waste loading for the alumosilicate ceramic matrix.

Dissolver residues from the reprocessing of spent fast breeder reactor fuel elements (burnup 76 GWd/tHM) of the KNK II-reactor have been incorporated into the ceramic matrix (type KAB 78) with waste loadings of 20, 30, 40 and 50 wt.-%.

The basic chemical composition of the different ceramic pellets is given in Table I.

From the resulting ceramic pellets the following properties have been determined so far: chemical composition, specific α-activity (9 E 8 Bq/g-2.2 E 9 Bq/g), density (3.20 - 3.90 g/cm^3), mechanical strength (51 - 46 N/mm^2) and open porosity (2 - 3 vol%).

Table I: Basic chemical composition of alumosilicate-based ceramics, loaded with 20, 30, 40 and 50 wt.-% of dissolver residues from the reprocessing of fast breeder reactor fuel elements

waste loading degree Component	20	30	40	50
Matrix Al_2O_3, SiO_2,...	80	70	60	50
Actinides PuO_2, UO_2,...	14	22	29	36
Fission products Ru, Mo, Tc,...	< 4	< 5	8	10
Stainless steel oxides Fe_2O_3, Cr_2O_3, NiO	< 2	< 3	3	< 4

Conditioning of Nuclear Cladding Waste by High Temperature Melting in Cold Crucible

Contractor: CEA, Marcoule, France
Contract N°: FI 1W - 0014 F
Working Period: October 1986 - March 1989
Project Leader: R. MAZOYER

A. OBJECTIVES AND SCOPE

The conditioning of zircaloy and stainless steel hulls by high temperature melting in cold crucible is being developed by the C.E.A. in France. The feasibility of this process which does not require any metallic additive is demonstrated, at industrial scale with an inactive prototype.

In order to carry out experiments involving radioactive hulls, laboratory scale facilities have been set up inside a new shielded cell : the melting unit is able to produce small metallic ingots weighing about 3.5 kg, 18 cm long and 5.7 cm in diameter.

The objectives of this program are :

- to qualify the cell process under cold conditions,
- to realize active ingots with genuine stainless steel hulls coming from the PHENIX reactor,
- to realize ingots with active zircaloy hulls coming from the OBRIGHEIM reactor.

The project includesthe characterization of the final waste materials (inactive and active ingots, glasses used as conditioning matrix for slags) and the evaluation of their leach resistance.

B. WORK PROGRAM

B.1. Definition of standard working conditions involving either stainless steal hulls or zircaloy hulls. Development of suitable operating methods for characterization of ingots and slags.
B.2. Realization and characterization of inactive stainless steal and zircaloy ingots.
B.3. Realization and characterization of active stainless steal ingots.
B.4. Realization and characterization of active zircaloy ingots.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In order to define standard working conditions, about 20 preliminary experiments involving inactive materials have been performed since the beginning of 1986. Most of the difficulties that came up, such as melting or drawing troubles, seem to be resolved. At present :

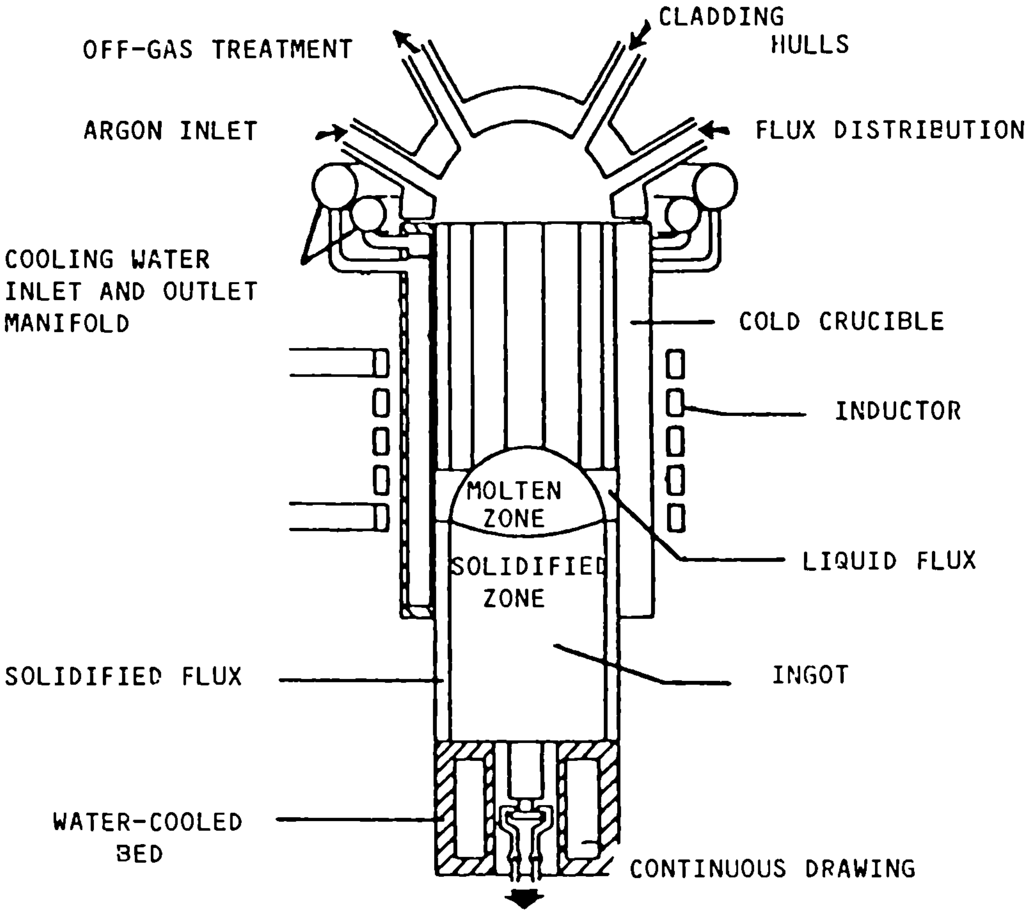
- some experiments must still be performed under cold conditions with master-slave manipulators.
- inactive reference tests must be carried out in order to qualify the whole process.

The cell conformity with hot safety standards is under official approval.

Progress and results

1. Cold crucible melting process

A schematic diagram of the cold crucible is given in the following figure :



The furnace consists of water-cooled copper tubes in cylindrical arrangement, surrounded by a solenoid inductor. During the melting phase :

- the cold crucible is continuously fed with hulls and small pellets of oxide or fluoride slag ($\simeq$ 2 % in weight of metal).
  This slag is used as electric and thermic insulant between the metal and the cold crucible.
- the water-cooled bottom of the crucible is moved downward continuously in order to maintain a constant level of molten metal. This level is given by the inductor self-inductance coefficient.

The great electromagnetic stirring inside the crucible enables oxides present in the molten metal bath to be decomposed and trapped by the slag. The final metallic ingot is surrounded by a thin layer of solidified slag which separates from the metal during the cooling.

2. Cell process development (B.1.)

The most important points wich were investigated during the preliminary experiments are :

- the electrical parameters
- the airtightness of the cold crucible
- the melt starting conditions
- the ingot drawing conditions
- the gaz treatment parameters

After this previous work, 11 stainless steal and 3 zircaloy ingots have been realized under cold conditions, without any trouble.At present further tests are being carried out to verify the working method with master slave manipulators.

Conditioning of Fuel Hulls and Structural Materials by High Pressure Compaction

Contractor: KfK, Karlsruhe, D
Contract N°: F I 1W-0020-D (B)
Working Period: July 1986 - December 1989
Project Leader: G. Boehme

A. Objectives and Scope

In the Karlsruhe Reprocessing Plant (WAK) the LWR hull and structural materials wastes (H + S wastes) are embedded into concrete in 120 l insert drums without reduction in volume, packaged into 200 l hooped barrels and transferred to an intermediate storage facility.

The concept chosen for conditioning H + S wastes from the Wackersdorf reprocessing plant (WAW) is analogous to the WAK process with the difference that the wastes are embedded into concrete in 330 l insert drums and packaged into 400 l barrels.

A drawback of this method is that a relatively great number of barrels are produced and that sufficient space must be provided for intermediate and ultimate storage. Likewise, the release of gaseous activities and H_2 from the waste fixed into concrete during operation of the repository might be associated with drawbacks.

KfK has been developing an alternative conditioning method according to which the waste is compacted by cold pressing and can be package into HLW canisters without matrix.

B. Work Programme

B.1. Inactive investigations of the behavior of hulls under high pressure in laboratory - and technical scales.

B.2. Determination of the surface of inactive compacts as a function of the compacting pressure.

B.3. Design and manufacture of press-dies and press-punches as prototype tools.

B.4. Conceptual design of a press facility for active H + S waste compacting

B.5. Investigations of gaseous activities release from active compacts.

C. Progress of work and obtained results

Summary

It is the aim of the technique developed to save storage space by reduction in voume of the H + S bulk and to improve repository relevant properties of the waste form produced. The waste form is anhydrous and more resistant to temperatures. No radiolytic hydrogen is generated. The large retention of gaseous activities from the waste form is ensured by its gas tight packaging. The outer dimensions of the packaging are identical with those of the HLW glass canister. This allows to apply a transport and storage technique which is similar to that used for solidified HLW. Given the low amount of nuclear heat released from H + S wastes as compared with solidified HLW, the specific heat load of the common salt borehole can be diminished with this type of mixed storage. The general work progress status is as follows:
- Description of goal and advantages of the technique
- Determination of reference data for the industrial planning.

Progress and results

1. Behavoir of hulls under pressure (B.1.)

Cold pressing tests involving inactive H + S bulks have shown that the volume can be reduced by the factor 6.5. This corresponds to an increase in density to about 80 % T.D. The tests were performed with a 50 MN hydraulic press. The die was 300 mm in diameter; the ultimate pressing effect attained was 400 MPa (Fig. 1).

2. Draft of press facility (B.4.)

In cooperation with an industrial manufacturer of large hydraulic presses the concept of a pressing facility for hot cell operation has been elaborated. The maximum pressing force is 50 MN. The press serves to produce compacted waste forms for loading into canisters of 400 mm diameter (COGEMA canister). The canned waste is compacted into pellets in the matrix and then ejected into the accomomdating rack. The fully loaded rack is lowered into the canister (Fig. 2).

From the point of view of mounting and dismounting as well as of disposal of large press parts this concept is still not satisfactory. The maximum single load to be handled by the cell crane of about 60 tons is relatively high. Up grading the concept up to the planning stage of industrial maturity includes the design task of reducing weights and dimensions of large press parts.

In order to be capable of evaluating the economic advantage of cold pressing a cost estimate was made. It takes into account costs of fabrication (capital service, operating costs, container costs), transport and ultimate disposal of H + S waste forms. The comparison of costs for 200 l WAK and 400 l WAW barrels has shown that the economic advantage resulting from maximum compaction is only moderate. Savings in transport and ultimate disposal caused by lower numbers of barrels are compensated by extra expenditure for fabrication. In a concept involving intermediate storage the economic benefit could be attractive (Fig. 3).

List of publications

H. Frotscher, Semi-annual report II. 1986
KfK - N° 04.02.06 P 09C, Dec. 1986

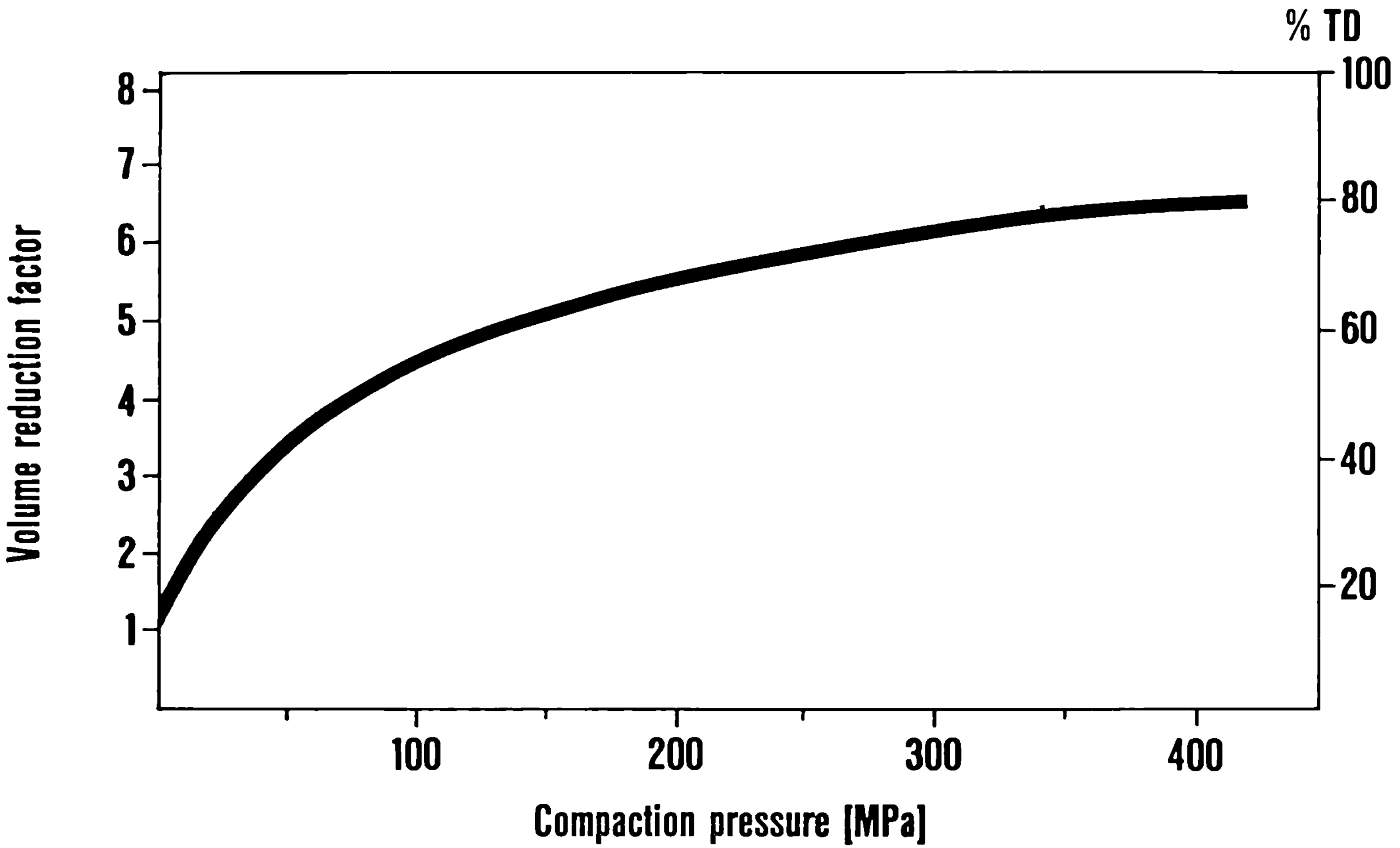


Fig. 1 Densification of unirradiated cladding hulls and fuel hardware

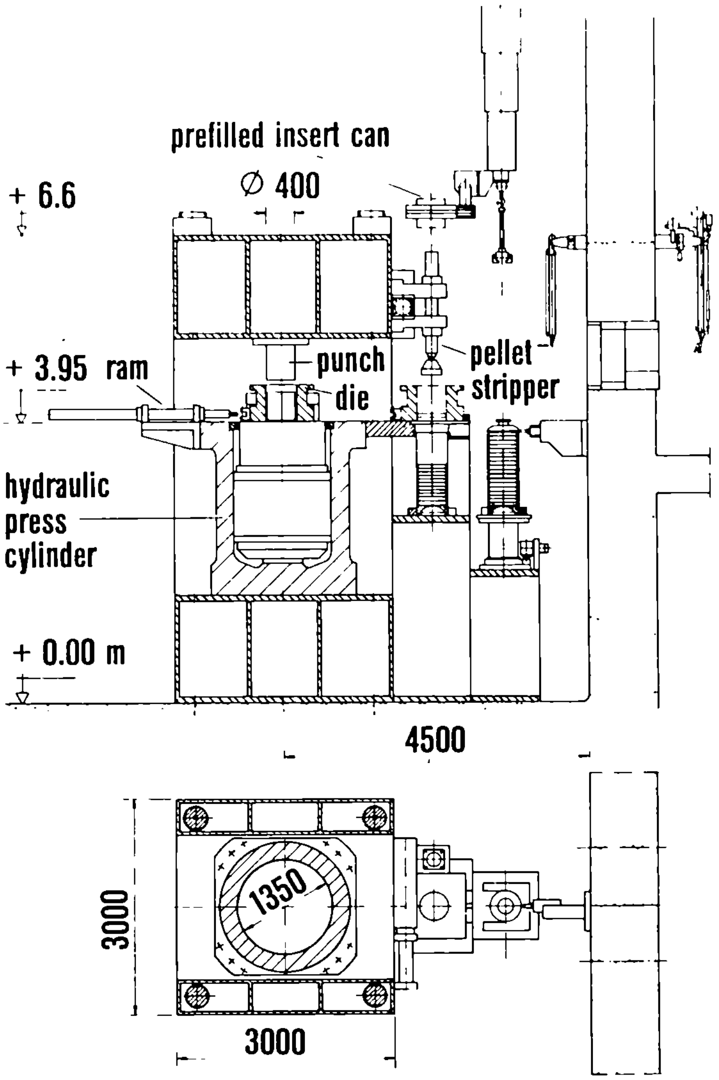


Fig. 2 Press facility for H + S-waste compacting

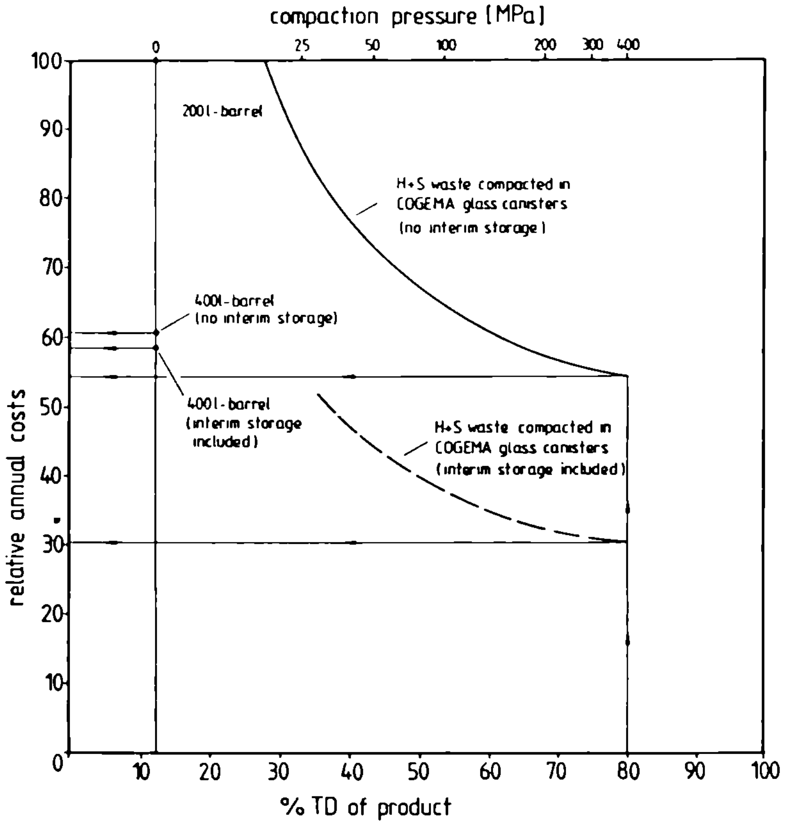


Fig. 3: Relative annual costs for conditioning, shipping, (interim storage) and disposal of H+S waste

Decontamination of solid alpha wastes and recovery of the plutonium (PROLIXE facility)

Contractror : CEA, CEN-FAR, FRANCE
Contract n° : FI1W/0013
Working period : October 1986 - December 1987
Project Leader : G. KOEHLY

A. Objectives and Scope

Nuclear activities in the Radiochemistry building of FONTENAY-AUX-ROSES nuclear research center 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 β γ emitters for hot-cells studies and with α emitters only for glove-boxe experiments.

In order to improve the management of these wastes it has been decided to build new facilities :

a/ a group of three glove-boxes for the treatment of α active solid wastes,

b/ a hot-cell (PROLIXE facility) for the treatment of α β γ active solid wastes.

In these facilities we will develop leaching processes in order to :

1/ Decontaminate these wastes expecially in α emitters to obtain a level of alpha contamination $< 0{,}1$ Ci x t^{-1} of the conditionned wastes which will be suitable for surface site disposal,

2/ recover actinide elements, particularly the highly valuable plutonium.

These two items constitute the main objectives of the present programme.

B. Work Programme

B.1. WASTES ANALYSIS to determine their composition and the nature and activity of the radiocontaminants.

B.2. WASTES CRUSHING : characterization of the size of particles obtained after the crushing of the wastes according to their nature.

B.3. PRETREATMENT : in the specific case of the treatment of ashes produced in other facility, the pretreatment procedure to eliminate chloride ion will be defined.

B.4. LEACHING TESTS : according to the nature of the wastes to be treated specific leaching experiments will be performed. Different leachants will be used : nitric acid, acidic leachants with electrogenerated reducing or oxidizing agents.

B.5. EQUIPMENT DESIGN : the electrolyzer for the generation of reducing or oxidizing agents will be defined.

B.6. SECONDARY WASTES : an optimisation of the management of secondary wastes (gazeous wastes, distillates) will be realized. The opportunity to recover some chemicals like silver will be considered.

B.7. RECOVERY AND PURIFICATION OF ALPHA EMITTERS : the study of the recovery of alpha emitters, especially the plutonium using extraction chromatography technique will be realized.

B.8. DESIGN OF PROCESS FLOWSHEETS : for the different wastes to be studied, special process flowsheets will be designed. A comparison of the performances of these processes with those of conventionnal techniques will be achieved.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The construction of the two facilities to be operated during the present programme is actually finished. The pilot glove box facility will start active runs in March 1987 ; in that facility series of cold tests have been made to study the behavior of each device = crusher, leaching machine, dryer, concentrator, etc... For the PROLIXE facility the test of each apparatus is under-way. Concerning the development of the leaching process special efforts have been made on the use of AgII oxidizing leachant to recover plutonium contained in incineration ashes and to process stainless steel pieces contaminated with nuclear fuel materials. In the case of the treatment of ashes, plutonium recovery yield close to 98 % have been obtained during the treatment of ≃ 0,8 Kg of active ash batches. For the treatment of Pu contaminated stainless stell pieces FD(Pu) = 1.4 10^4 has been obtained, the remaining Pu contamination was ≃ 0,14 Ci/t.

Progress and results

1/ Wastes crushing (B2)

Cold tests studies of waste crushing have been made in the pilot glove box facility. The crusher is a ROTAC 44136 apparatus made by AUREC S.A. (FONTAINEBLEAU, FRANCE), equipped with two disc-blades mounted on two parallel driving shafts. The rotation speed is 66 r.p.m. Crushing experiments have been realized with separate inactive materials : polyethylen, PVC, elastomers, plexiglass, cellulose, glass, electric wires. No problems were encountered during these tests ; the mean volume reduction factor is close to 5 and the size of the crushed particles is comprised between 7 to 8 mm.

2/ Leaching tests (B4)

A laboratory study was realized in order to define the experimental conditions to process plutonium contaminated ashes by leaching with a nitric acid solution containing electrogenerated AgII. The ashes treated were produced in UP1 Marcoule plant facility ; they possess different composition = Cl^- = 6 to 23 %, SiO_2 = 13 to 40 % in mass. Their plutonium content was always found to be close to 3 %. The ashes were first submitted to a water washing steep prior to operate the treatment with AgII ions. Laboratory experiments were realized in a small electrolyser of 1.3 l total capacity on 100 to 300 g of ashes per batch. Using the following conditions = anolyte = 1 liter, HNO_3 = 4 M, $AgNO_3$ = 0,1 M, θ =25°C, current intensity = 20 A, stirring = 750 r.p.m, an overall yield of plutonium solubilization of 98 % was obtained after 9 hours of electrolysis. Application of that process was done on a larger scale using 800 to 900 g batches of ashes. Experiments were realized in a larger electrolyzer of 6 liters of total capacity. Experimental conditions were identical to those described previously except for the current intensity which was rosen to 80 A. After 7 hours of electrolysis a 98 % plutonium recovery yield was also obtained (see figure 1).

Oxidizing AgII treatment was also applied to the decontamination of stainless stell pieces contaminated with nuclear fuel materials. For that treatment high plutonium decontamination factor (DF(Pu) = 1.4 x 10^4) was obtained and the remaining plutonium contamination was estimated to be close to 0.14 Ci/t. Nevertheless these performances have been obtained using three successive leaching steps ; an improvement of the decontamination rate will certainly by obtained be improving the contact between the metallic pieces and the leachant.

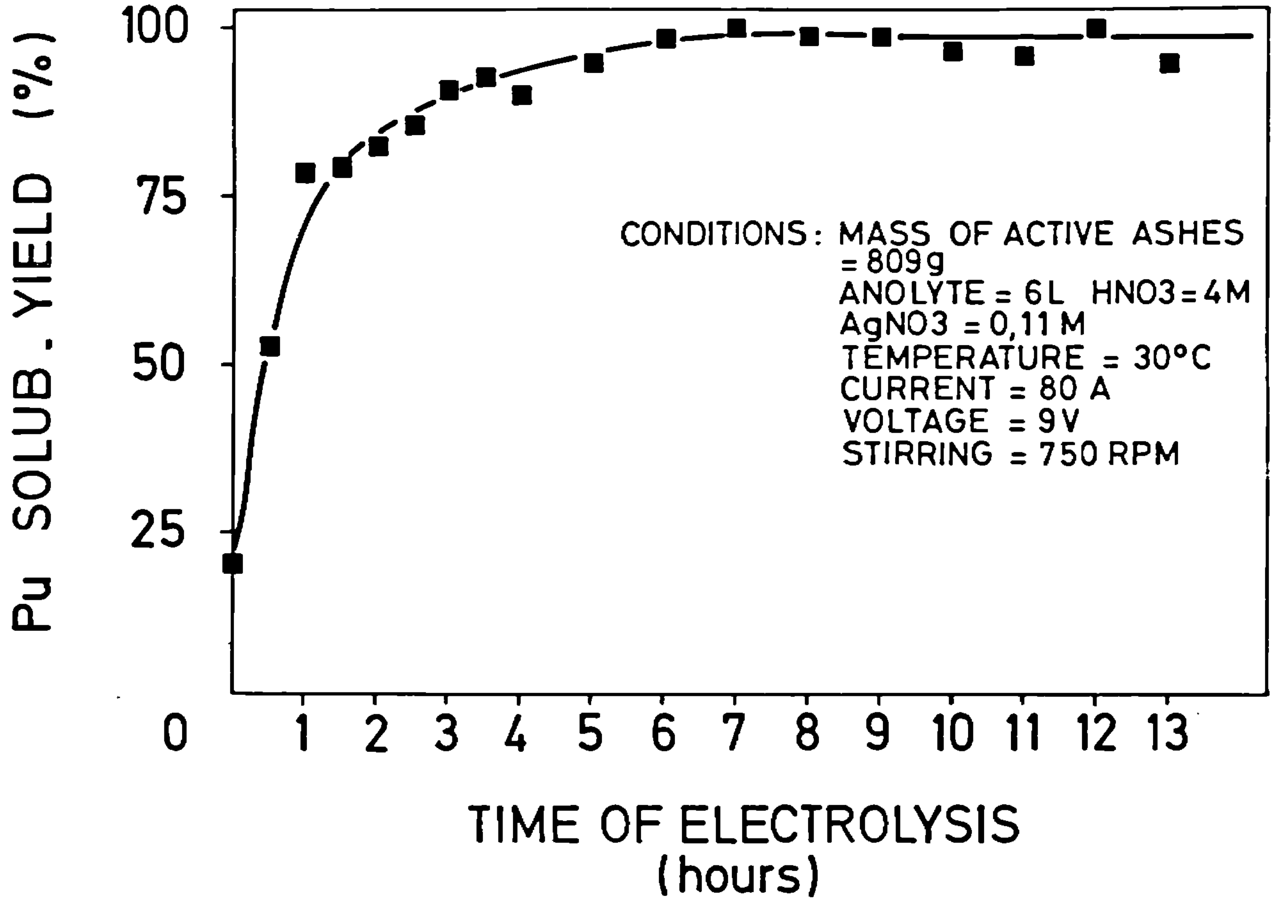

Pu SOLUB. YIELD (%)
100
75
50
25
0
1
2
3
4
5
6
7
8
9
10
11
12
13
TIME OF ELECTROLYSIS
(hours)
CONDITIONS: MASS OF ACTIVE ASHES = 809g
ANOLYTE = 6L HNO3 = 4M
AgNO3 = 0,11 M
TEMPERATURE = 30°C
CURRENT = 80 A
VOLTAGE = 9V
STIRRING = 750 RPM

FIGURE 1

Active Pilot Plant for the Decontamination of ILW Solutions by Chromatographic Processes

Contractor:	KfK, Karlsruhe, West Germany
Contract No:	FI1W-0022
Duration of contract:	July 1986 - December 1987
Project Leader:	W. Faubel

A. OBJECTIVES AND SCOPE

In the F.R.G., low and intermediate level liquid wastes arising during reprocessing operations are currently mixed and evaporated. The resulting waste called "reprocessing concentrate" is then conditioned into cement of gamma emitters (e.g. Cs-134/137, Ru-106, Sb-125 ...) important shielding of the waste product containers has to be provided thereby increasing by far the weight and volume of waste to be transported and disposed of. Noticeable economical savings are expected to be achieved if reprocessing concentrate can be split into a highly active fraction which could be added to high level waste for vitrification and a low active fraction capable to be managed without cement shielding. To this end, previous studies have shown that decontamination factors higher than 280, 12 and 6 should be reached for caesium, antimony and ruthenium, respectively.

Because decontamination of reprocessing concentrate revealed difficult or ineffective by means of chemical precipitation especially for antimony and ruthenium, this research activity foresees the implementation of inorganic ion exchange and extraction chromatography as treatment processes.

Therefore the main objective of this contract is to assess the performances of these alternative treatment processes for decontamination of reprocessing concentrate on the basis of lab-scale experiments performed on simulated and genuine samples of relevant waste. These could be a basis for subsequently scaling-up the process to an active pilot plant (100 litre-scale) in the frame of a possible new contract (1988-89).

B. WORK PROGRAMME

B.1. Experiments in a 1 l scale in columns filled with:

B.1.1 Bio Bed 7 (or Lewapol R) for removing traces of organic products (TBP, DBP and dodecane) and glass wool for filtration.

B.1.2 Ammoniummolybdato phosphate (AMP-1) for Cs separation (used as suspended bed column).

B.1.3 Antimonypentoxid (Sb_2O_5) and manganese dioxide (MnO_2) for Sb removal.

B.1.4 N-N'-diphenylthiourea for Ru retention.

B.1.5 N-Octyl(phenyl)-N-N'-diisobutylcarbamoylmethylphosphine oxide (CMPO) for rare earths and actinides separation.

B.2. Treatment/conditioning of the waste arising

B.3. Data evaluation

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In the frame of decontamination of intermediate level waste solutions from reprocessing of spent fuel elements, the feasibility of the chromatographic processes for the separation of cesium with the recently developed "AMP-1" column has been demonstrated in a 1 l scale. Furthermore the separations of Sb, Am, Eu, Ce and Ru have been successfully performed with genuine waste solutions in a ml scale according to the agreement of the EG-contract. For the Sb separation one experiment in a 1 l scale has been already shown the expected decontamination factor greater 100.

The general work progress status is as follows:
B.1.1., B.1.2. are completed.
B.1.3., B.1.4., B.1.5., B.2., B.3. are processing normally.

Progress and results

1. Cesium separation (B.1.1., B.1.2.)

Due to the high amount of precipitate and organic impurities the aqueous, nitric acid ILW-concentrate solution was first purified by filtration with glass wool and absorption of the organic species on a Bio Bed SM 7. After that the "in-line" method was continued by feeding the purified ILW directly into the "suspended bed column" filled with AMP-1. The retention was 100 % (DF > 60 000) at a throughput of 10 volumes of the column per hour.

2. Antimony separation (B.1.3.)

Sb-125 ($T_{1/2}$ = 2.8 years) has been successfully separated with DF's > 100, in ml and in a 1 l scale employing antimony pentoxide or manganese dioxide, using "on-line" directly the effluent of the "suspended bed" column where the Cs-137 has been completely removed.

"On-line" means in this case that 1 l of the genuine ILW-solution was transported by one pump in one step through the filter, Bio Bed SM 7, the "AMP-1 suspended bed" column and the mixed MnO_2/SbO_2-column.

3. Americium and R.E. separation (B.1.5.)

Am-241, Eu-154, Eu-155 and Ce-144 were separated in a ml scale from simulated and genuine ILW remaining after the Sb-125 separation using the technique of extraction chromatography. The best performance was found for the resin consisting of 0.6 M CMPO dissolved in TBP on SM 7.

Decontamination factors DF > 100 have been reached and first experiments concerning multiple use of this column have been promising.

4. Ruthenium separation (B.1.4.)

Ru-106 ($T_{1/2}$ = 1 year) is retained in this system (Fig. 1) in three different stages:

- At the filtration of the ILW-concentrate (R = 45 %)
- On the manganese dioxide column (R = 50 %)

- The remaining Ru is retained by extraction chromatography in 5 ml ILW-experiments on diphenylthiourea (DPTU) to 80 % and after a pretreatment with a reduction medium to 90 % and it is also possible to reach 95 % by an additionally extraction with aliquat.

Thus, at least, by a very conservative estimation the required decontamination factor of 6 will be reached and probably exceeded for the separation of ruthenium taking into account the multiplicity of the DF's of the filtration, sorption on MnO_2 and sorption on DPTU.

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2. W. Faubel and Sameh A. Ali, Nucl. Techn. 69, 178 (1985)
3. W. Faubel and Sameh A. Ali, Radiochim. Acta 40, 49 (1986)

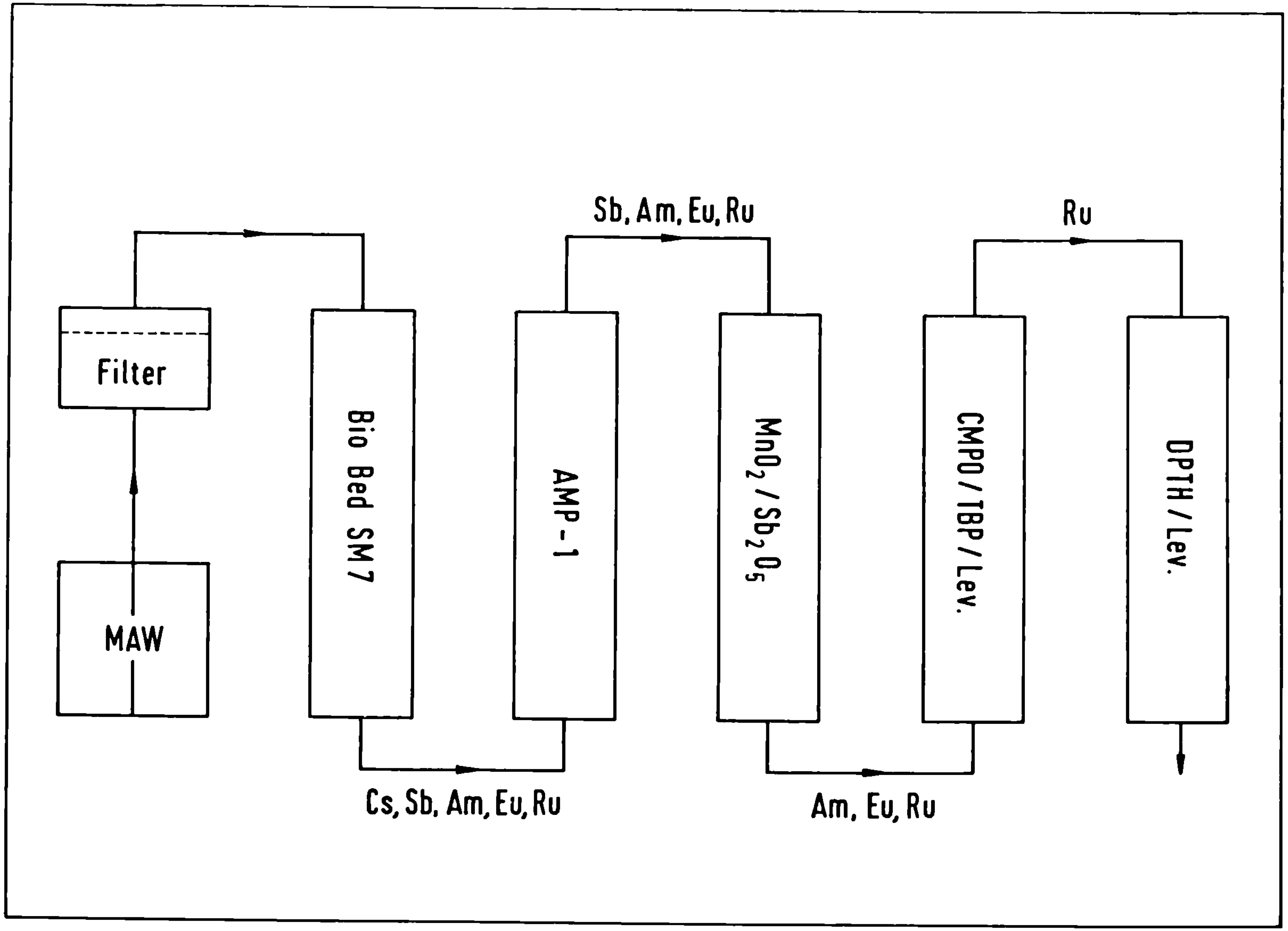

Fig.1: Flow-sheet of the chromatographic decontamination of ILW.

SEPARATION OF ACTINIDES AND LONG-LIVED FISSION PRODUCTS FROM HLW AT THE EUREX PLANT MTR FUEL REPROCESSING

Contractor: ENEA-CRE CASACCIA, Rome, ITALY
Contract n°: FI1W-0011
Duration of contract: July 1986-March 1988
Project leader: L. Pietrelli

A. OBJECTIVES AND SCOPE

The purpose of this research project is to simplify the pre-disposal management of the stored liquid HLW at the ENEA EUREX pilot plant. This waste consists of aqueous raffinate of the first extraction cycle (1AW) from the reprocessing of MTR-type fuel.

The EUREX liquid waste consists of 85 m^3 of a 1.1 M HNO_3 solution with 27 g/l of Al, and other minor costituents, including fission products and reprocessing chemicals. Table I gives the estimated chemical and radiochemical composition of 1AW-MTR waste.

The direct vitrification of these liquid wastes would require a complex vitrification plant resulting in a large amount of vitrified waste because these wastes contain a large amount of inactive chemicals (essentially aluminum, sulphates, mercury). Therefore, the objective is to separate this liquid waste into two parts:

- a small-volume highly radioactive fraction (Cs, Sr and Actinides);
- a larger-volume of LLW fraction containing the majority of inactive salts present in the waste.

In Figure 1 is shown a conceptual flowsheet for the management of 85 m^3 1AW-MTR liquid wastes. The direct vitrification of HLW solution, using the hot version of the IVET pilot plant (the inactive italian prototype vitrification plant) /1/ and taking into account the maximum allowable amounts of sulphates (1.2% w/w) and aluminum (13% w/w as Al_2O_3) should give about 500 canisters (50 l, 150 Kg) of vitrified product.

The application of a "declassification" process reduces the vitrified product to about 30 canisters.

B. WORK PROGRAMME

B.1 Development of chemical flowsheets for the quantitative separation of Cs, Sr and actinides from the 1AW-MTR solution.

B.2 Development of suitable sampling method for 1AW-MTR storage tank.

B.3 Design and realization of a minipilot plant to test the flowsheets with real 1AW-MTR feed solution;

B.4 Chemical and radiochemical analysis of real 1AW-MTR solution.

B.5 Tests in the equipped hot cell with real 1AW-MTR solution.

B.6 General considerations and Final Report.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Summary

In order to fulfil these objectives, some chemical flowsheets for the separation of actinides and long-lived fission products from the bulk salt matrix (essentially aluminum nitrate) are being investigated.

The studies related to this report concern the following conceptual flowsheets:

- the **acidic flowsheet,** based on the separation of Cesium by Phosphotungstic Acid (PTA), and on the separation of Strontium and Actinides by Polyantimonic Acid (PAA), directly from the acidic 1AW-MTR solution;

- the **alkaline flowsheet,** based on the alkalinization with sodium hydroxide of the 1AW-MTR solution to pH 13 (in order to trasform the aluminum in the water soluble sodium aluminate); at this pH value, the iron present (see Table I) precipitates, and the Strontium and the actinides are separated by co-precipitation with Ferric Hydroxide; the Cesium is then separated by selective precipitation by Sodium Tetraphenylborate(NaTPB) or by ion exchange with Zeolites.

Development of chemical flowsheets

Acidic flowsheet

Cs separation by CsPTA precipitation.

The precipitation of Cs by means of PTA occurs in acidic conditions /2,3/ and therefore in our case it can be carried out directly in the feed solution (1.2 M HNO_3) without pH adjustment.

According to the literature the PTA concentration does not appreciably influence the reaction efficiency, provide that PTA reactant is added as solid powder. In any case the mgPTA/mgCs=62 ratio has been used in all experimental tests.

In Figure 2 is shown the behaviour of Cs Decontamination Factors (DF) by PTA precipitation from simulated 1AW-MTR waste solution. More than 17 hours were required at 25°C to obtain both Cesium DFs and particle size suitable to perform an efficient separation.

Sr and Pu separation by ion exchange with PAA.

According to the informations available in the literature /4/ the PAA is the only compound which can give high DFs both for Sr and actinides in acidic media.

However, there are not information about the performances of PAA in aluminum nitrate concentrated solutions such as the 1AW-MTR.

Table II shows the results of preliminary batch tests on simulated and traced 1AW-MTR solution with PAA; additional data related to some other exchangers have been added for comparison.

These results confirm that even in a concentrated aluminum nitrate solution PAA is the only exchanger giving good decontamination factors for Sr in acidic medium.

The adsorption of Pu carried out by batch technique at room temperature shows that Pu DF increases slowly with the time, but even for long contact time the obtained values are not satisfactory for a good decontamination of the waste solution. Infact, after shaking 20 ml of traced solution with 1 g of PAA, DF=9.2 (Kd=160) has been obtained after 20 hours.

Basic flowsheet

Aluminum solubilization and Sr, Pu removal.

The aluminum separation from the active fraction is possible by transformation of the insoluble Al-Hydroxide to soluble Na-Aluminate. This transformation is done at pH 13 by adding excess of concentrated NaOH solution.

Some tests were carried out to find optimal conditions for the 1AW-MTR solution alkalinization. The results have shown that the best conditions are realized by adding very slowly the 1AW-MTR waste solution to the necessary amount of 10 M NaOH solution and not vice-versa. In this case the direct aluminate formation occurs without troubles during agitation and the precipitate volume is minimized.

A sistematic study of the Sr and Pu removal from 1AW-MTR solutions by means of Ferric Hydroxide precipitation has shown that Sr and Pu can be effectively separated; on the contrary, as well known, Cs is poorly removed.

The coagulation of Ferric Hydroxide occurs when the OH^- ions are added to Iron (III) solutions. Strontium and Plutonium are removed from solution by the Iron hydroxide coagulation-flocculation, provided the final pH of the solution is in the range from 7 to 13. This separation does not appreciably occur below pH=7.

The pH effect on the Sr removal at constant Iron concentration is shown in Figure 3. The removal of Sr, at constant Sr and Fe concentrations, increases linearly with pH. The removal process takes place rapidly, and no substantial differences have been observed increasing the digestion time from 30 minutes (curve a) to 20 hours (curve b). At pH 7 the difference is due to the competition effect with H^+ ions.

The DF found in all the tests carried out at laboratory scale using simulated waste traced with Pu-239, Sr-85 and neutralized by 10 M NaOH solution, have been generally about 10^3.

Separation of Cesium by Sodium Tetraphenylborate (NaTPB).

For the selective precipitation of Cs from the supernatant coming from the alkalinization, the tetraphenylborate anion is added in the form of water soluble NaTPB.

The effect of several experimental parameters such as pH, Na^+ and NaTPB concentrations on the Cs removal from the 1AW-MTR liquid waste via CsTPB precipitation have been investigated.

The Cesium DF is strongly effected by the Sodium ion concentration, in fact the NaTPB solubility decreases from about 0.9 M in water to 1.1×10^{-3} M in a supernatant containing 7 M Sodium.

The highest Cesium DF can be obtained by adding NaTPB excess to the alkalinized waste solution. For a reaction time of 30 minutes a sufficiently high Cs removal (99%) from simulated waste solution was obtained when NaTPB concentration was more than 200 mg/l (see Figure 4).

The pH effect at two different contact times is shown in Figure 5. As it can be observed at pH 3 the supernatant Cesium concentration increases with time. This effect has been ascertained to be due to the CsTPB destruction by the acidic media /5/.

Cesium adsorption by Zeolites

Before the Zeolites treatment the simulated 1AW-MTR waste solution must be alkalinized with 10 M NaOH solution according to the procedure before mentioned. The Zeolites, in fact, cannot be used directly in the case of acidic solution.

After centrifugation the supernatant has been used directly for the laboratory tests.

To check the Zeolite performances both for Cs and Sr the waste solutions were traced after the alkalinization. The adsorption tests were performed using batch tecnique at room temperature.

The results of the Cs and Sr adsorption by different Zeolites is reported in Table III. The IE-96 and Zeolon-900 (after NaOH pre-treatment) Zeolites seem to give the best results. The tests by using columns must be performed to confirm this behaviour.

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/3/ BRAY,L.A., et al. Fuel Reprocessing and Waste Management. Jackson 1984.Proceedings pp. 345-356 Vol. 1.
/4/ DOZOL,J.F., et al. CEN-Cadarache, Report D.R.D.D. n°56 (1985).
/5/ PIETRELLI,L., ENEA-RTI COMB MEPIS 21 (1985).

Table I Estimated chemical composition of the 1AW-MTR solution.

Element	Conc.		Ci/l
Al	27.01	g/l	-
Fe	0.56	"	-
Hg	1.34	"	-
Si	0.14	"	-
Zr	35	mg/l	-
Nd	35	"	-
Mo	27	"	-
Ce	20	"	-
Cs	17	"	0.6
Ru	13	"	negl.
Ba	12	"	0.56
Sr	7.8	"	0.6
Sm	7.3	"	1.2E-2
Y	5.0	"	0.6
Np	1.8	"	1.3E-6
Pu	2.5	"	1.4E-3
Pm	0.07	"	6.3E-2
Am	4E-3	"	1.3E-5
H+	1.1	M	
S04--	0.006	M	

Table II Exchange capacity Qt for Cs and Sr.

Exchanger	Qt(mg/g)	
	Cs	Sr
PAA	1.183	0.944
Zr-Phosphate	0.202	-
NH4-Phospho Molybdate	1048	-
PHOMIX (*)	10	-

(*)mixture of NH4-Phosphotung. and Zr-Phosphate.

Table III Cs and Sr adsorption by Zeolites: Kd values=(Ci-Ce)V/MCe

	Cs	Sr
Zeolon-900(*)	154	663
Zeolon-900(**)	100	18
IE-96 (Na form)	111	374
IE-95 (H form)	97	219

Ci=initial activity
Ce=equilibrium activity
V=ml of 1AW-MTR solution
M=grams of exchanger

(*) 10 M NaOH pre-treatment
(**)NaCl pre-treatment

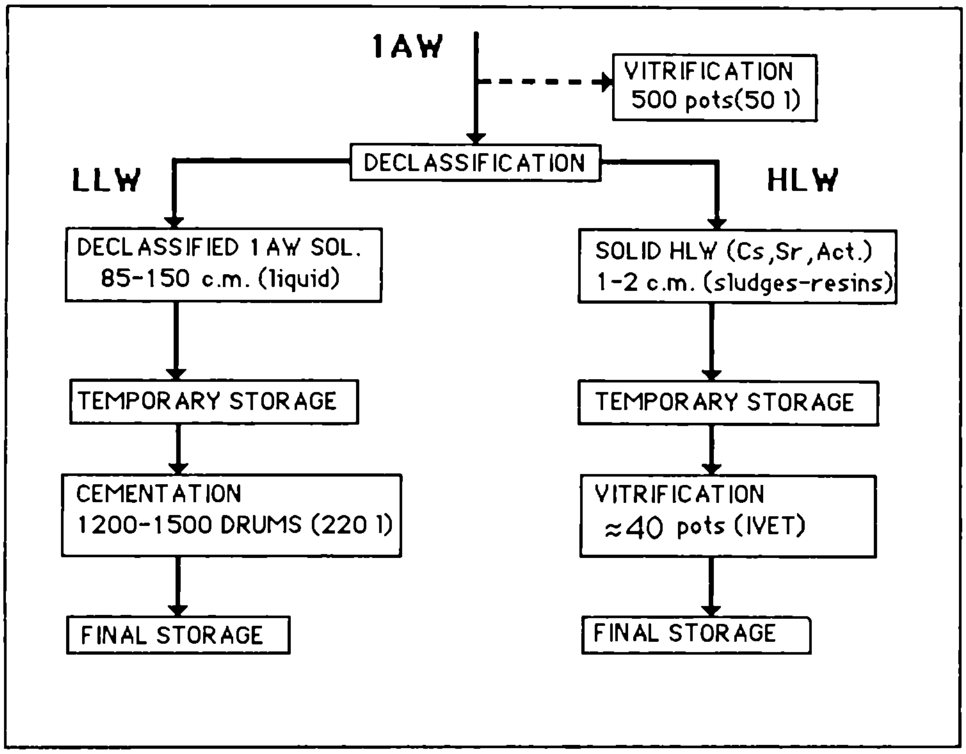

Fig.1 Conceptual flow-sheet for the management of 1AW-MTR liquid wastes.

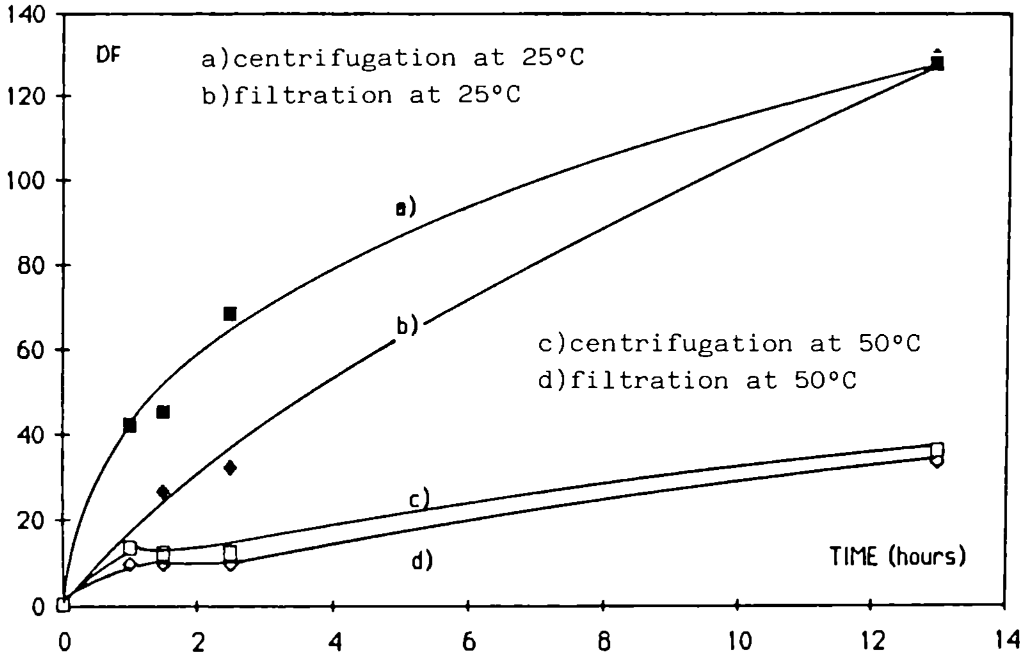

Fig.2 CsPTA precipitation:DF vs time

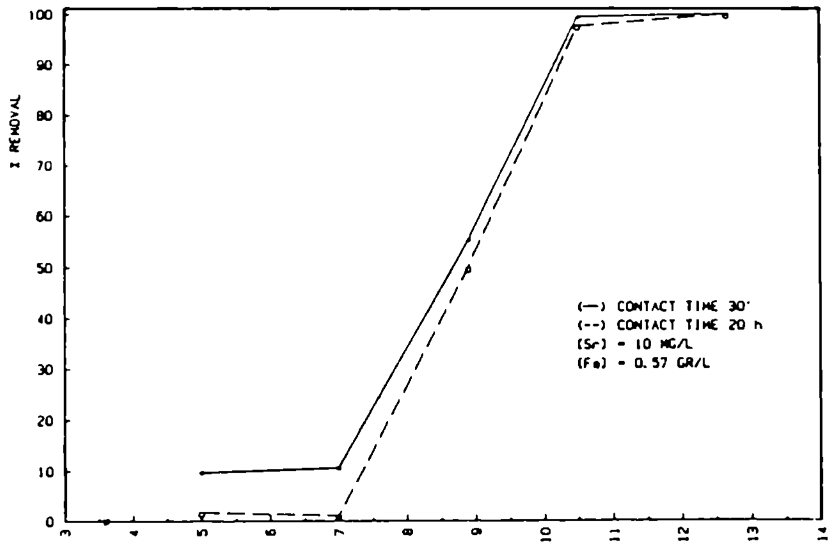

Fig.3 The effect of pH on percentage removal of Sr by Fe-hydroxide flocs. T=25°C

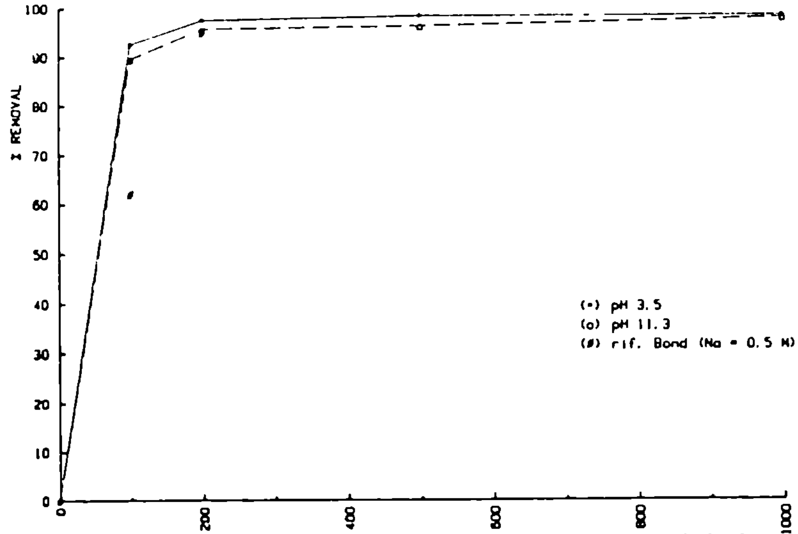

Fig.4 EFFECT OF NaTPB CONCENTRATION ON PERCENTAGE REMOVAL OF CESIUM-137. INITIAL Cs 20 MG/L , CONTACT TIME 30'

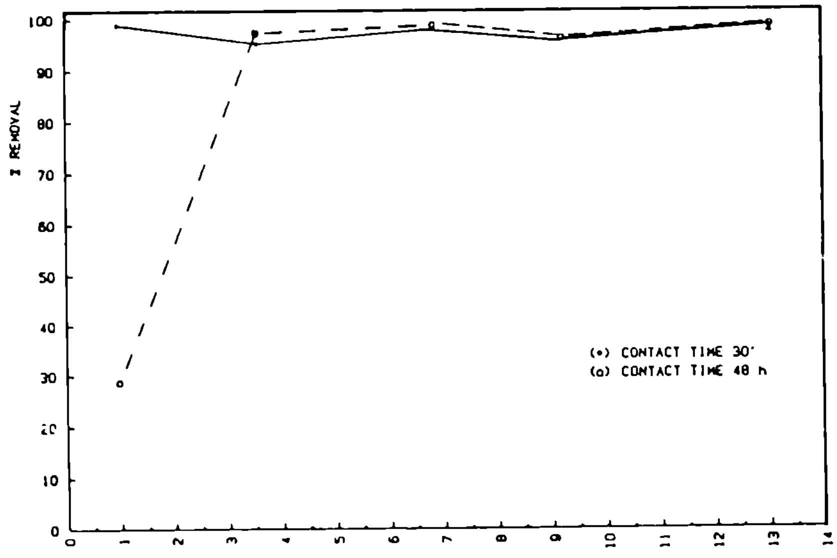

Fig.5 The effect of pH on percentage removal of Cs by TPB precipitation. Initial Cs 20 mg/l , TPB=1 gr/l

TREATMENT(SEPARATION AND RECOVERY TRANSURANIC ELEMENTS)FROM LIQUID WASTES PRODUCED BY PLUTONIUM PLANT OF CRE-CASACCIA

Contractor:	ENEA-CRE CASACCIA, Rome, ITALY
Contact n°:	FI1W-0012
Duration of contract:	July 1986-March 1988
Project Leader:	M.Casarci

A.Objectives and Scope

The liquid wastes produced by Casaccia Plutonium Plant,due to the content in alpha emitters,must be considered,according to the present national regulation(guida tecnica N°26 ENEA-DISP)as included in"category 3"(highest risk wastes).

The main purpose of the research work related to this contract is to study and develop in laboratory and pre-pilot scale a general purpose transuranic element extraction and recovery process.

To implement this process,the selected extracting agent is the Octyl(Phenyl)-N-N'-Diisobutylcarbamoylmethylphosphine oxide(CMPO)

The study under this contract will permit to verify:

*the feasibility of a simultaneous separation of U,Pu and Am from liquid wastes of different composition with a single extraction procedures;

*the flexibility of the process;

*the easiness of management of the process;

*the recovery of actinides in a suitable form to allow their rework;

*the volume reduction,minimizing the production of secondary wastes.

B.Work Programme

B.1 Identification and classification of liquid wastes to be treated

B.2 Procurement of the CMPO extractant

B.3 Purification of CMPO,and purity evaluation test

B.4 Preparation of simulated wastes and interaction studies with the solvent

B.5 Choice of diluent

B.6 Decontamination tests at laboratory scale with real solutions

B.7 Modelling of the flowsheet

B.8 Pre-pilot scale tests with real solutions

B.9 Technical and economic valuation and final report.

C.Progress of work and obtained results

Summary

In the first semester of the activities under contract the B.1,B.2,B.3 items have been investigated.
The main TRU waste sources in Plutonium Plant of CRE Casaccia have been identified(B.1).
All this type of liquid wastes have been collected in 2 litre bottles.
Until now about 700,2 l. bottles have been produced.
The CMPO has been supplied(B.2) by M&T Chemical Inc. as 84% pure grade.
The present cost of this product is about ten dollars for gram.
A major problem associated with the use of O(o)D(iBu)CMPO has been to obtain sufficently pure material(B.3).
There are some methods to purify CMPO:Distillation,Mercury Salt Purification,Crystallization and Ion Exchange.
After purification,it's important to verify the purity grade and the presence/absence of acidic impurities.
We have been utilized two methods to obtain this information:Americium test and Gas-Chromatographyc study.
The general work progress status is as follows:
B.1,B.2,B.3 are completed.
B.4,B.5,B.6 are progressing normally.

Progress and Results

B.1 Identification and classification of liquid wastes to be treated

The main TRU waste sources in Plutonium Plant of CRE-CASACCIA have been:
-Purification of Plutonium Solution;
-Pu(IV) oxalate processes;
-Sol-gel processes;
-Analytical Methods utilized for Pu/U determination.
All this type of liquid wastes have been collected in 2 litre bottles,when the estimated Pu concentration was higher than 1 mg/l and in 25 l container for lower estimated Pu concentrations.
About 700,2 l bottles have been produced.
Each of these bottles has been controlled,in order to verify:
-the integrity of the containment;
-the pH of the solution;
-the presence of suspended solids or precipitates;
-the presence of organic phase;
-the bulk actinide(U,Pu)concentration,by non destructive neutron-based techniques.

Chemical analysis has been performed on spot samples.

After this inspection procedure,the liquid wastes have been stored in new bottles,and collected in homogeneus categories,according the 4 types described before.

A summary of the information concerning the typology,and U/Pu total amount is reported in the table 1 and 2.

B.2 Procurement of the CMPO extractant

For this work,CMPO has been supplied by M&T Chemical Inc. as 84% pure grade.

The present cost of this product is about ten dollars for gram.

Due to the very strong interest on further application of this compounds,expecially in U.S., other firms are interested in commercialization of large amounts of CMPO.

Therefore,a decrease of its price can be foreseen for the future.

B.3 Purification of CMPO and Purity evaluation test.

There are at present four methods to purify CMPO:Distillation,Mercury salt purification,Crystallization and Ion exchange.

In these work only crystallization and Ion exchange have been utilized.

The acidic impurities of CMPO are likely to be phosphinic acid,then it should be possible to purify CMPO by using an anionic exchange resin.

Amberlyst A-26,a macroporous resin in Cl form has been generally used for this purpose.

In our case to obtain an even better product,the CMPO purified by I.E. has been also crystallized.

To this purpose,crystal seeds of pure CMPO have been addend to the I.E. purified solution and after a few hours,the crystalline material was obtained.

To determine the presence of indesiderable impurities,it's possible to use the Americium Test.

In fact,these acidic impurities can reduce the efficency of the Am(III) stripping at low acidity.

A tracer amount of Americium in 0.01,0.02,0.05,0.1,0.2,0.5,1,2,6 M $HNO3$ was equilibrated with an equal volume of extractant 0.1 M in Diethylbenzene.

Fig.1 show the D o/a for Am vs. equilibrium acqueous phase $HNO3$ concentration.

The difference at low acidity between the commercial and purified CMPO is clearly visible.

The commercial CMPO resulted 86% pure from G.C. analysis.

An accetable solvent extraction purity grade is at least 95% CMPO.

Purities of CMPO were also determined with Gas-Chromatographic methods.

The column used was a capilary column(22 mm x .32 mm)with DB5 phase (film=0.3 m).
A programmed temperature of 40°-260° was used.
The preliminary results are shown in Fig.2
There are at least eight impurities in the commercial as received CMPO and their total amount is 14%.
After purification the purity level of CMPO increases to 98% which is accetable for extraction applications.
Further investigation is in progress to determine the chemical nature of at least some of these impurities.

D.REFERENCES

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/5/E.P.Horwitz et al. Sol.Extr.and Ion Exch.4(3),449(1986)
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Table 1 Total Volume and U/Pu total amount

Material Description	Volume(l)	Pu(gr)	U enriched(gr)
Nitric solution	952	244	63
Oxalic solution	154	51	9.2
Analytical solution	86	33	1885*(natural U)
Sol-Gel solution	15	14	---
Other Solution stored in Plutonium Plant			
Pu nitric solution	6.5	21	---
Pu and U nitric sol.	27	3.2	5.7
U nitric sol.	4		0.7

Table 2 Typology of wastes

Type 1 waste	Nitric solution 3-7 M
Type 2 waste	Nitric acid 1 M Oxalic acid 0.6 M Pu oxalate
Type 3 waste	Pu variable concentration NH4OH 11 M NH4NO3 0.5 M CCl4 Tetrafurfurilic alcool 0.5 M
Type 4 waste	Solphamic acid 0.1 M Ferrous sulphate 0.1 M Phosphoric acid 2 M Nitric acid 0.5 M Molybdenium Ammonium trace Diphenyl Barium trace Potassium Bichromate trace Uranium 1 g/l Plutonium variable Silver nitrate 20 g/l Ferrous sulphate 0.01 M Alluminium nitrate trace Solphamic acid trace Cerium solphate trace Pu 0.25 g/l U variable

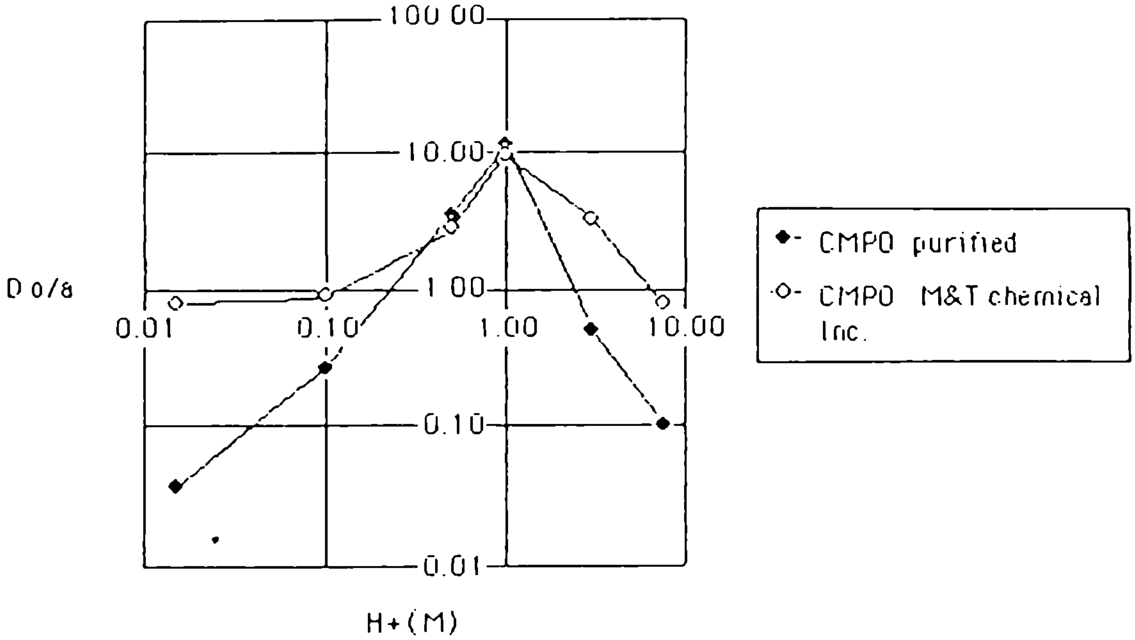
100.00
10.00
1.00
0.10
0.01
D o/a
0.01
0.10
1.00
10.00
H+(M)
◆- CMPO purified
◇- CMPO M&T chemical Inc.

Fig.1


A
INJECT
11 1
0
6.93
8.94
9.41
10.92
14.36
14.74
17.62
18.31
18.93
23.09
23.65
24.01
48.64
B
INJECT
11 1
0
9.47
14.48
17.78
18.44
19.03
19.07
23.28
24.19
48.93

Fig. 2

Electrochemical Ion-exchange/Sorption for Medium Active Liquid Waste Treatment

Contractor: UKAEA, Harwell Laboratory, UK
Contract No: FI.IW.0018.UK(H)
Working Period: June 1986 - May 1990
Project Leader: A.D. Turner

A. Objectives and Scope

The specific aim of this contract is to develop electrochemical ion-exchange/sorption processes (EIX) from a bench top to a demonstration pre-pilot scale, and verify their capabilities in the treatment of synthetic and genuine liquid waste streams at flow rates of 0.1-1 m^3/h for the removal of both βγ and α activity.

The programme is directed at optimizing equipment design and process control, and obtaining sufficient performance data on the relationships between flow rate, electrical current, stream decontamination and overall volume reduction factors so that realistic flow sheets may be drawn up. These could subsequently be a basis for evaluating the potential of a full scale plant. Other practical issues such as the degree of feed clarification needed before treatment will also be considered - examining the possibility of desorbing any colloidal fouling during the subsequent elution half cycle. In addition, the effect on EIX performance of the presence of potentially inteferring ions that adversely affect normal ion-exchange and floc process (e.g. complexing agents) will also be evaluated.

Another important technical goal of the programme is to compare the performance of these electrochemical processes with existing treatment routes - such as ion-exchange, flocculation and evaporation - and demonstrate advantages in plant compactness, operation and effectiveness.

B. Work Programme

B.1. The design, construction and commissioning of a 0.1 m^3/h EIX module and its ancillary pumps, tanks and control gear for the treatment of βγ waste solutions.
B.2. Evaluaton of 0.1 m^3/h module performance on the treatment of genuine waste streams. Small scale supporting work on interferring ions.
B.3. Design, construct and commission a 1 m^3/h EIX unit, incorporating any modifications arising from the previous tasks.
B.4. Evaluate performance characteristics of the 1 m^3/h unit for the treatment of genuine βγ waste streams for flow sheeting purposes.
B.5. Develop high capacity electrosoprtive electrodes for the treatment of α bearing wastes. Examine the effect of interferring ions.
B.6. Design, construct and commission a 10 ℓ/h module based on the results of B.5.
B.7. Evaluate the performance of the 10 ℓ/h module on genuine α waste streams.
B.8. On the basis of B.7 results, design, construct and commission a 0.1 m^3/h plant for the treatment of α wastes.
B.9. Evaluate the performance of the 0.1 m^3/h α removal plant on genuine wastes.

C. Progress of work and obtained results

Summary

Long term trials of electrochemical ion-exchange (EIX) have just been terminated after 2 years of continuous use - comprising 2190 cycles of absorption and elution. Little change in performance or appearance of these modules was observable - thus demonstrating the robustness of the process.

The design and construction of a 0.1 m^3/h EIX unit (together with ancillary equipment) has now been completed, so work has begun on the fabrication of the 0.4 m^2 electrodes required for this cell. A small scale automated test rig (100 cm^2) has been comissioned to evaldate new electrode designs and fabrication routes more suited to this larger scale. Currently, alternative binder systems are being examined, as well as the proportion of binder needed in the EIX electrode for effective performance. A range of new exchange media (both inorganic and organic) have been obtained for evaluation on both small and large scale.

An inorganic ion-exchange electrode (zirconium phosphate), developed for the selective removal of Cs from a Na containing stream, has been demonstrated to be resistant to radiation damage up to at least 10 MGy, with no marked deterioration in EIX performance. While previous work using an opposed pair of zirconium phosphate electrodes has shown enhanced selectivity when used with periodic polarity reversal, modifications to this cell design have displayed improvements in kinetic performance for the treatment of high salt content streams.

Work has also been initiated to extend the application of EIX to plutonium containing liquid streams. Equipment has now been installed in a glove box to evaluate the behaviour of small EIX electrodes which have been fabricated using known Pu absorbing materials. The general work progress status is as follows:

. B.1 is progressing normally
. B.5 is delayed
. B.6 is as far advanced as B.5 will allow.

Progress and results

1. 0.1 m^3/h EIX module for $\beta\gamma$ waste treatment (B.1, B.2)

As the purpose of this programme is to demonstrate the treatment of relatively large throughputs of liquid waste, this has necessitated the movement of the work to a laboratory more suited to this scale of operation. A significant proportion of the resources deployed during this period have therefore been expended in rebuilding existing equipment and in the purchase, construction and installation of new apparatus. A 3 m^3 feed tank will be used in conjunction with the 0.1 m^3/h EIX unit, and an additional 4 m^3 of storage capacity for the 1 m^3/h module. A variable speed pump capable of operating over the 0.1 - 1 m^3/h range has been purchased and installed. The work programme has been divided into four subsections.

- Electrode scale-up

  Previous electrodes used in bench-top development trials were typically 100 cm^2 in area /1/. These were manufactured by the application of ion-exchange powder as a viscous slurry in a toluene solution of an elastomeric binder to the platinized titanium metal mesh current feeder. Although larger electrodes (700 cm^2) have been fabricated by this technique, it proved to be less than ideal. As a result, work has been initiated to develop a new method of electrode preparation more suited to large scale production. Alternative, non-flammable solvents (e.g. 1,1,1 trichloro-ethane) for the currently used styrene-butadiene copolymer binder, and a two-part silicone are being investigated, and are showing signs of promise. Initially, this work is being carried out on 100 cm^2 test electrodes, so that their performance can be evaluated and compared with the previously well characterised electrode assemblies. As one extreme of a series of tests, a binderless electrode has been successfully demonstrated - the exchanger beads being retained in the proximity of the current feeder by a microporous polyamide cloth restrained by the counter electrodes. Although this performed adequately, it was not as good as a bound electrode due to a degree of mobilization of the beads by the small amount of gas generated at the current feeder. However, this result does confirm that absorbers may be used in the form of beads rather than just a fine powder, and also that only sufficient binder to immobilise the media may be required, without having to completely fill the interstices.

- Flow cell development

Based on the performance characteristics of a previous flow cell (FC/4) /1/, which had a surface area of 700 cm^2, a scaled-up module has been constructed to accommodate an electrode of 4000 cm^2 - capable of treating a 0.1 m^3/h flow of 200 ppm caesium solution. The experimental unit, 1 m in length and 0.2 m wide, is constructed of perspex with a rubber gasket sealing the two halves. Flow profiles of the feed through this cell have been followed by dye injecton. While the 'V' shaped inlet gives a good plug flow distribution over the majority of cell length, the single outlet at the top does produce some channelling. It is proposed to eliminate this by modifying a future sealed unit with a corresponding 'V' shaped channel outlet.

- Ion-exchange selection and development of electrode design

Continuing work is required throughout the course of this programme on the demonstration over significant lifetimes of the effectiveness of the electrodes manufactured by new routes and to new designs, as well as the evaluation of alternative absorbers - including inorganic exchangers and organic chelating resins. To this end, a small scale test rig has been constructed and fully automated to test novel 100 cm^2 electrodes - either in stirred batch or flow cell mode. Several exchangers available commercially on the 1 kg scale required for the 0.4 m^2 EIX electrode, will also be evaluated in the 0.1 m^3/h module. These will include Amberlite IRC 84 (either as beads or as a powder), Amberlite CG 50 (as a powder) and zirconium phosphate (granules and powder).

- Cell configuration

During 1985/6, a cell design was developed comprising a pair of zirconium phosphate cation exchange electrodes. By polarity reversal as the feed progressed up the cell, the selectivity towards caesium removed from a sodium rich solution was greatly enhanced. As the specificity of activity removal is more important for the treatment of higher salt content wastes, it is significant that recent experiments have demonstrated that unrestrained electrodes are even more effective for the treatment of such streams. Preliminary results have shown that these unrestrained electrodes are mechanically stable under the periodic potential reversal regime used to enhance selectivity, due to the suppression of any gas formation at the current feeders.

2. Actinide sorption (B.5-B.9)

Work has also been initiated to extend the application of EIX to plutonium containing liquid streams. Previous studies have investigated Pu(IV) removal from nitric acid solutions at Pt, Ti, stainless steel and graphite electrodes as a function of potential, acid concentration (1-5 M) and Pu concentration (0.01 - 1 g/ℓ). The most significant adsorption was observed under those conditions where ion-exchange might be expected at electrolytically formed surface oxide films (PtO, TiO_2, Cr_2O_3, -COOH). Essentially complete desorption could be effected by changing the applied potential. Having demonstrated the possibility of electrical control for actinide adsorption and deposition at thin oxide films on simple plane electrodes (with a capacity of ∿ 40 MBq/m^2), it is the goal of this part of the programme to investigate whether EIX electrodes composed of such Pu specific adsorbers as polyantimonic acid, titania or graphite are effective in increasing the specific absorption capacity.

To this end, small EIX electrodes made of these materials and a small scale test cell have been fabricated and installed in an alpha active glove box to evaluate their performance in removing plutonium from a range of nitrate streams. Analysis of residual plutonium content in the feed will be carried out by liquid scintillation spectrometry. Initially, experiments will be conducted on a batch basis prior to flow cell work.

Publications

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Immobilisation of Cladding Waste by Press Compaction and Conditioning for Final Disposal by Encapsulation in a Lead Containment

Contractor: S.C.K./C.E.N., Mol, Belgium
Contract N°: FI1W-0019-B
Working Period: May 1986 - December 1989
Project Leader: L. Geens

A. Objectives and Scope

At present, cladding waste is either temporarily stored under water, or conditioned by embedment in cement. An alternative conditioning method consists of press compaction, followed by enclosure in a seamless lead containment. The main advantages are the important volume reduction and the corrosion resistance of the conditioned product in clay as a final disposal medium. The process has already been demonstrated on pilot scale under inactive conditions, in a simulated hot cell /1/.

The main aims of the actual project are:

- the further development of the press compaction technology on pilot scale ;
- the active demonstration on pilot scale of the conditioning technique with representative cladding waste ;
- the evaluation of the characteristics of the products obtained, in view of their final disposal.

The work is carried out in close collaboration with KfK-Germany, where the press compaction technique will be developed on the industrial scale.

B. Work Programme

B.1. Further development of press compaction technolgy under inactive conditions.
B.2. Equipment of a hot cell facility for press compaction and conditioning of radioactive cladding hulls.
B.3. Transport of representative cladding waste and compaction products.
B.4. Press compaction of radioactive hulls.
B.5. Conditioning of compacted radioactive hulls in a corrosion resistant containment.

C. Progress of work and obtained results

State of advancement

The further development of the compaction technique was focussed on the addition of soft metals to the hulls, in order to improve the characteristics of the compaction product. No effect resulted from the addition of lead granulates. With addition of lead or aluminum sheets of various thickness, compacted discs were obtained with smoother and less curved bottom and top surfaces. However, it did not really improve the cohesion of the product in view of further manipulation. Moreover, disc dimensions and weight increased, resulting in a smaller volume reduction. In the actual compaction process, the hulls are stacked in a tin can before compaction. The use of a basket instead of the tin can will be investigated in the next year.

The equipment of a hot cell facility is going on. The stainless steel alfa box of the cell is being mounted. Some parts of the equipment have been purchased and are being adapted for use in a hot cell. Other parts have been designed and are under construction in our workshops.

The radioactive cladding waste for the active demonstration will be obtained from the WAK-Karsruhe. The transport of hulls from Karlsruhe to Mol will be arranged by KfK ; the transport of compacted discs to Karlsruhe by the SCK/CEN. For these two transports, respectively a German and Belgian company will be responsible. However, the incompatibility of the reception and handling systems in Karlsruhe with those in Mol creates some problems, which will have to be solved in 1987.

Progress and results

1. Further development of the press compaction technology (B.1.)

The active hulls, coming from the WAK, will have a length of 50 mm. Since all the experience available was obtained with 25 mm chops, a series of compaction tests were carried out both with carbon steel and zircaloy chops of 50 mm. This is considered as the limit for the press used, which has a press diameter of 105 mm. The chops are compacted, stacked in a tin can of 750 cm^3. Although the stacking density is lower with the 50 mm chops, the density of the compaction product is the same as with the shorter chops. The density of the compacted disc increases with decreasing wall thickness of the chops.

In a second series of compaction experiments, the addition of soft metals to improve the coherence of the compaction product was investigated. The soft metals used were lead and aluminum. The use of lead granulates resulted in no effect at all, except that the weight of the compaction product increased. Consequently, lead and aluminum sheets with thicknesses from 0.5 - 03 mm were put on the bottom of the tin can and on top of the hulls. This resulted in smoother and less curved surfaces of the compacted discs. However, it did not significantly improve the handling and manipulation in view of their further conditioning. Moreover, disc dimensions and weight did even increase, resulting in a smaller global volume reduction. As a result, the addition of these metals will not be further applied during the active demonstration.

Compaction in successive steps has also been tested. However, the press is not really designed for this kind of operation. Compaction of 50 mm zircaloy chops, with a diameter of 10.5 mm and a wall thickness of 0.75 mm, in two steps decreased the compaction product density from 80 to 74 % of the theoretical zircaloy density. No further experiments in this field are planned. In view of the gas evolution experiments, foreseen by KfK, compaction of hulls in a basket instead of a tin can will still be investigated in the future.

2. Equipment of a hot cell facility for press compaction and conditioning of radioactive cladding hulls (B.2.)

For the active demonstration of the hulls conditioning technology, a hot cell facility is being equipped. The facility consists of an alpha-thight hot cell, shielded with 1 m of concrete. The alpha-thightness is assured by a stainless steel box, installed in the hot cell area. The mounting of windows, doors, passages and peripheral equipment, like ventilation, is going on. For the handling of heavy objects in the cell, a jib-arm of own SCK/CEN design was constructed. The apparatus, which has a lifting power of 250 kg, has been tested and some minor improvements are still being implemented.

Some parts of the cell equipment were available already from the previous cladding waste programme /1/. New units have been purchased or ordered, while other ones have been designed and constructed. A hulls distribution unit and the 3000 kN press were already adapted for remote operation and maintenance during the previous programme. A gamma scanning apparatus to measure the distribution of the gamma activity on the hulls has been designed and it is being constructed in the SCK/CEN workshops. A new semi-automatic gas cooled TIG-welding unit, for the welding of the triple containment of the compacted hulls, has been ordered. It differs from the one previously used in this way, that the container to be welded remains fixed and that the welding torch is rotating. The unit has the possibility of oscillating the torch while rotating, for the welding of the lead containment. A helium leak detector, to be used for the quality control of the stainless steel inner container, has been purchased. For the general surveillance of the cell and for close visual control of some operations, a monitoring system consisting of in-cell disposable cameras linked to a video screen outside the cell will be installed.

3. Transport of representative cladding waste and compaction products (B.3.)

The possibility to have radioactive hulls transported from Karlsruhe to Mol and vice versa was one of the conditions for the approval of the research contracts by the C.E.C. The transport of hulls from Karlsruhe to Mol will be arranged by KfK ; the transport of the compacted discs to Karlsruhe by the SCK/CEN. For these two transports, respectively a German and a Belgian company will be responsible. Originally the use of a TN-6 container was foreseen for both transports. Due to the rather large volume of 100 kg hulls, KfK proposes to have the transport done in 200 dm^3 drums, shipped in the appropriate transport container. As no reception facilities for such drums exist at the SCK/CEN, reception under water is being envisaged at the moment. The specific technical aspects related herewith are being investigated.

List of publications

GEENS, L., C.E.C. Contract N° FI1W-0019-B, Semestrial Report May-December 1986.

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2 c) Optimization of waste management at source

Minimization of volume and Pu content of wastes from a plutonium fuel fabrication plant

Contractor : BELGONUCLEAIRE N.V., Dessel, Belgium
Contract N° : FI1W/0024
Duration of contract : May 1986 - October 1988
Project Leader : G. Vanhellemont

A. Objectives and Scope

The main objective of the programme is to conceive, to develop and to apply at BELGONUCLEAIRE's Pu fuel fabrication plant a series of techniques, working procedures and equipment aiming at a minimisation of the volume and Pu content of the waste arising during the operation of the plant and/or at the dismantling of the installations.

The amount and the nature of the Pu contaminated waste generated by future Pu fuel fabrication plants have been estimated within the framework of past R & D programmes. In the present programme, the interests of which are of both an ecological and an economical nature, the various waste streams will be characterized in a qualitative and quantitative way in order to allow the elaboration of a waste minimization strategy by the development and application of techniques, concepts and systems leading to a reduction of the volume and/or Pu content of the various waste forms produced. The principle of reduction of the waste at the originating source will be put into practice up to a maximum.

B. Work Programme

B.1. Determination of the characteristics of the equipment used at the BELGONUCLEAIRE plant for measuring the Pu content of the waste.
B.2. Results from the application of techniques, concepts and systems for :
B.2.1. -the confinement of Pu bearing powders within tight equipment.
B.2.2. -the limitation of the contamination within the glove boxes.
B.2.3. -the transfer of Pu bearing materials in reusable containers.
B.2.4. -the transfer of Pu bearing materials using new purged posting systems.
B.2.5. -the reduction of waste with high Pu content by the gradual replacement of destructive testing by non destructive testing.
B.3. Qualitative and quantitative characterization of the waste generated at a Pu fuel fabrication plant; identification of the waste producing fabrication steps; classification of the waste as a function of the conditioning and final disposal criteria.

C. Progress of work and obtained results

State of advancement

Work on the tasks B.1., B.2.1. and B.3. has started as scheduled in the work programme and is progressing normally.

As to the task B.1., the waste drum scanner has been adapted in order to reduce the variation of its geometric efficiency. Measurements performed before and after the modification show that this variation has been improved by a factor of about 2.

Work on the task B.2.1. consisted of a survey of the literature on dust formation within alpha-tight enclosures and of the development of an equipment allowing the emptying of PuO_2 cans with a maximum limitation of dust spread.

The main activity within the framework of the task B.3. has been the starting and analysis of detailed waste production statistics, which will enable to evidence the reduction of both the volume and Pu content of the waste in the course of the present programme.

Progress and results

1. Determination of the characteristics of the equipment used at the BELGONUCLEAIRE plant for measuring the Pu content of the waste (B.1.)

Almost the whole of the solid radioactive waste produced at the BN plant is packed in tin cans the volume of which is about 25 liters. Their Pu content is determined by means of an apparatus of the HLNCC type (High Level Neutron Coincidence Counter), i.c. the model DRC-100 from the IRT Corporation, San Diego, USA.

The detector unit consists essentially of a cylindrical sample cavity surrounded by a crown of 30 ^3He proportional neutron counting tubes. The tubes themselves are sunk in an annular matrix of moderating polyethylene provided with a cadmium lining. Additional moderation is provided by polyethylene disks at the top and bottom of the sample cavity.

The geometric efficiency of the system, i.e. the response to a fission source placed at any position within the sample cavity has to be as constant as possible since in practice the position of the Pu in a waste can is not known. Since the apparatus as purchased had a too high geometric efficiency variance, the detector unit has been modified in order to get a more constant geometric efficiency.

For the high-sensitive configuration, the modifications consist in a partial replacement of polyethylene by pure graphite on the top and bottom plug of the sample cavity in order to minimize the loss of neutrons through the ends and to increase the efficiency near the ends. Furthermore, the inner Cd liner has been partially removed near the top and the bottom of the sample cavity. In the medium part, the thickness of the polyethylene matrix has been reduced and an additional Cd liner has been installed, reducing in this way the efficiency of the counting tubes in this zone.

For the low-sensitive configuration, the use of the graphite bottom plate and top plug of the high-sensitive configuration limits the loss of efficiency near the ends.

The tests have been performed by placing a PuO_2 sample containing 18.1 g $^{240}Pu_{equivalent}$ at 37 different positions within the sample cavity and recording the response of the apparatus. The counting time was set at 100 s and 6 counting runs were made for each position of the PuO_2 sample.

As can be seen from the summarized results given in table I the geometric efficiency variation has been improved by a factor of about 2 as compared with the unmodified system.

2. Results from the application of techniques, concepts and systems for the confinement of Pu bearing powders within tight equipment (B.2.1.)

As evidenced by a survey of the literature on dust formation within alpha-tight enclosures one has to deal with Pu bearing powders the particle size of which may range from a few tenths of a micrometer up to 100 micrometers. Concepts are being worked out to confine this powder within tight equipment kept at a negative pressure with respect to the internal glove box pressure. A first achievement of BELGONUCLEAIRE in this field is an equipment used to introduce the powdery PuO_2 feed material into the fuel manufacturing line with a maximum limitation of dust formation.

3. Qualitative and quantitative characterization of the waste generated at a Pu fuel fabrication plant (B.3.)

Solid Pu suspected waste is generated within the controlled area but outside the glove boxes. It is selectively collected according to the classification system imposed by NIRAS-ONDRAF, the Belgian National Radioactive Waste Authority. The relative amounts of solid Pu suspected waste produced during a typical LWR-MOX fabrication campaign are given hereafter :

. combustible	74.2 % by volume
. non-combustible, compactible (except filters)	4.4 % by volume
. non-combustible, compactible filters	19.0 % by volume
. non-combustible, non-compactible	2.4 % by volume

The total volume of solid Pu suspected waste produced per kg of Pu in the final product, i.e. in the fuel pins, amounts to about 60 l. Detailed information has been gathered concerning the origin of this waste and some 20 waste producing operations have been identified.

Solid Pu contaminated waste is generated within the glove boxes; before leaving the glove boxes it is also sorted according to its nature (combustible or not, compactible or not). The relative amounts of solid Pu contaminated waste produced during a typical fuel fabrication campaign are given hereafter :

. combustible	48.6 % by volume,	containing 38.6 % of the total $(Pu+^{235}U)$ content of the solid waste
. non-combustible, compactible	43.6 % by volume,	containing 37.2 % of the total $(Pu+^{235}U)$ content of the solid waste
. non-combustible, non-compactible	7.8 % by volume,	containing 24.2 % of the total $(Pu+^{235}U)$ content of the solid waste

The tables II and III show the distribution of this type of waste as a function of the $(Pu+^{235}U)$ content per 25 l-can.

Table I : Geometric efficiency variation of the DRC-100 waste drum scanner : coincidence counts per second per g ^{240}Pu equivalent.
Source : PuO_2 sample containing 18.1 g ^{240}Pu equivalent.

POSITION OF THE SAMPLE		LOW-SENSITIVE CONFIGURATION		HIGH-SENSITIVE CONFIGURATION	
		Before modification	After modification	Before modification	After modification
Total sample cavity volume (37 positions)	Median value (*)	7.89	11.25	12.23	23.83
	Variation	± 41 %	± 19.9 %	± 52 %	± 8.4 %
	Minimum-to-maximum ratio	$\frac{4.67}{11.11} = 0.42$	$\frac{9.00}{13.51} = 0.67$	$\frac{5.87}{18.59} = 0.31$	$\frac{21.83}{25.83} = 0.84$
Cavity volume corresponding to the volume of a waste can of the 25 l-type	Median value		10.22	24.15	23.83
	Variation		± 12 %	± 18.4 %	± 8.4 %
	Minimum-to-maximum ratio		$\frac{9.00}{11.45} = 0.79$	$\frac{19.70}{28.60} = 0.69$	$\frac{21.83}{25.83} = 0.84$
Empty 25 l-can	Median value				23.98
	Variation				± 7.7 %
	Minimum-to-maximum ratio				$\frac{22.14}{25.83} = 0.86$
25 l-can filled with a simulated waste matrix	Median value				23.83
	Variation				± 4.7 %
	Minimum-to-maximum ratio				$\frac{22.71}{24.95} = 0.91$
Along the central axis of the cavity volume	Median value	6.75	9.50	22.75	23.25
	Variation	± 19 %	± 5.3 %	± 13.5 %	± 6.1 %
	Minimum-to-maximum ratio	$\frac{5.47}{8.03} = 0.68$	$\frac{9.00}{10.01} = 0.90$	$\frac{19.70}{25.80} = 0.76$	$\frac{21.83}{24.67} = 0.88$
Along the radius of a cylindrical cavity volume corresponding to the volume of a 25 l-can	Median value	9.50	9.72	21.29	22.95
	Variation	± 15.8 %	± 7.4 %	± 7.5 %	± 4.8 %
	Minimum-to-maximum ratio	$\frac{8.03}{11.00} = 0.73$	$\frac{9.00}{10.44} = 0.86$	$\frac{19.70}{22.88} = 0.86$	$\frac{21.85}{24.05} = 0.91$

(*) Calculated as the arithmetic mean of the minimum and maximum value

Table II : Relative volumes of solid, Pu contaminated waste generated during a typical fuel fabrication campaign

Group limits according to the(Pu+^{235}U) content per can		Combustible	Non-combustible, compactible	Non-combustible, non-compactible	Subtotal
Lower	Upper				
0 g	0.4 g	27.8 %	12.2 %	1.6 %	41.6 %
0.4 g	2 g	8.6 %	16.2 %	0.5 %	25.3 %
2 g	5 g	4.7 %	7.7 %	0.4 %	12.8 %
5 g	10 g	3.8 %	3.1 %	0.6 %	7.5 %
10 g	15 g	1.3 %	1.8 %	2.6 %	5.7 %
15 g	30 g	0.9 %	1.2 %	1.3 %	3.4 %
30 g	50 g	0.7 %	1.0 %	0.7 %	2.4 %
50 g	100 g	0.7 %	0.4 %	0.1 %	1.2 %
100 g	-	0.1 %	0 %	0 %	0.1 %
Subtotal		48.6 %	43.6 %	7.8 %	100 %

Volume of solid, Pu-contaminated waste per kg of Pu in the final product (pins) : 50.8 l/kg Pu

Table III : Relative amounts of (Pu+^{235}U) in the solid, Pu contaminated waste generated during a typical fuel fabrication campaign

Group limits according to the(Pu+^{235}U) content per can		Combustible	Non-combustible, compactible	Non-combustible, non-compactible	Subtotal
Lower	Upper				
0 g	0.4 g	0.9 %	0.5 %	0.1 %	1.5 %
0.4 g	2 g	1.7 %	3.7 %	0.1 %	5.5 %
2 g	5 g	3.1 %	4.7 %	0.3 %	8.1 %
5 g	10 g	5.5 %	4.7 %	1.0 %	11.2 %
10 g	15 g	2.9 %	4.5 %	7.8 %	15.2 %
15 g	30 g	3.3 %	5.9 %	7.6 %	16.8 %
30 g	50 g	6.1 %	7.9 %	5.3 %	19.3 %
50 g	100 g	11.2 %	5.3 %	2.0 %	18.5 %
100 g	-	3.9 %	0 %	0 %	3.9 %
Subtotal		38.6 %	37.2 %	24.2 %	100 %

Pu content of the solid waste :
0.98 % of the Pu in the final product (pins)

Optimization of waste management at source

Contractor: Associated Nuclear Services,
Contract No: FI1W/0023
Working Period: November 1986 - November 1987
Project Leader: Mr. A. Martin

A. Objectives and Scope

The objectives of the study are to collate and review information on measures taken at nuclear installations to minimize waste arisings, looking particularly at the segregation and measurement of wastes at the point of arising, and those factors which currently limit efficient segregation of suspect contaminated solid wastes.

The programme of work is jointly funded by the Commission of the European Communities and the UK Department of the Environment (DoE) under contracts FI1W-0023-UK(H1) and PECD 7/9/383. The start date for these contracts being 1 December 1986 and 1 November 1986 respectively.

B. Work Programme

B.1. To complete a literature review of the state-of-art in waste minimisation and segregation techniques for suspect contaminated solid wastes.

B.2. To undertake visits to nuclear installations both in the United Kingdom and Europe, with the objective of identifying successful measures taken in minimizing and segregating solid wastes.

C. Progress of work and obtained results

State of advancement

A literature review of the state-of-art in waste minimizing and segregating techniques was initiated in November 1986. This search, while providing a source of useful information on the general topic of waste minimization has so far identified very little information on the specific aspects of segregating suspect contaminated solid wastes.

The approach of gathering details of practical experiences, by undertaking visits to nuclear sites, also commenced in November 1986, with a visit to the Dounreay Nuclear Power Development Establishment. The site visit provided details of successful waste minimization methods introduced at Dounreay.

The status of the work progress on both approaches B.1. and B.2. used in this study is considered satisfactory.

Progress and results

1. Review of literature (B.1.)

Work was started at ANS in November 1986, on a literature review of the state-of-art waste minimization and segregation techniques. Initially an on-line computerised literature search of the International Nuclear Information System database (INIS) was undertaken. From this search some fifty-five reports and papers were identified as containing useful and relevant information on waste minimization and related topics. Those documents not in the ANS library have been ordered and only some fifteen are still outstanding. This review will continue in 1987.

2. Site visits (B.2.)

A visit to the Dounreay Nuclear Power Development Establishment by ANS on the 14 November 1986, was very successful. The decision to reprocess Prototype Fast Reactor (PFR) irradiated fuel at Dounreay had necessitated a complete re-appraisal of the management philosophy and practices for solid waste, for the following reasons:

- the PFR fuel contains about one thousand times more plutonium and higher actinides than fuel from Dounreay Fast Reactor (DFR);
- it was intended to increase the throughput by about a factor of ten.

As a result of the re-appraisal the following means of reducing waste arisings have been used:

- the incorporation of bagless posting techniques for high, medium and low activity waste operations;
- shredding and washing of PCM;
- replacing PVC with other plastics which do not give problems of HCl generation;
- improved instrumentation;
- introduction of a pneumatic transfer system for small samples;
- education of personnel;
- liquor recycling and monitoring.

It is estimated that the above measures have reduced the volumes of high alpha, low beta-gamma waste by 25-30% and the volumes of high beta-gamma waste by about 20%. An additional benefit is that handling of the waste is now safer and cleaner.

Further site visits to other nuclear power plants, reprocessing plants and to users and producers of radioisotopes will be undertaken in 1987.

CHAPTER 3

TASK No. 3 : EVALUATION OF CONDITIONED WASTE AND QUALIFICATION OF ENGINEERED BARRIERS

CHAPTER 3

TASK No. 3 : TESTING AND EVALUATION OF CONDITIONED WASTE AND QUALIFICATION OF ENGINEERED BARRIERS

A. Objectives

Assessment and modelling of the long-term behaviour of engineered barriers (waste conditioning matrices, containers, buffer materials, etc ...)

Establishment of quality assurance in radioactive waste management

Integration of European research effort in the above fields.

B. Research topics dealt with under the 1980-1984 programme

Characterization of medium-activity waste forms :

- Work was carried out on the stability of ten of the commonest forms of low- and medium-activity wastes in the Community (e.g. ion exchange resins fixed in epoxy matrices, reprocessing sludges cast in cement or bitumen, etc ...).

Characterization of solidified high-activity waste forms :

- Several reference materials (e.g. borosilicate and vitreous ceramic glasses) were defined and investigated in the framework of a co-ordinated Community action. The investigations concerned :
  - the leaching of glasses,
  - the effects of leachants,
  - the thermal stability,
  - the radiation damage,
  - the mechanical strength and fracture mechanics.

Work on engineered barriers :

- Selection of materials for high-activity waste containers and assessment of their long-term behaviour

- Selection and characterization of suitable buffer materials.

C. 1985-1989 programme

a) Research on medium-active waste form characterization

- Long-term leaching behaviour :
  - Modelling of nuclide release phenomena in various repository environments

  - Experimental studies to investigate the associated mechanisms and to validate predictive models.

- In addition to these studies, investigations on the most important synergistic and radiation induced effects, such as swelling, shrinking, fissuring, gas release and possible reactions between waste and matrix materials, will be carried out.

b) Research on high-active waste form characterization

- On the basis of the results of the preceding programme, characterization research on solidified high-level waste will be carried out on a limited number (3-4) of reference borosilicate glasses.

- The data obtained from the above-mentioned research will be validated and the relevant mechanisms will be modelled.

c) Other engineered barriers

- The following subjects will be investigated :

  - Completion of the testing programme started during the 1980-1984 period, on corrosion behaviour of selected materials for high-activity waste containers and subsequent modelling of corrosion phenomena.

  - Characterization, on a laboratory scale, of candidate buffer materials and linings

  - Long-term effects of irradiation on barriers.

d) Development of standard test methods

- A major action will be launched to harmonize test methods for the research outlined in the preceding paragraphs.

e) Development of test for quality control and quality inspection purposes

D. Programme implementation

26 contracts have been signed and the available information is listed thereafter.

3 a) Medium active waste form characterization

EMBEDDED WASTES AND LEACHATES ANALYSIS

Contractor : CEA - CEN CADARACHE FR
Contract n° F 11 W/0095/1 - task 3
working period : 1986-1989
project leader : A. SAAS
Executant : C. POLETIKO - CEN CADARACHE

A. OBJECTIVES AND SCOPE

To characterize low level and intermediate level activities in nuclear wastes, we must develop analytical methods required for alpha and pure beta emitters.

For such measurements we must obtain a liquid sample, this implies a complete destruction of each matrix (bitumen, cement and thermosetting resins).

The finally objective of the programme is to provide an acceptable set of methods for the characterization of each type of embedded waste.

B. WORK PROGRAMME

B.1. Full destruction of embedded thermosetting resins.
B.2. Measurement of pure beta emitters (63 + 59 Ni ; ^{55}Fe, ^{99}Tc).
B.3. Mineralization of bitumen matrices and solubilization of sludges used to coprecipitate nuclides.
B.4. Solubilization of cement matrices.
B.5. Measurement of ^{14}C and ^{3}H in all matrices.
B.6. Method for concentration and separation of alpha emitters from each solution of mineralization.
B.7. Isolation of gamma emitters, at low concentration (such as ^{94}Nb).

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The destruction of embedded thermosetting resins has been achieved (B.1) ; this procedure has been associated with B.5 programme. The main difficulty is to get a solution which permits easy operations for chemistry or radiochemistry determinations.

The measurement of both ^{59}Ni et ^{63}Ni has been achieved, the critical point is the determination of chemical nickel concentration in such a complex solution.

Progress and results

The starting point for the destruction of resins is sampling. The difficulty is to crush such samples, in order :

- to get a suitable geometry for gamma counting
- to perform a good mineralization.

gamma counting is an important step ; thanks to this procedure we can determine the activity of solid sample and check whether the yield of attack is good.

The mineralization is based upon a digestion, of crushed sample, with concentrated sulfuric acid at about 200°C, gas emitted are either condensed (H_2O) or trapped in a bubbler containing sodium hydroxide (for CO_2), these solutions are used for liquid scintillation counting.

Full oxidation of sample is obtain thanks to hydrogen peroxide addition.

The resulting clear solution is used to proceed in further determinations i.e. chemistry or radiochemistry (^{90}Sr, $^{59+63}$Ni).

$^{59+63}$Ni measurements are achieved thanks to a complexation with dimethylglyoxime (DMG) and addition of Ni carrier used also for yield determination. This complex is extracted in chloroform ; after elimination of chloroform, DMG complex is destroyed with nitric acid, the solution may be concentrated to be used for liquid scintillation counting.

List of publications

- technical report for ^{63}Ni (internal CEA)
- technical note for resins attack (internal CEA)

Full-scale leaching tests, scale effects, lysimeter tests

Contractor : CEA - CEN-CADARACHE - FR
Contract N° : F 11 W/0095/1
Task 3 :
Working period : July 86 - Dec. 90
Project leader : A. SAAS
Executant of task 3 : J.C. NOMINE - CEN SACLAY FR

A. Objective and scope

The knowledge of Radionucleides migration from full-scale packages containing ML or LLW to the biosphere is recognized to be one of the most important parameter for the radwaste management.

With this in mind, several kinds of characterization tests have been scheduled ; among them we proposed to do full-scale leaching tests on real active blocks, coming either from french or foreigners CEC Radioactive producers facilities (lysimeter experiments, and R and D action, like the study of scale effect in leaching experiments.

B. Work programme

B1. Knowledge of leaching exchanges between full-scale packages of real active waste, embedded in different matrices, and the biosphere.
B2. Comparison between leaching and lysimetric datas.
B3. Scale effect studies in the area of the leachability of active waste embedded in hydraulic binders.

C. Progress of work and obtained results

Summary

The previous CEC contrat which covered the period 1980-1985 gave us the opportunity to do full-scale leaching experiments, including several types of solidified waste form (ex : RWF2, RWF8, RFW7...), the actual program will procure the possibility, either to continue tests undertaken formerly (ex : KfK cement-concentrates block) or to start new experiment (ex : Harwell cement magnox cladding hulls, spanish blocks...). Within the same programme, attention will be focused on others important aspects like : balance of activity released, especially with α emitters, effect of the size of the samples on activity Fraction Released (scale effect) ; for this purpose we intend to compare several cement blocks doped with ^{137}Cs, which volumes will cover the range 0.2 to 200 l ; in the same point of view, we intend too to observe, with lysimetric experiments the influence of alternate (dried or saturated situations) periods on the leachability of the samples.

B1 and B3 are progressing normally and B2 will start soon.

Progress and Results

B1. Full-scale leaching tests

The KfK cement-concentrates block of 170 l is essentially concerned here. Originally this specimen is constitued with a PZ45F cement (150 kg) mixed with a $NaNO_3$ concentrate (100 l or 120 kg) containing α, β and γ emitters.

The total salt content represents 9.3 % of the total weight.

The leaching test is operated in a stainless steel vessel with the following parameters.

Leachant : tap water of Saclay, maintened at a constant temperature of 23 ± 3°C ($\frac{\text{V leachant}}{\text{S of the block}} = 14,3$).

Method : static with periodical leachant renewal.

The main elements which were analyzed are respectively ^{137}Cs, ^{90}Sr, ^{60}Co, ^{239}Pu, ^{241}Am, ^{238}U for the radiochemical aspects.

Dry extract, nitrates... for chemical aspects.

After a total duration of 446 days (9 runs with renewal of leachant) the results concerning the leachates (non filtered) are :

Radionuclide	Initial activity Ao (Ci)	Total amount of activity released (Ci) Σ an	Total fraction released Σ an/Ao
^{137}Cs	$2,10 \times 10^{-2}$	$2,48 \times 10^{-3}$	$1,18 \times 10^{-1}$
^{90}Sr	$1,06 \times 10^{-2}$	$7,97 \times 10^{-6}$	$7,52 \times 10^{-4}$
^{60}Co	$1,54 \times 10^{-3}$	$3,24 \times 10^{-6}$	$2,10 \times 10^{-3}$
^{239}Pu	$5,19 \times 10^{-3}$	Non detectable	
^{241}Am	$2,18 \times 10^{-2}$	Non detectable	
^{238}U	$4,11 \times 10^{-4}$	Non detectable	

TABLE 1

In order to make a first balance of the total activity released, some more analysis have been undertaken :

1) On the sludges deposited on the leaching loop.

2) On the solution (HNO3 HN) which has been used to decontaminate the vessel.

The results obtained after a duration of 77 days are summarized Table 2.

Radionuclide	Initial activity Ao (Ci)	Total amount of activity released in the leachates A_L (Ci)	Total activity in the sludges A_S (Ci)	Total activity deposited in the loop by contamination A_C (Ci)
^{137}Cs	$2,1 \times 10^{-2}$	$1,05 \times 10^{-3}$	$6,12 \times 10^{-9}$	$3,66 \times 10^{-5}$
^{90}Sr	$1,06 \times 10^{-2}$	$5,16 \times 10^{-6}$	$1,38 \times 10^{-8}$	$3,85 \times 10^{-5}$
^{60}Co	$1,54 \times 10^{-3}$	$1,18 \times 10^{-6}$	non detectable	$9,61 \times 10^{-5}$
^{239}Pu	$5,19 \times 10^{-3}$	non detectable	$2,43 \times 10^{-10}$	non detectable
^{241}Am	$2,18 \times 10^{-2}$	non detectable	$6,4 \times 10^{-10}$	$1,75 \times 10^{-4}$
^{238}U	$4,11 \times 10^{-4}$	non detectable	non detectable	non detectable

TABLE 2
BALANCE OF ACTIVITY RELEASED AFTER 77 DAYS

The first conclusions about this experiment are :

- Important released activity for ^{137}Cs.
- Non detectable released activity for α emitters, except for ^{241}Am, but at a very low level.
- A beginning of degradation of the block (cracks on the top).

B2. Lysimeter data

Three subroutine have been undertaken :

- A bibliography to register the main parameters influencing lysimeter experiment.

- The construction of a first kind of laboratory scale lysimeter which permit to observe the hydraulic flow within some inert materials (sand, sand + clay) (see figure 1).

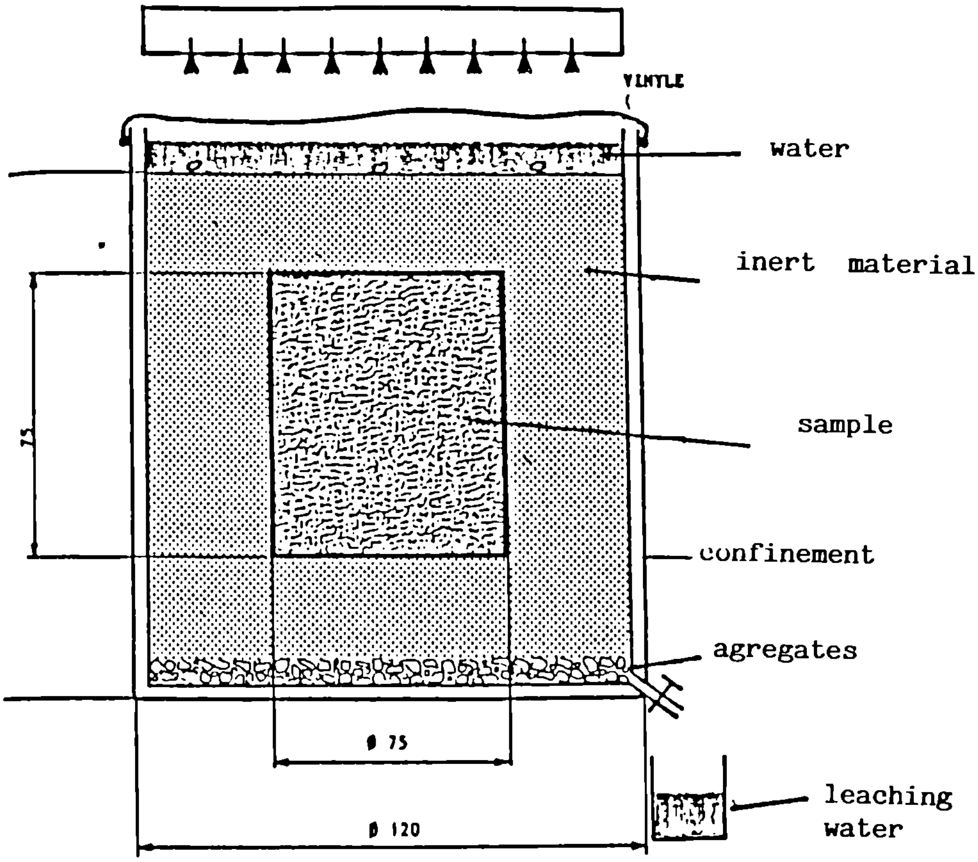

FIGURE N° 1
FIRST LABO-SCALE LYSIMETER

- The preparation of a programme based on the influence of driying cycles in the leachability.

Scale effect in leaching test

Preliminary tests, in order to wasrant a good homogeneity of the sample have been undertaken.

For this purpose several inactive or weakly doped 200 l drums have been fabricated ; they permit :

- the control of the density distribution by sampling core on two 200 l drums : average values like 1,92 ± 0,01 and 1,94 ± 0,01, starting from 12 samples in each drum have been obtained,

- the control of the activity dispersion on a weakley traced 200 l drum ($UO_2(NO_3)_2$) by counting in different places (150 ± 10 c/s).

After these previous experiments, we have fabricated the real sample with the same batch using the following formulation (for 1 l).

Cement CPA55 : 1300 g
Sand : 850 g
Absorbant : 90 g
Water : 380 cm^3 (w/c = 0,47)
Contaminant ^{137}Cs : 10 mCi/l.

The real characteristics of the different samples submitted to the leaching tests are summarized in Table 3.

We made 4 samples of 2 l in order to have indications on the homogeneity of the material and on the reproductibility of the leaching experiments.

The samples are now in water and we have edited a special protocol both for the leaching experiment and the analysis.

Samples	Diameter (cm)	Height cm	Volume cm^3	Surface cm^2	Weight kg	$\frac{\text{Leachant volume}}{\text{surface of the sample}}$ ( )	Contact dose rate in mrad/h
200 l	57,0	77,7	198272	19017	420,000	15	1200
20 l	26,5	40,9	22558	4508	45,200	15	950
2 l	12,3	17,9	2127	929	4,318	15	400
2 l	12,3	17,7	2103	921	4,348	15	400
2 l	11,0	20,7	1967	905	4,020	15	400
2 l	11,0	20,8	1977	909	4,027	15	400
0,2 l	5,8	8,6	227	209	0,457	15	100

TABLE 3

Speciation of the transuranium elements stemming from low intermediate and high activity level wastes

Contractor : CEA - CEN-CADARACHE - FR
Contract N° : F I1 W/0095/1 Task 3
Working period : July 86 - December 89
Project leader : A. SAAS
Executant : D. STAMMOSE - CEN SACLAY FR

A. Objective and scope

For storage of nuclear wastes, it is necessary to provide for all eventualities, in particular the arrival of water in contact with blocks containing radioactive wastes. In this case, it is important to know on which form are present radionucleides carried in solution. Then behaviour in the biosphere depends on their chemical form. Essentially we have taking an interest in α emitters.

During this program, we are going to work on leachates issued from different matrices.

- Glass (in collaboration with Marcoule center).
- Cement, concrete : we expect to use leachates coming from the SEL*, if their activity is high enough to allow us measurement by alpha spectrometry.
- As a special case, a few cement blocks, artificially charged with α emitters, which are able to be used in a scale effect experiment will provide valuable leachates.
- Furthermore, leachates from other participants of the CEC are welcome if possible.

B. Work program

B1. Improvement of speciation

Setting off complementary methods in determination of insoluble part of leachate for example electrodialyse. Development of new techniques of speciation among different oxydation degrees of a named element.

B2. Try to find a relation between the nature of the matrix and the chemical forms of α emitters in leachates.

B3. Make speciation of α emitters in the solutions issuing from leaching of the glasses R7T7 fabricated at Marcoule Center.

C. Progress of work and obtained results

State of avancement

The adjusting of method of preparation of PuVI at trace level is finished and we are going to test this element as an oxydation degree tracer in selective coprecipitation by neodyme fluoride (NdF_3).

We have analysed some leachates coming from SEL, but α emitters activity is too low to allow us any speciation.

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* Station for Experimental Leaching/CEN Saclay (France).

A piece of glass R7T7 containing 1,85 10^7 Bq has been leached by 30.10^{-6} m^3 of bidistilled water at 90°C. For each sequence, we put fresh bidistilled water in place of leachate.

A speciation among particle size has been done by filtration and ultrafiltration and spectation on soluble part as soon as activity is detectable.

Progress and results

B1. Improvement have been made by using plutonium as a tracer at the + VI oxydation degree. Stability, and use have been assessed and experiments are made to check the validity of the experimental protocol.

B2. At a point, at the present time. We need more experimental results to correlate the chemical forms in solution with the nature of the matrix.

B3. Speciation of α emitters in the low activity solution issued from the leaching of α doped glasses.

	^{239}Pu	^{238}Pu	$^{238}Pu/^{239}Pu$
Soluble part + insoluble species destroyed by HNO_3 0,1 M	$3,48.10^2$ (83 %)	$1,11.10^2$ (85 %)	0,32
Insoluble species destroyed by HNO_3 1 M	44,4 (11 %)	11,1 (8,5 %)	0,25
Insoluble species destroyed by warm HNO_3 8 M	27,8 (7 %)	7,4 (5,5 %)	0,25
Total activity	$4,2.10^2$ (100 %)	$1,3.10^2$ (100 %)	

TABLE I
RESULTS IN Bq

Chemical treatment on soluble part		^{239}Pu	^{238}Pu
Selective coprecipitation by NdF_3	PuIII + PuIV	$1,4.10^4$	$2,33\ 10^7$
	PuV + PuVI	$3,9.10^4$	9,62.10
Extraction by TTA	PuIV	$5,2.10^3$	$1,4.10^3$
	PuIII+PuV+PuVI	$4,3.10^4$	9,99.10
Coprecipitation by $Fe(OH)_2$	Pu	$6,7.10^4$	$1,6.10^4$

TABLE II
RESULTS IN $Bq.m^{-3}$

We have made several sequences of leaching. First we noted than the most important part of radioactivity is setted on an insoluble form. In some cases activity in soluble part is impossible to detect.

We have made a more precise speciation of insoluble forms on 4 sequences. Results which are presented on the figure (1) show than radioactivity is essentially (95 %) fixed on particles whose size in greater than $0,22.10^{-6}$ m.

To try to precise the nature of these insoluble forms (hydroxyde, colloïdes or pseudo colloïds) we have determined the proportion of these particles which are solubilised by nitric acid at different concentration.

Table I collects results concerning study of leachate corresponding to a period of 14 days of contact between solution and glass. For an other sequence representing same conditions of leaching we have observed that only 0,5 % of plutonium activity is present on a soluble form.

After a first acidic treatment (HNO_3 0,1 M) we find 83 % of activity in the soluble part. These particles very easily solubilized are probably plutonium hydroxydes recently polymerized and sop easily destroyed. The second treatment by nitric acid 1 M destroyed 10 % of particles and it has been necessary to use HNO_3 8 M warm to solubilize 6 % still present in solution.

At least we have made a determination of different chemical forms of plutonium in soluble part ($NdFO_3$) herefore we used selective coprecipitation wich carries plutonium on valence states III and IV, coprecipitation by $Fe(OH)_2$ carrying all oxydation degrees of plutonium and extraction of Pu^{4+} by TTA (thenoyltrifluoracetone). We observe than activities determined by these methods are very similar. They show that there is twice more plutonium on degrees V or VI than plutonium tri or tetravalent. This result has soon been noticed in others medias (lakes, pounds, seas...). There speciation experiments have been made without tracers. We work now on a synthetic leachate with 2 tracers one a tetravalent and other is hexavalent. We will try to test this method issuing from leachates on solutions glass containing Pu in same conditions except for temperatures which is fixed at 90°C.

Colloids Related to LLW and ILW

Contractor: UKAEA, Harwell, UK
Contract N°: FIIW/0090/1
Working Period: July 1986 - December 1986
Project Leader: J.D.F. Ramsay

A. Objectives and Scope

A recent review /1/ carried out for the Department of the Environment indicates the considerable importance of colloids in radionuclide transport processes. This review and our initial experimental investigations has confirmed that this subject is complex and in general the sources, characteristics and migration behaviour of colloids are very poorly understood, particularly in regard to cement waste forms.

Our objectives in this contract are:

- to charactetise and investigate the mechanisms by which colloids may form in cement leachates, with particular attention to the composition, age and structure of the cement,
- to determine the properties of colloids which may occur in repository environments and establish the effects of the near-field aqueous chemistry on their behaviour, and
- assess the radionuclide incorporation and sorption of such colloids.

This investigation is seen as providing basic information of cement leaching mechanisms and reference data for the transport modelling of colloids in the near-field environment. It is also envisaged that expertise in colloid characterisation techniques (e.g. light scattering) can complement other projects concerned with radioactive waste leach testing carried out within Task 3. It is further anticipated that this contract will provide background for a second phase of experimental investigation of colloid migration and sorption behaviour which will have a direct application for transport modelling.

B. Work Programme

B.1. Studies of colloids in cement leachates.
B.1.1 Develop procedures for cement formulation and leaching.
B.1.2 Establish light scattering techniques for characterisation of colloids in leachate samples.
B.1.3 Use ultrafiltration, ultracentrifugation and dialysis to fractionate leachate colloids - characterise fractions by light scattering and identify by electron microscopy and chemical analysis.
B.1.4 Investigate effects of cement composition and additives on colloids in leachates.
B.1.5 Investigate radionuclide association with colloids.
B.2. Characterisation of colloids in repository environments - near-field chemical interactions.
B.3. Determine colloid sorption behaviour.

C. Progress of work and obtained results

Summary

A representative range of possible cement grout formulations has been prepared for long-term colloid leach test studies at different temperatures. These include pure ordinary Portland cement (OPC), and mixtures containing pulverised fuel ash (PFA), blast furnace slag (BFS) and silica fume. Other samples containing nuclide tracers, either separately or in association with ferric hydroxide floc, have also been prepared for tests under B.1.5.

From dynamic light scattering measurements it has been shown that there is a release of colloids in all leachates studied - in some cases very pronounced. These measurements provide data on colloid diffusion coefficients, hydrodynamic diameters, and concentration. The effect of ultrafiltration on colloid retention has been investigated in parallel with light scattering and scanning electron microscopy (SEM). These studies show that colloidal aggregates of primary particles (diameter $\lesssim 5\mu m$) exist together with clumps of rod-shaped particles (length $\lesssim 1\mu m$). Electrophoretic light scattering shows these two components to have different surface charge. There is evidence that the spherical particles arise by a process of nucleation and growth in solution. Chemical analysis on individual particles by EDAX shows a predominance of Si; Ca and traces of Ti and Al are also present with BFS cements. Initial inductively coupled mass spectrometry (ICP-MS) measurements on leachates from Co-doped cements show that a dominant fraction released is associated with colloids. Background investigations on different ultrafiltration membranes under B.1.3 show that blocking and interaction of colloids in pores may occur with cement leachates and that ultracentrifugation is a preferable colloid/liquid separation procedure.

Progress and results

1. Studies of colloids in cement leachates (B.1)

Procedures for cement formulation and leaching (B.1.1)

A representative range of possible cement grout formulations has been selected for study. Typical formulations are listed in "Table I".

Standard pellets were cast using sealed 10 ml polystyrene containers as moulds. 8-10g of wet mix in the form of a reasonably mobile paste were placed in each mould to give a cylindrical pellet (25mm diameter, 10mm long). The capped mould was then sealed in a second container in the presence of soda-asbestos (to exclude CO_2) and the mix allowed to set at room temperature (RT) for a minimum of 28 days. In some cases curing was accelerated in water at 60°C.

With some cement formulations this was accompanied by a noticeable release of a gelatinous white solid from the pellets. This was especially marked with the pellets containing fume silica (018).

After curing the cement samples have been leached as follows:

The demoulded pellets were rinsed in distilled water at the end of curing and then placed in distilled water (typically 250 ml/pellet) in a conical flask. The flask and water were then purged with nitrogen and sealed. Static leaching was then carried out at 25, 60 and in some cases 90°C with a range of different samples. (Leach tests at room temperature were carried out in the dark to prevent algae formation.)

Characterisation of colloids in leachates by light scattering (B.1.2, B.1.3)

Several leachate samples from different cement formulations have been characterised by photon correlation spectroscopy. In this technique /2/ information on the rate of diffusion of colloid particles is derived from fluctuations in the scattered light from an incident laser beam. Such fluctuations can be transformed to give a broadened frequency distribution about the monochromatic incident frequency, the width of which is dependent on the diffusion coefficient, D_T, of the colloid particles. From the latter a hydrodynamic radius, R_H, can be obtained; this is equivalent to the geometric radius in the case of monodispersed spherical particles.

The time integrated intensity (static light scattering) of the scattered light is dependent on the size and number concentration of particles. Typical results for the latter are shown for an OPC leachate in "Figure 1", after sequential ultrafiltration through membranes of decreasing nominal pore sizes. From this it is evident that considerable retention of particulates occurs when the pore size reaches $\lesssim 1\mu m$. Furthermore, for a pore size $<0.5\mu m$ scattered intensities are in general very low. Moreover we have found that the retention behaviour (for the same nominal pore size) is markedly affected by the type of membrane employed. In this case we show results for tortuous cellulosic and polycarbonate membranes respectively. These features arise from a combination of reasons due to colloid membrane interactions and pore blocking effects - the latter being particularly significant for colloids composed of particle aggregates as we have found here. We have investigated such effects in some detail since they have far broader implications in leach testing.

Values of R_H (as derived from D_T) ("Figure 2") corresponding to the same sequential filtration experiment, demonstrate the presence of colloidal aggregates: here we note that R_H is significantly larger than the nominal filter pore size. This implies that colloidal aggregates may be disrupted and aligned when forced under high shear through the ultrafilter pores. Such shear degrading effects are known to occur with high molecular water soluble polymers (e.g. polyacrylamides) and highlight the problems of colloid size determinations based solely on ultrafiltration.

Ultrafiltration/light scattering studies have also been undertaken with OPC/BFS cements (B.1.4). Although it is not appropriate to report in detail we have noted that the colloid concentration is lower and that there is less evidence of aggregates.

Scanning electron microscopy (SEM) of leachate colloids (B.1.3)

In parallel with our ultrafiltration/light scattering studies of cement leachate colloids, we have also developed techniques to examine colloid particles which are retained on the ultrafilter membranes. These investigations, performed after more prolonged leaching (5 months) than in (B.1.1), have provided important insight into the morphology and mechanism of formation of the colloids. Thus, in leachates from OPC we have observed two types of colloidal particle. The first are composed of large clusters ($>10\mu m$) of rod-shaped particles ($\sim 0.5\mu m$ long, $\sim 0.1\mu m$ thick). Other evidence, not reported here, indicates that these are composed of a silica-rich Cristobolite phase. The second type occurs as spherical particles with diameters in a range from $\sim 5\mu m$ to $<0.5\mu m$. The latter are frequently present as chain-like aggregates, and presumably correspond to the colloid particles detected by light scattering at an earlier stage of growth. These spherical particles have an internal microstructure which further suggests that they have nucleated and undergone growth in the leachate solutions. Currently we are investigating the possible formation of smaller colloidal particles ($\ll 1\mu m$) in leachates by light scattering (these are too small for detailed SEM study). Our preliminary SEM investigations of OPC/BFS leachates show important differences. Thus, although we observe colloidal particles, these are less regular in shape and fewer in number, and furthermore show less tendency to aggregate - an observation in keeping with the light scattering studies. Such differences may arise from the different chemical compositions of the leachates and will be explored further.

Another valuable technique being used in conjunction with SEM is energy dispersive X-ray analysis (EDAX). From this the elemental composition of individual particles can be obtained from the energies of the characteristic X-ray emission. Initial measurements made on particulates ultrafiltered from OPC/BFS leachates show the presence of several elements (Si, Ca, Al, Ti) the proportion of which depend on particle size and morphology. However, in general, most colloidal particles contain silicon predominantly.

References

/1/ RAMSAY, J.D.F., Harwell Laboratory Report AERE-R 11823 (1985).
/2/ RAMSAY, J.D.F. and BUNCE, J., Harwell Laboratory Report AERE-R 11017 (1983).

TABLE I
Range of Cement Grout Compositions Studied

Sample Code	Parts by Weight				
	OPC	PFA	BFS	FUME SILICA(1)	WATER SOLIDS
014	1	1	-	-	0.3
015	1	-	9	-	0.4
016	1	-	3	-	0.4
017	1	-	-	-	0.4
018	1	-	-	0.4	0.4(2)

OPC = ordinary Portland cement (Blue Circle)
PFA = pulverised fuel ash
BFS = blast furnace slag, ground granulated (CEMSAVE)

(1) 0.06:1 Superplasticiser: silica
(2) Water/OPC = 0.34

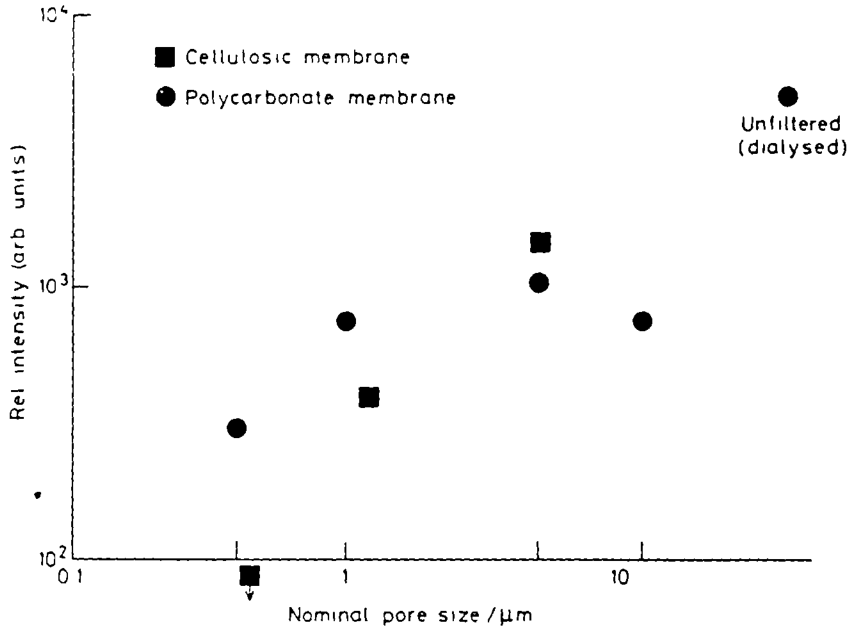


FIG 1 INTEGRATED SCATTERED INTENSITY FROM OPC (W/C 0 4) LEACHATES (298K)
N B Sample passing through filter size indicated

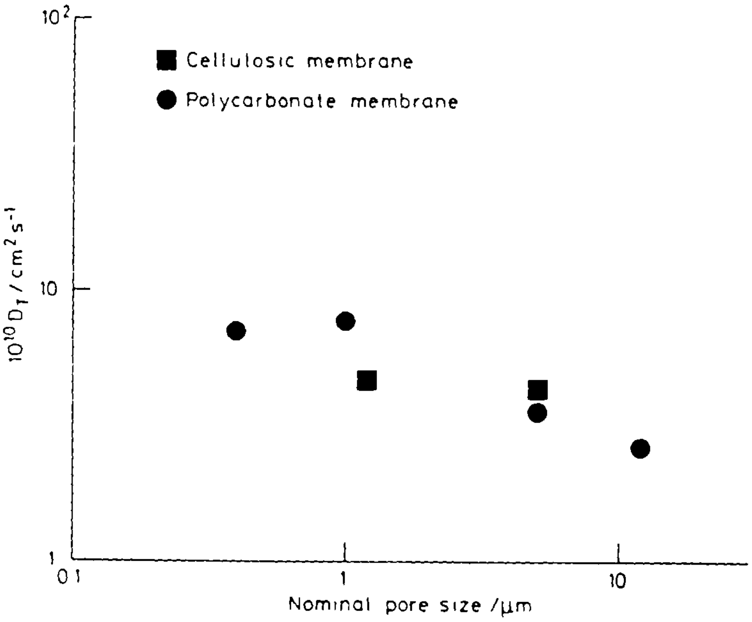


FIG 2 SELF DIFFUSION COEFFICIENTS OF COLLOIDS IN CEMENT (OPC) LEACHATES

Physico-chemical characterization of bituminized Eurochemic medium level waste

Contractor: S.C.K./C.E.N. Mol, Belgium
Contract N°: FI1W/0094
Duration of Contract: 1/08/1086-31/12/1989
Project Leader: P.Ph. Van Iseghem

A. Objectives and Scope

The present programme is a continuation of research carried out in the framework of the previous CEC R&D programme (1981-1984), under action 1 (characterization of low and medium level waste forms), covered by the contract n° 302-83-15 WASB.

In the previous programme, a number of real Eurobitum samples has been stored, to measure after various times the physico-chemical properties ("ageing"). Results for one year ageing were obtained. The corrosion behaviour of small, real Eurobitum samples in two media (pure water, clay-water mixture) was investigated, and important data on the swelling, leaching of the waste salts and of the radionuclides were gathered.

In this programme, the study of the ageing behaviour will be continued. Extrapolation of the swelling data on small samples to full size containers will be attempted by performing swelling tests on inactive specimens of increasing size. The study of the corrosion behaviour of real, fully active Eurobitum samples will be extended by performing tests in clay related media at repository-like pressure (4.0 MPa).

The experimental work will be elaborated in collaboration with Belgoprocess (ex-Eurochemic).

B. Work Programme

B.1. Effect of specimen size

Swelling experiments on inactive Eurobitum samples with specific surface area of 6.25, 2.20, 0.70 and 0.25 cm^{-1}, to conclude about the swelling behaviour of full size blocks (0.1 cm^{-1}). The experiments are conducted in two media.

B.2. Effect of pressure

Corrosion tests on real, small Eurobitum samples at ambient or the clay repository like pressure of 4.0 MPa, in interstitial clay-water and wet clay. Particular attention is given to the radionuclide release.

B.3. Ageing behaviour

Measurement of some physico-chemical properties (density, softening and self-ignition point, penetration, thermal properties, ...) on real Eurobitum samples stored for periods of 4 and 6.5 years.

C. Progress of work and obtained results

State of advancement

Preparations have been made for the experiments. Two actions were undertaken:

- The assembly of both inactive (see B.1.) and active (see B.2.) samples.
- The design and elaboration of the corrosion containers, consisting either in the differently sized containers for the tests under B.1., or the small containers for the tests under B.2., in active conditions and under pressure.

A delay of a few months has occurred for the assembly and delivery of both inactive and active Eurobitum samples.

Progress and results

Effect of specimen size

Two inactive, full size Eurobitum blocks have been identified as being potentially useful to provide inactive samples. The conformity of the bitumen with the product specifications will be controlled by an analysis of the nitrate concentration at various places in the block.

The experimental conditions for the corrosion tests have been defined as follows:

- Corrosion media: distilled water and clay-water mixture (100 g l^{-1}).
- Specific surface area: 6.25, 2.20, 0.70 and 0.25 cm^{-1}.
- Test duration: 14, 90, 365 days.
- Temperature: 23°C; surface area to solution volume ($SA.V^{-1}$): 0.1 cm^{-1}.

Effect of pressure

Part of the on-line, 50 ml Eurobitum samples (each 25 containers) will be used to conduct the experiments with active samples. The sample dimensions will be similar to those used in the previous CEC experimental programme on Eurobitum.

The experimental programme will consist of two parts:

- Tests at ambient pressure
  Inactive and active Eurobitum samples will be corroded at 23°C in synthetic interstitial claywater or wet clay for durations until two years.
- Tests at clay host repository pressure
  Active Eurobitum samples will be corroded at 23°C in synthetic interstitial claywater or wet clay for durations until two years.

Ageing behaviour

A number of measurements of physical properties are in preparation on some real Eurobitum specimens stored since beginning of 1983: density; self-ignition, flash and softening point; penetration; occurrence of exothermic reactions.

Mechanisms and interaction phenomena influencing release in low- and medium-level waste disposal systems.

Contractor: Risø National Laboratory, Denmark
Contract No: FI 1W-0089-DK (B)
Working Period: July 1986 - December 1987
Project Leader: K. Brodersen.

A. Objectives and Scope

Improved understanding of interaction phenomena influencing the nearfield in disposal systems for conditioned low- and medium-level radioactive waste is necessary for advanced safety assessments of such systems.

One topic is the diffusive transport from waste through barriers of concrete or clay as influenced by e.g. corrosion products from steel containers. The composition of water in equilibrium with various types of waste and concrete is important for concrete corrosion and for the possibility of crack-healing in concrete barriers. The influence of pore type distribution on diffusive transport through concrete will be demonstrated. SANS-measurements are used in an attempt to follow the structure of degrading concrete.

Some Bituminized waste products tend to swell and may thereby damage the outer barriers when exposed to water. Pressure build-up due to this mechanism will be followed. Metabolic products from growth of micro-organisms on bitumen may have indirect influence on solubility-controlled leaching and will be investigated. Measurements of flow properties of bituminized waste will be used to demonstrate ageing effects in the materials.

B Work Program

B.1. Diffusive transport in porous barriers.
B.2. Leaching compared with diffusion through slabs.
B.3. Self-healing of cracks or macro-pores in concrete.
B.4. Reactions with thin plates of cement paste.
B.5. SANS-measurements.
B.6. Volume stability of cemented ion-exchange resins.
B.7. Hygroscopic properties of bituminized or cemented waste.
B.8. Swelling forces due to water uptake in bituminized waste.
B.9. Diffusion through bitumen membranes.
B.10. Microbial degradation of bituminized materials.
B.11. Flow properties of ageing bituminized materials.

C. Progress of work and obtained results

Summary

The work during the first half-year of the contract has mainly been concentrated on characterization of concrete used as barrier material. The experimental part of B.2. is nearly finished. B.1., B.3. and B.5. are well under way. B.4. gives som experimental difficulties and B.7. to B.11. are delayed due to uncertainties about sample composition.

Progress and results

1. Diffusion in concrete (B.1., B.2.)

An extensive series of leaching and diffusion experiments using ^{134}Cs and TOH as tracers in various types of concrete is nearly completed and is expected to confirm previous work /1/ on pore structure in concrete. Final conclusions are not yet available.

Work on the use of the COLUMN code to describe interactive diffusion of leached components through clay barriers is well under way.

2. Concrete as material (B.3., B.4., B.5.)

Equilibrium compositions (Ca,K,Na,$SO_4$and pH) for water in contact with various amounts of granulated hardened pure cement paste or cement paste containing silica fume have been determined.

Water conditioned by contact with a silica-rich (or a pre-leached) type of concrete is likely to result in precipitation when passing through a pore or crack in a more alkaline concrete. This may result in closure of such cracks, and possibly in some sort of self-healing mecha- nism for damaged concrete barriers. Preliminary indications for such an effect have been obtained but the present experimental technique is unsatisfactory.

SANS (Small Angle Neutron Scattering) measurements are new for us, and so far the time has mainly been used to get aquainted with the principles and to develop methods for preparation of suitable samples of degraded (strongly leached) cement paste. High quality measurements over a large range of neutron wave-lengths can now be obtained, but it is still too early to draw any conclusions about the relevance of the method for waste characterization purposes.

3. Cemented ion-exchange resins (B.7.)

In lack of specifications for this reference waste type some preliminary experiments based on samples cast according to Swedish recommendations /2/ are in preparation. The samples are cast in spherical shape in a silicon rubber form.

4. Bitumen (B.8., B.9., B.10., B.11.)

Two sets of experimens with diffusion of ^{134}cs and TOH through thin membranes of pure Mexphalte 40/50 have recently been finished. Calculations are not yet available, but the cross-contamination problem encountered in some previous experiments is now eliminated.

The intention was to base most of the bitumen experiments on samples cast from inactive Eurobitumen. However, the availability of representative material is uncertain, so the experiments may have to be made with simulated material prepared in lab-scale.

References

/1/ BRODERSEN, K., Development of waste unit for use in shallow land burial. EUR report in press.

/2/ BEIJER, O., Casting granular ion exchange resins with medium-active waste in cement. Prav 1.36 (1980).

THE EFFECTS OF RADIATION ON INTERMEDIATE LEVEL WASTE FORMS

Contractor: UKAEA, Harwell, U.K.

Contract No.: FI.1W.0093

Working Period: July 1986-December 1986

Project Leader: D.C. Phillips

A. OBJECTIVES AND SCOPE

The purpose of this programme is to determine the effects of radiation on the properties of intermediate level waste forms relevant to their storage and disposal. It has two overall aims: to provide immediate data on the effects of radiation on important European ILW waste forms through accelerated laboratory tests; and to develop an understanding of the degradation processes so that long-term, low dose rate effects can be predicted with confidence from short-term, high dose rate experiments.

The programme will include cemented inorganic waste forms; organic matrix waste forms; and cement waste forms with a substantial organic component. Irradiation will be carried out by external gamma sources; by the incorporation of alpha emitters, such as ^{238}Pu; and, if appropriate, by the incorporation of beta emitters. The irradiated materials will include matrix materials, simulated waste forms and real waste forms.

Specific technical data which will be generated will include information on the effects on: mechanical integrity; dimensional stability; gas evolution; radionuclide release; and microstructure. Other information which will be generated will include models and predictive methodology for the assessment of long-term behaviour.

B. WORK PROGRAMME

B.1 Selection and procurement of specimens.

B.2 Gamma-damage experiments. Measure gas evolution and absorption. Provide specimens for B.4.

B.3 Alpha-damage experiments. Measure gas evolution and absorption. Provide specimens for B.4.

B.4 Assess radiation damage. Monitor dimensional stability, mechanical integrity, microstructural changes, leach rates.

B.5 Irradiation in vented containers.

B.6 Basic mechanisms. Develop theoretical models. Measure any additional necessary material properties.

B.7 Conclusions and feedback.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Summary

This programme has been in progress for six months. Detailed specifications of the reference waste forms, RMA, have not yet been agreed. A number of UK specifications have been drawn up and offered to the Commission. In the absence of RMA specifications experimental work is concentrating on generic studies of matrix materials and some limited experiments on waste form simulants which approximate to suggested RMA. Cemented borate wastes are known to disintegrate at 6-9 MGy when irradiated at high dose rate. Experiments have now been carried out at a lower dose rate and it has been shown that this waste form spontaneously fractures at the same dose at the lower dose rate, although less severely than at the higher dose rate. X-ray analysis indicates the growth, during irradiation, of an unidentified phase. Cement samples with a range of permeabilities have been manufactured to determine if there is a correlation between permeability and propensity to spontaneous fracture. Samples of polymer matrix simulated waste form, containing water and wet wastes, have been irradiated in vented containers, open top containers, and unconfined. Quantitative data on the effects of relative confinement have been generated.

Progress and results

1. Procurement of Specimens (B1)

The programme is to concentrate on those waste forms which are expected to be most affected by radiation and whose behaviour is still poorly understood: these are the organic matrix waste forms RMA 4 and 5; the cement waste forms containing inorganic waste RMA 2,6,8 and 10; and the cement waste forms containing organic wastes RMA 3 and 11. Detailed specifications for these RMA's have not yet been agreed by the Commission. Specifications for UK versions of RMA 3, 5, 6, 10 and 11 have been drawn up and offered to the Commission. In the absence of agreed RMA specifications initial work is proceeding on matrix materials and relevant RWF from the preceding 5 year programme.

2. Gamma-damage experiments (B2, B4)

Some cement matrix waste forms and matrices can disintegrate when irradiated. The mechanism of this process is not yet known with certainty but two possibilities are: the build-up of radiolysis gas in pores resulting in high pressures; and the radiolysis-induced growth of new solid phases producing strain. Radiation experiments have been carried out on samples of RWF2, a cemented borate, which has been shown previously to disintegrate at high dose rates of 10^4 Gy h^{-1} at 6-9 MGy. A lower dose rate of 10^3 Gy h^{-1} has now been used and gas analyses are shown in Tables I and II. Samples again spontaneously fractured at 6-9 MGy but the effect was less severe than at the higher dose rate. Thermal analyses did not identify any phase changes but X-ray analysis showed the growth of an, as-yet, unidentified phase.

Additives to cement, such as BFS and PFA, can change the permeability. Samples covering a wide range of composition have been manufactured and are being irradiated to determine if there is a correlation between propensity to spontaneously fracture, and gas permeability, measured in the saturated condition by a newly developed hydrogen permeability technique.

The radiolysis of plastics and other organics, encapsulated in cement, will produce gases which may react with the cement. Samples consisting of single types of plastic embedded in cement are being produced to obtain some basic data.

3. Alpha-damage experiments (B3, B4)

Alpha-damage experiments are to be carried out at high dose rate by incorporating relatively large quantities of the alpha emitter Pu-238 or Pu-239 into the simulated waste form. Equipment for measuring and analysing α-active gases has been designed and is being constructed. Equipment for manufacturing α-active cement waste form specimens has been assembled and commissioned in α-active glove boxes. An Instron mechanical testing machine has been adapted for α-active work.

4. Irradiation in vented containers (B5)

An objective of the programme is to obtain data and information of relevance to both storage and disposal. To simulate storage conditions samples should be irradiated under dry conditions, preferably in a vented container. For disposal conditions, an extreme is provided by irradiating the unconfined material while immersed in water.

A comparison has been made of the behaviour of polymer matrix waste forms irradiated under the following conditions: unconfined; in close-fitting, open top, containers; and in vented containers. The simulated waste forms consisted of polyester and epoxide resins containing water or damp ion exchange beads. As expected water loss was considerably less from the vented container samples than from the unconfined samples. Quantitative data on weight loss and dimensional stability have been obtained. Analysis of these data and of gases absorbed and evolved will provide a basis for future theoretical modelling.

Table I: Radiolytic gas evolution from Pozzo 325 containing borate waste simulant + sodium silicate + calcium hydroxide

Dose Interval	Sample Mass	Radolytic Gas Evolution ml STP			$G(H_2)$ Molecules per 100 eV
MGy	g	H_2	O_2	N_2	
0-3	253.7	+38	-40	-2	0.02
3-6	"	+55	-42	+7	0.03
6-7	"	+34	-34	0	0.06
7-9	"	+61	-42	+3	0.05

Table II: Radiolytic gas evolution from Portland 425 containing borate waste simulant + sodium silicate + calcium hydroxide

Dose Interval	Sample Mass	Radolytic Gas Evolution ml STP			$G(H_2)$ Molecules per 100 eV
MGy	g	H_2	O_2	N_2	
0-3	259.7	+41	-41.1	-5	0.02
3-6	"	+43	-40.9	+11	0.02
6-7	"	+13.6	-27.4	0	0.02
7-9	"	+26	-40.7	+5	0.01

The influence of organic complexing agents upon the mobilization and migration of radionuclides from ILW contained in cement and bitumen under near-field conditions for a repository in a salt dome

Contractor : Freie Universität Berlin, D.
Contract No. : FI1W-0091
Duration of contract: July 1986 - December 1988
Project Leader : G. W. Marx

A. Objectives and Scope

The effects of the presence of organic residues such as TBP, oxalate, citrate etc. upon the release of radionuclides from the source term and the subsequent migration of those radionuclides through a repository's near-field have, until now, received relatively less attention in comparison to studies concerning the influences of other parameters. These organic molecules are however, very strong complexing agents and it is becoming increasingly apparent that the presence of such compounds may influence radionuclide release and mobility.

Investigations will be carried out into radionuclide solubility and release from conditioned ILW under laboratory conditions representing those for a waste repository in a deep salt environment, with special attention being focused upon the rôle that certain man-made organic molecules may play in the release scenario. Subsequent migration studies involving salt columns will indicate the influences that such organics may have upon radionuclide mobility and retardation in salt.

B. Work programme

B.1 Source term solubility studies

B.1.1 Determination of equilibrium solubilities of plutonium(IV), americium(III) and neptunium(V) hydroxides, sodium diuranate, cesium chloride, silver iodide and silver iodate in concentrated salt solutions under the influence of the presence of TBP, DBP, EDTA, citrate and oxalate.

B.1.2 Determination of the tendency towards colloid formation by means of ultrafiltration.

B.1.3 Determination of radionuclide leachability from conditioned ILW in concentrated salt solutions in the presence of organics mentioned above.

B.1.4 Determination of the tendency towards colloid formation of radionuclides in waste leachates by means of ultrafiltration.

B.1.5 Solidification of selected organics in cement and determination of their leachabilities.

B.1.6 For selected actinides only: solidification of complexed actinides in cement and determination of their leachabilities.

B.2 Sorption and migration in the near-field.

B.2.1 Determination of mobility and sorption properties of radionuclides derived from B.1.1 and B.1.6 through columns filled with crushed sodium chloride and site-specific rock salt.

B.2.2 Determination of mobility and sorption properties of radionuclides in waste leachates derived from B.1.3 by the use of salt columns.

B.2.3 Determination of the sorption behaviour of selected radionuclide systems upon salt by the use of batch-type experiments.

C. Progress of work and obtained results

State of advancement

Upon receipt of the contract from the Commission during mid-October, work began immediately on those aspects originally forseen for July to December 1986 (B.1.1, B.1.2 and B.1.5). This work is progressing satisfactorily although the delayed start and the systems' themselves mean that no definitive results are as yet available. Completion is, however, expected during April-May 1987. Work has also commenced ahead of schedule on B.1.3, B.1.4 and B.1.6, necessitated because of long equilibration times required.

Progress and results

1. Sample preparation (B.1.1, B.1.5)

All solutions, radionuclide compounds and waste samples have now been prepared or are available for investigations with the exception of that listed under B.1.6.

- Solutions

Two concentrated salt solutions, a saturated sodium chloride solution and a quinary salt solution at its equilibrium point Q (the so-called "Q-solution") have been equilibriated with samples of inactive cement matrix (under aerobic conditions at 298K) and their physical chemical parameters (Eh, inorganic carbonate concentration) checked with results previously obtained under other contracts (1.2). The solubilities of the organic reactants mentioned under B.1.1 in these solutions are currently being measured.

- Standard radionuclide systems

Actinide hydroxides and sodium diuranate have been prepared as described elsewhere (1.2) and have already been brought into contact with salt solutions containing organics in a series of preliminary experiments. The remaining radionuclide compounds have also been prepared and are awaiting investigations.

- Waste systems

Samples of RMA 8 and 9 have been brought into contact with salt solutions containing EDTA and TBP and are currently being leached. Parallel to these experiments analyses techniques for the measurement of leached radionuclides are being improved and developed (partly reported in B 1).

Inactive cement samples have been doped with TBP, EDTA and citrate for separate studies into the release of these organics from waste matrices.

2. Speciation tests (B.1.1, B.1.3)

Ongoing studies in the Department of Radiochemistry into the polarographic and voltammetric determination of actinides in systems of high salinity are currently being extended to include complexation by organic chelating agents such as EDTA. Within the frame of a preceeding contract /1/ the properties of plutonium in standard saline systems are described, work has just begun into determining the influence of TBP complexation upon the plutonium(III)-plutonium(IV) equilibrium. In conjunction with this, extraction tests involving PMBP, and TTA for actinide(III)-actinide(IV) separations have been developed. First indications are good, results pointing to complete extractability of thorium(IV) and plutonium(IV) and Eu(III) by PMBP and TTA respectively, even from saturated salt solutions. It is hoped to be able to apply such extractants in order to support investigations concerning the chemical state of dissolved radionuclides in the systems of B.1.1.

3. Radionuclide mobility studies (B.2.1, B.2.2)

Already existing column migration apparati has been successfully modified to cope with an increased volume of experiments as a result of this contract. Long-term tests at low linearly hourly space velocities ($< 1.5\ cm^3\ h^{-1}$) are currently being undertaken with tritium and thorium containing solution in order to assess aparative stability.

References

(1) Flambard, A.R. and Marx, G., "Solubility and speciation of actinides in salt solutions and migration experiments of Intermediate Level Waste in Salt formations" CEC Contract No.: 415-83.7 WAS D(B), BMFT Contract-No.: KWA 5313 2, Final Report, Freie Universität Berlin, to be published by the CEC (1987).

(2) Marx, G., Flambard, A.R., Eßer, V.H.-G., Fusban, H-U. and Keiling, Ch. D., BMFT Contract-No. 02 U 5715, First Annual Report for 1985.

(3) Flambard, A.R., Keiling, Ch., Fusban H.-U. and Marx, G. Proc. 66th PTB Seminar "Chemie and Migrationsverhalten der Aktinoide und Spaltprodukte in natürlichen aquatischen Systemen, München 1986, PTB-SE-14, 28 (1986).

INVESTIGATION OF LLW AND MLW CEMENT PRODUCTS RESULTING FROM REPROCESSING

Contractor : Kernforschungszentrum Karlsruhe GmbH
Institut für Nukleare Entsorgungstechnik (INE)
Contract No. : FI1W/0092-D(B)
Duration of contract : July 1, 1986 - December 31, 1989
Project leader : P. Vejmelka

A. OBJECTIVES AND SCOPE

The proposed laboratory investigations include experiments with real samples from the waste treatment facility at KfK and experiments with simulated samples containing Pu, Am and Np.

With these samples detailed investigations will be performed to describe the long term activity release in the case of leaching. The experiments will be performed at room temperature using water and salt brine as leachants. The aim of the investigations is to determine the thermodynamically defined equilibrium concentrations of Pu, Am and Np in the system waste form/brine as well as the leaching kinetics. The investigations on the real samples will be performed in order to verify the numerous results from experiments on simulated samples and to obtain values for the realistic long term activity release.

B. WORKING PROGRAMME

B.1 Investigations with real samples. Determination of the kinetics of the activity release. Determination of the equilibrium concentrations for Pu, Am, Np in the system waste form/brine.

B.2 Investigations with simulated samples. Determination of the kinetics for the release of Pu, Am-241, Np-237.
Determination of effective diffusion coefficients for the release from corroded samples (Pu, Am-241, Np-237).

C PROGRESS OF WORK AND OBTAINED RESULTS

Summary

The experiments were started using real samples. The results for the release kinetics show that the most abundant isotopes in solution are the Cs-isotopes Cs-137 and Cs-134. The time dependence as well as the cumulative amount released of these isotopes corresponds very well with the results obtained in experiments with simulated samples.

Results for equilibrium concentrations under the experimental conditions are available for Am-241. The values are about 10^{-10} moles/l in Q-brine and about 10^{-11} moles/l in dist. water and NaCl brine, respectively. The values in Q-brine are significantly lower than the Am-concentrations obtained from solubility experiments with AmO_2 and $Am(OH)_3$. Further experiments are under way in order to separate Pu from the leachants and determine the Pu using alpha-spectroscopy. The general work progress is as follows

B.1 is progressing normally

B.2 experiments have started by the end of 1986, first preliminary results are already available.

PROGRESS AND RESULTS

Investigations with real samples (B.1)

For the investigations with the real samples, two types of specimens were used. One experimental series was performed using samples from the waste treatment facility at KfK which were also delivered to the EC for experiments in the frame of the MIRAGE-Project. The other kind of specimens were produced in the laboratory using a real evaporator concentrate. The composition of the samples is given in Table I. For the leach experiments the cylindrical specimens were placed in polyethylen bottles. The leachants used were Q-brine and dist. water. During the leach experiments no changes of the leachants were made. After defined time intervalls 2 ml samples of the leachants were taken and filtered through 1,5 nm filters (Amicon system). 1 ml of the filtered sample was diluted with water to 10 ml for measuring the gamma-spectrum and for determining Am-241 using the 59 KeV-gamma-line. The results of the MCA-measurement indicate that the main isotopes in solution are Cs-137 and Cs-134. Besides the cesium only tracer amounts of Ru-106 and Co-60 were detected. The time dependence of the Cs-release is shown in Figure 1. The results obtained are in good agreement with results from experiments with simulated samples. The gamma-measurements show, that the Am concentrations in the first period of the experiments are below the detection limit under the conditions used of about 2-4 Bq/10 ml.

After a period of 6 months there is a measurable amount of Am-241 only in Q-brine which remains constant for longer time periods. The value amounts to about 10-20 Bq/10 ml which corresponds to about 10^{-10} moles/l. In dist. water the Am-241 values are always near the detection limit for the whole experimental period. The maximum Am-concentration derived from the detection limit amounts to 10^{-11} moles/l. These values agree very well with the results from experiments using crushed samples with a high specific surface to reach the equilibrium concentration in shorter time periods.

For the measurement of Pu in the leachants by alpha-spectroscopy which requires a separation from the salt solution, from the fission products and from the other alpha-emitters, experiments are under way to test different methods for the separation of the Pu.

In summary, the results obtained up to now indicate already that the results from experiments with real samples are comparable with those from experiments with simulated samples.

TABLE I: COMPOSITION OF THE REAL EVAPORATOR CONCENTRATE USED FOR THE PREPARATION OF THE CEMENTED WASTE FORM (RWF 8)

compound	content
U	3.980 mg/l
Pu	1.4 mg/l
Am-241 *)	0.99 mCi/l
Np-237 *)	10.3 µCi/l
Sr-90 *)	27.1 mCi/l
Cs-134 *)	6.1 mCi/l
Cs-137 *)	43.3 mCi/l
Fe	625.0 mg/l
F^-	219.0 mg/l
Cl^-	288.0 mg/l
SO_4^{2-}	1.266.0 mg/l
$C_2O_4^{2-}$	10.0 mg/l
salt content ($NaNO_3$) dried at 105°C	275.0 g/l
calcined at 800°C	113.5 g/l
density	1.17 g/ml

*) corrected to the sampling date: July 12, 1983

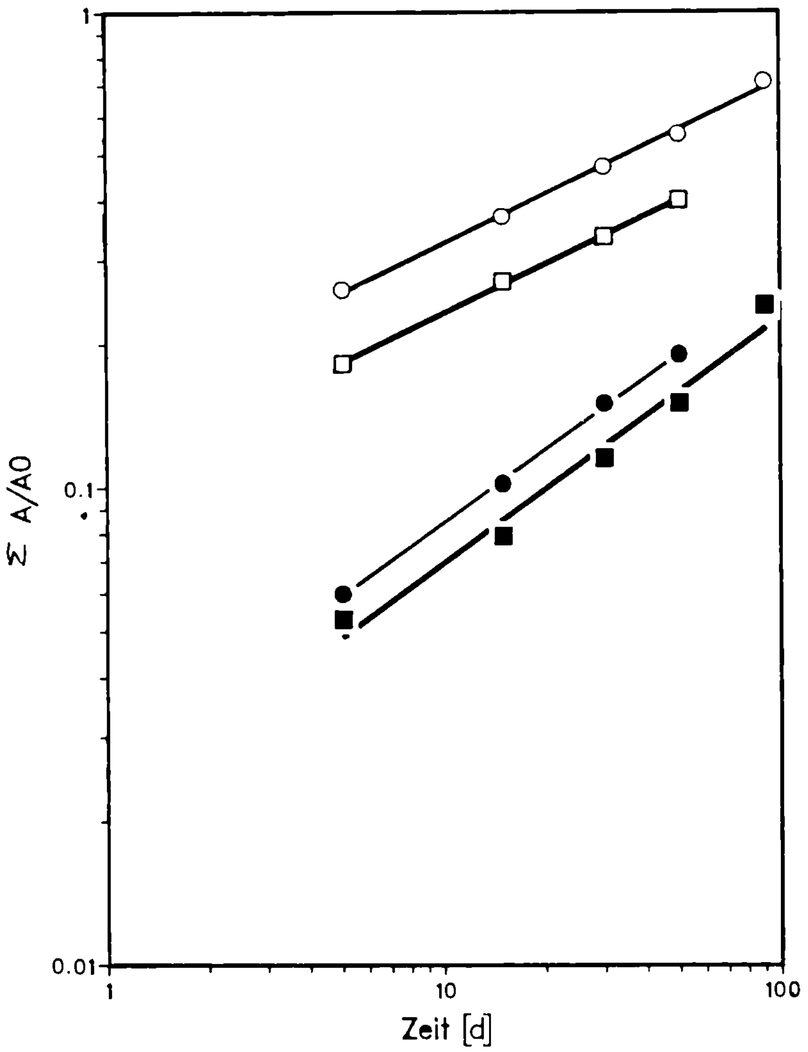


Fig. 1: Cumulative Cs-leaching from real cemented waste forms (RMA 8, S/V = 1,8 cm^{-1})
Q-brine (●,■) and dist. water (○,□) at room temperature

○, ● samples from the waste treatment facility
(OPC 45, w/c = 0.48, salt content 9 weight%)

□, ■ laboratory samples
(OPC 35, w/c = 0.4, salt content 5 weight%)

Study of Leaching Mechanisms of Ions Incorporated in Cement or Simple Polymer

Contractor: Greek AEC, "Demokritos" Center, Greece
Contract No.: FI1W/0026/00
Duration of Contract: May 1986 - June 1988
Project Leaders: S.G. Amarantos, J.H. Petropoulos

A. Objectives and Scope

Further elucidation of the factors and mechanisms which govern the elution of various ions from solidified low and medium level radioactive wastes in contact with water is important. Here further laboratory studies of the mechanisms of leaching with water of Cs and Sr ions from solids simulating cemented waste concentrates are carried out. Previous studies with model systems consisting of a - soluble or insoluble - salt embedded in a simple polymer are continued. Preliminary studies with epoxy resins are also envisaged. The experimental work is complemented with the development of pertinent more sophisticated theoretical models of the kinetics of ion release.

The basic aim of the project is the improvement of the method used in the evaluation of the risk of long-term environmental radioactive pollution (via natural waters) from waste disposal sites.

B. Work Program

B.1 Cement

(i) Leaching kinetics of Cs in relation to the distribution of the ion in the specimen at various stages of the leaching process.
(ii) Examination of the effect of temperature on leaching rate by means of parallel experiments at different temperatures.
(iii) Effect of changing the thickness of the sample on the elution curve.
(iv) Examination of the possibility of setting up a theoretical model for the representation of the elution kinetic curve of Cs.
(v) Effect of atmospheric CO_2 on the elution of Sr, in relation to the Sr content of the sample.

B.2 Polymer

(i) Further experimental investigation of the cellulose acetate-salt system (effect of salt solubility, salt content, salt particle size or polymer water content).
(ii) Development of a more sophisticated theoretical model to describe the elution kinetics of soluble salts in particular.
(iii) Preliminary investigation of leaching of specimens of a simple salt embedded in epoxy resin.

C. Progress of Work and Results Obtained

Summary

The laboratory work was concerned with the study of leaching kinetics of Cs^+ at different temperatures and sample thicknesses. The distribution of Cs^+ in the cement sample was determined at various stages of the elution process and compared with theoretical Fickian concentration profiles. The diffusion coefficient at 30° and 70°C, and the activation energy of diffusion were determined.

The theoretical work involved the formulation of a new model describing the elution of a soluble salt from a polymer matrix with simultaneous inbibition of water by the matrix. A computer program for application of the model has been developed and successfully tested.

The general work progress status is as follows: B.1(i), B.1(ii), B.1(iii) are progressing normally, B.1(iv), B.1(v), B.2(i), B.2(iii) are delayed, B.2(ii) is nearly completed.

Progress and results

1. Studies with cemented specimens (B.1(i), B.1(ii), B.1(iii))

Three series of cylindrical cemented specimens of height $\ell \simeq 4$ cm (Series A and B) or $\ell \simeq 1.2$ cm (Series C) and diameter ~ 4 cm containing a concentration of cesium sulphate of $C_o \simeq 3.4\%$ by wt have been subjected to leaching by stagnant distilled water (with only one flat surface exposed to leachant) at 30°C (Series A,C) or 70°C (Series B). At appropriate stages of the elution process certain specimens were withdrawn and sliced into seven slices for determination of the distribution of non eluted Cs.

Typical results of fractional amount eluted ($\Sigma\alpha_n/A_o$) as a function of time t are presented in Figure 1. The resulting $\sqrt{t}$ plots are reasonably linear in accordance with Fick's law. The diffusion coefficients D and activation energy of diffusion E_a were calculated from

$$\Sigma\alpha_n/A_o = 2(Dt/\pi\ell^2)^{\frac{1}{2}}; \qquad D = D_o\exp(-E_a/RT)$$

yielding $D = 3.6\text{-}4.7\times10^{-7}\ \mathrm{cm^2s^{-1}}$ at 70°C (Series B),
$D = 2.4\text{-}4.0\times10^{-8}\ \mathrm{cm^2s^{-1}}$ at 30°C (Series A,C), and
$E_a = 12\text{-}14$ kcal/mol.

The distribution profiles of non eluted Cs corresponding to $\Sigma\alpha_n/A_o \sim 10\%$ or $\sim 20\%$ are shown in Figure 2 (where C=measured concentration of Cs in a slice of the specimen located at distance x from the exposed surface). The theoretical curves of this figure were calculated from the appropriate Fick law solution /1/

$$\frac{C-C_1}{C_o-C_1} = \mathrm{erf}\,\frac{x}{2\sqrt{Dt}}$$

with the surface concentration $C_1 = 0.2\ C_o$ and $D = 5.5\times10^{-7}\ \mathrm{cm^2s^{-1}}$.

2. Model for the elution of soluble salts from polymer matrices (B.2(ii))

The objective is to develop a theoretical model describing simultaneous elution of salt (particularly a highly water soluble salt) and inbibition of water, free from the defects inherent in presently available treatments /2/.

The new model has been formulated in terms of diffusion equations based on chemical potential gradient driving forces (instead of the concentration gradient driving forces previously used /2/). For unidimensional diffusion along x in a slab ($0 \leq x \leq \ell$; ℓ=thickness of the slab), with one surface (at x=0) exposed to liquid eluant (water) and all other surfaces blocked, we obtain /3/

$$\frac{\partial C_W}{\partial t} = \frac{\partial}{\partial x}\left(D_W S_W \frac{\partial a_W}{\partial x}\right); \qquad \frac{\partial C_N}{\partial t} = \frac{\partial}{\partial x}\left(D_N S_N \frac{\partial a_N}{\partial x}\right) \tag{1}$$

where the subscripts W and N refer to water and salt respectively; C denotes the concentration of the relevant species in mol per unit volume of the unswollen matrix; a represents the corresponding activity; S and D are the relevant "thermodynamic" sorption (partition) and diffusion coefficients respectively /3/; and t is the time.

In the case of water, a_W is approximated to by the relative vapor pressure and S_W is an increasing function of both a_W and C_N, which may reasonably be modelled by

$$S_W = C_W/a_W = (K_{W1} + K_{W2}a_W)(1+K_{W3}C_N) \tag{2}$$

where K_{W1}, K_{W2}, K_{W3} are constants. Eq. (2) permits evaluation of the local value a_W, at any point within the matrix, given the local values of C_W and C_N.

In the case of salt, the total concentration C_N present at any point in the matrix must, in general, be split into mobile (dissolved) and immobile (dispersed) parts represented by C_{NS} and C_N-C_{NS} respectively. We then have

$$C_{NS} = k_s C_W \bar{V}_W c_{NS} \ ; \quad a_N = c_{NS}/c^o_{NS} \ ; \quad S_N = C_{NS}/a_N = k_s C_W \bar{V}_W c^o_{NS} = K_{N1}C_W \tag{3}$$

where c_{NS} denotes salt concentration in aqueous solution; c^o_{NS} is the aqueous solubility of the salt; $\bar{V}_W$ is the molar volume of water and k_s=const. (and hence K_{N1}=const.). Thus, S_N represents the saturation value of C_{NS} and, at any point within the matrix, we have

$$C_{NS} = S_N,\ a_N=1,\ \text{if } C_N \geq S_N; \quad C_{NS}=C_N,\ a_N=C_{NS}/S_N,\ \text{if } C_N<S_N \tag{4}$$

The diffusion coefficients are generally increasing functions of C_W of the form

$$D_W=D_{WO}\exp(\beta_W C_W); \qquad D_N=D_{NS}\exp(-\beta_N/C_W) \tag{5}$$

where D_W, D_{NS}, β_W, β_N are constants (D_{NS} is the diffusion coefficient of the salt in aqueous solution).

A computer program has been developed, in which eqs. (1) are solved simultaneously by an explicit finite difference method, subject to eqs. (2)-(5) with appropriate input parameters and to the boundary conditions

$$a_W=a_{WO};\quad a_N=a_{NO};\quad C_N=C_{NO} \quad \text{at} \quad 0<x\leq\ell \quad \text{and } t=0 \tag{6}$$

$$a_W=1;\quad a_N=0;\quad C_N=0 \quad \text{at} \quad x=0 \text{ and } t\geq0 \tag{7}$$

$$\partial a_W/\partial x = \partial a_N/\partial x = 0 \quad \text{at } x=\ell \quad \text{and } t\geq0 \tag{8}$$

where a_{WO}, a_{NO}, C_{NO} = const. Integration of the resulting diffusion profiles $C_W(x,t)$, $C_N(x,t)$ then yields the total amount of water taken up, or of salt eluted, at various times t.

The program has been tested successfully. Typical results are shown in Figure 3.

References

/1/ CRANK, J., The Mathematics of Diffusion, Chap. 3, 2nd Ed., Clarendon Press, Oxford (1975).

/2/ KORSMEYER, R.W. and PEPPAS, N.A., Proc. Int. Symp. Controlled Release Bioact. Mater. 10, 144 (1983).

/3/ PETROPOULOS, J.H. and ROUSSIS, P.P., J. Chem. Phys. 47, 1491 (1967).

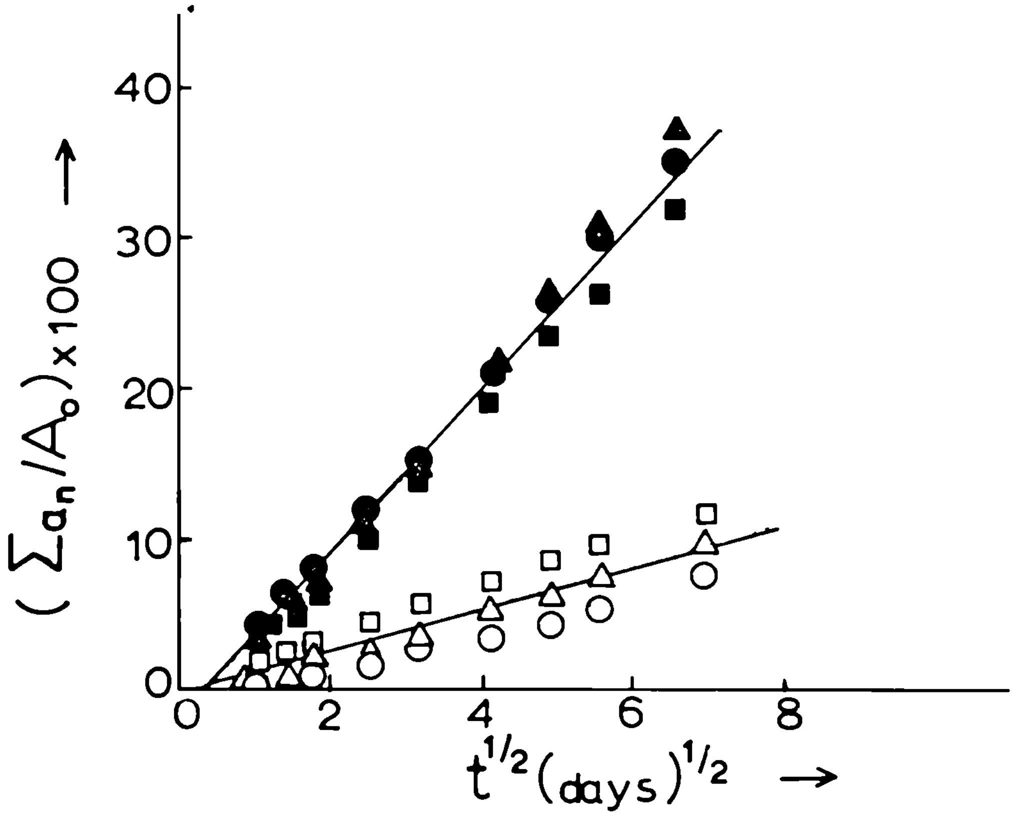


Figure 1. Elution curves of Cs from Cs_2SO_4-cement samples (C_o ∿3.4% wt) vs $\sqrt{t}$ at 30° (open points) or 70°C (filled points).

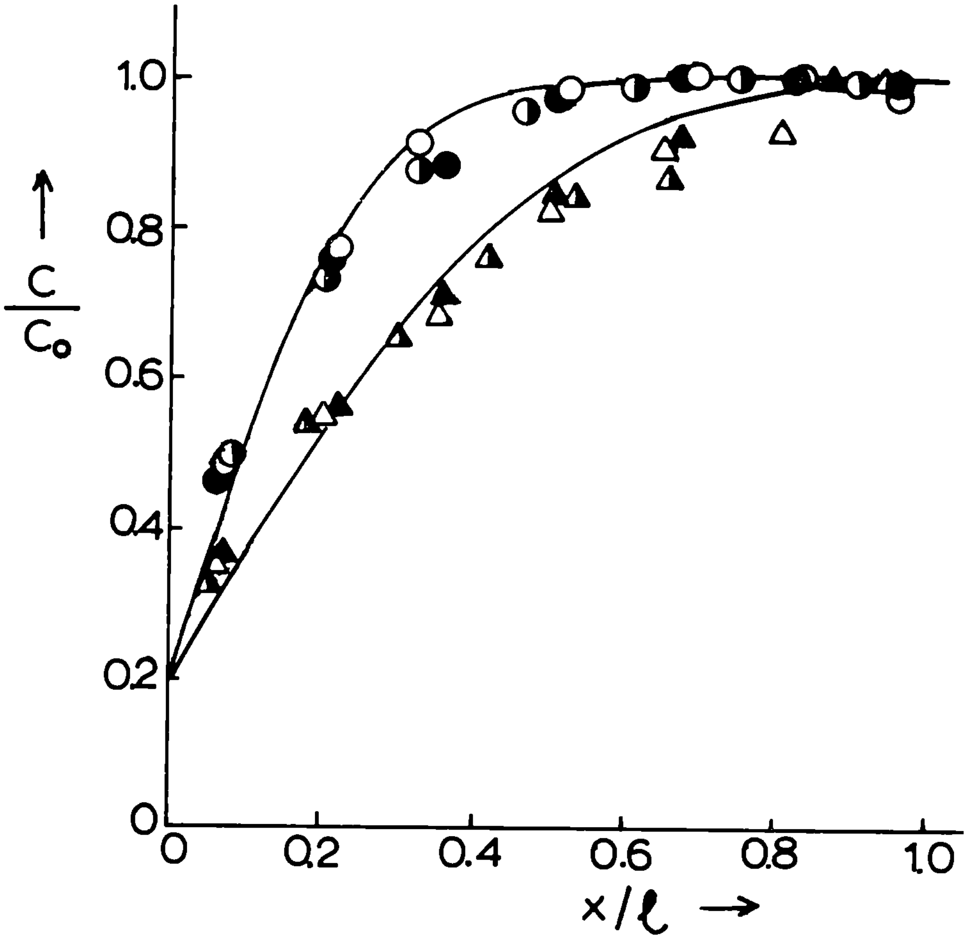


Figure 2. Distribution of Cs in triplicate samples (points) after 6 days (o,◑,●) and 21 days (Δ,◭,▲) of leaching at 70°C, compared with best-fitting theoretical Fick-law curves (see text).

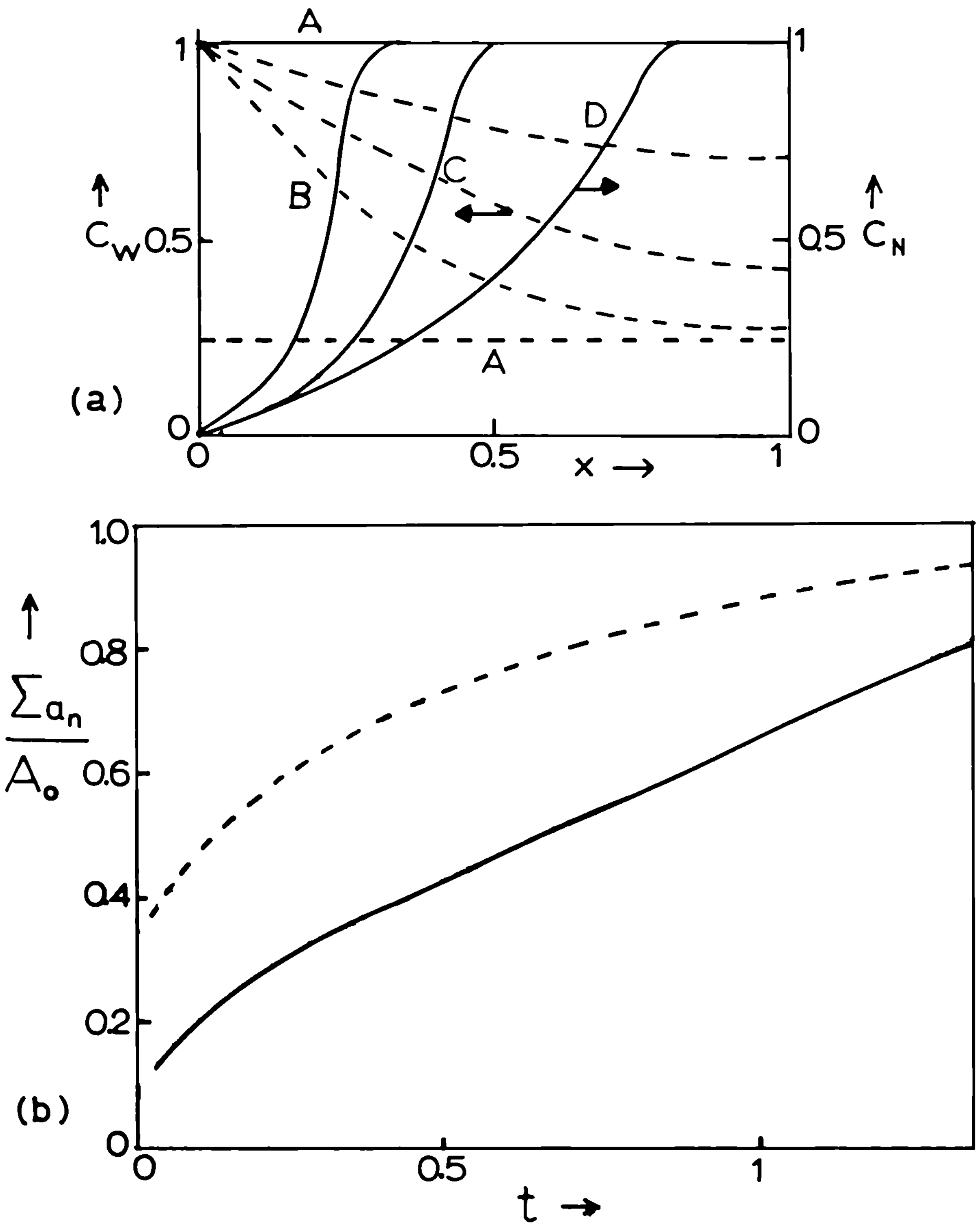


Figure 3. Results of a test model calculation based on eqs. (1)-(8) with $K_{W1}=0.4$, $K_{W2}=0.6$, $K_{W3}=0$, $D_{W0}=1$, $\beta_W=0$, $K_{N1}=1$, $D_{NS}=100$, $\beta_N=4.61$, $a_{W0}=0.4$, $C_{N0}=1$, $\ell=1$: (a) Diffusion profiles of salt (—) and water (---) at t=0 (A), 0.1 (B), 0.3 (C), 0.5 (D); (b) Water uptake (---) and salt elution (——) curves.

Evaluation and characterization of conditioned LLW and MLW

Contract N° : F 11 W/0095/1 - Task 3
(CEA-CADARACHE) : Bitumen and polymer characterization - C.COURTOIS
Project leader : A. SAAS

This part of contract includes three main items.

I. Biodegradation studies (Mme LANGOMAZINO - CEA/CADARACHE)

A. Point of these studies

Biodegradation studies of bitumen matrixes (WF9) have shown first that CO_2 production measurement (final product of hydro carbon oxydation by microorganisms) allowed to point upon the action of microorganisms against bitumen.

A soil sample and a mixed culture remote from this soil (with at least three different types of bacteria) induce a weak but non negligible attack of bitumen matrixes : pure bitumen, RWF9, silicagel, bitumen (in powder) and maltene - silicagel).

- The mixed culture gives CO_2 production rates on maltene two times higher than rates reached on bitumen. Soil sample is more active on these substrates than mixed culture.
- Bitumen and embedded wastes in pieces, give CO_2 production rate less important than the rates obtained when substrate is powdered. Contact surface is one of the limiting factors of biological attack.
- Biological attack is confirmed by chemical analysis of part of bitumen . CO_2 comes from this part (paraffinic part) for the main production.

Preliminar studies in anaerobic conditions allowed to measure a CO_2 production . This part of the study needs further investigations.

B Work programme

The following studies will include :

- The measurement of biodegradation of bitumen by : mixed or pure cultures remoted from natural environment ; pure cultures of bacterias (5), yeasts (2), mushrooms (1) well known for hydrocarbon degradation.

It's important to study the action of a great variety of microorganisms to try to define what are the real risks of bitumen biodegradation.

This complex matrix can only be attacked by multi enzymatic systems which have few chances to be encountered in a lone bacterium.

The important risks of biodegradation will be attributed to many associated microorganisms we have to study.

The biodegradation rates are established by CO_2 production measurements versus time by gas chromatography for each microorganisms studied on following supports :

- bitumen
- embedded wastes
- main parts of bitumen separated on sicilica columns

on aerobic conditions.

Studies are conducted first in closed vessels and the restricting factors of the bitumen biodegradation are inquired.

At the end of each growth of each culture, a chemical analysis of bitumen or of part of bitumen is done to define what are the hydrocarbons attacked and in what ratio.

A study of the factors having an influence on biodegradation rates will be also began.

2. Diffusion coefficent studies (M. DE TASSIGNY - SPR/CEN-G)

A. Objectives and scopes

Characterization test of ageing of embedded wastes in polymers is looking for. The methodology will be looking for among several spectroscopic, methods adapted to the analysis of different polymeric matrixes. Comparison between old and reference samples will be studied mainly with epoxid and polyester materials.

B. Work programme

B1. Bibliography

Bibliographic state of the research in this field will be done for the spectroscopic methods of studing the ageing of polymers.

B2. Study of the chemical state of degradation.

Analysis of UV and IR spectrum in polymers gives usefull information of a state of degradation in the structure of the polymeric matrix. Degradation profiles can be obtained by analysis of samples coming from old wastes ageed in real climatic conditions at the open air.

B3. Study of morphologic degradation.

Optical microscopic methods on thin layers cutted in samples will give informations on thermomechanic ageing of the matrix.

B4. Test of degradation.

Correlation between these different kinds of analysis may give test for defining a state of ageing.

C. Progress of work

State of advancement

During the last months of 1986 the programme started as following :

- Significant samples were found and prepared:polymers of 5 and 6 years old ageed at the open air in real climatic conditions and reference samples of the same composition.
- Bibliographic research was begun.
- Method of controling ageing by spectroscopy were choosen.

3. Leaching studies

A. Wastes embedded in bitumen

Wastes are chemical precipitation sludges coming from a reprocessing plant and embedded in bitumen.

The leaching tests will be conducted on cylindrical samples made in laboratory (Ø 50 mm, h 50 mm).

The leaching surface is the upper part of the cylinder.

Radionuclides included in the matrix are 60 Co, 106 Ru, 134 Cs, 137 Cs, 238 Pu + 241 Am. The release of theses radionuclides will be studied.

The leaching will be done in static. Test will be an AIEA type Test spraying over one year.

The sampling periods for leachant can be 2, 7, 14, 21, 52, 90, 130, 220, 360 days after the beginning of the test.

B. Wastes embedded in polymers

These studies will be done on ion exchangers embedded in an epoxyde thermosetting resin.

The leaching tests will be conducted on little cylinders (Ø 80 mm, h 80 mm). These cylinders will include real wastes.

The characteristics of these samples will be the following :

- waste : Duolite ion exchanger, the active level is about one curie per ton.
- matrix : epoxyde thermosetting resin.
- the final product includes 50 % of waste.

The leaching test is one static test, AIEA type. The test duration will be one year, and the leachant sampling will he done 2, 7, 14, 21, 52, 90, 210, 300, 365 days after the beginning of the test.

In the leachant , the radionuclides 60 Co, 58 Co, 134 Cs, 137 Cs will be looked for.

During the last months of 1986 , the useful material for these leaching tests have been prepared.

After beginning of these active tests, other expriences of leaching of inactive bitumen samples (chemical sludges of reprocessing plants embedded in bitumen) will be conducted under pressure and temperature.

MEDIUM ACTIVE WASTE FORM CHARACTERIZATION : THE PERFORMANCE OF CEMENT-BASED SYSTEMS

University of Aberdeen
FI1W/0025-UK(H)
1 May, 1986 - 31 December, 1989

F. P. Glasser

A. Objectives and Scope.

The objective is to lay the foundation for a scientific basis for the immobilization of non-heat generating radioactive wastes in cement matrices. The practical application of the information enhances our ability to predict the behaviour of matrices, and their retentive characteristics, at ages longer than those for which test data was obtained. Among the other factors considered are : effects of heat, radiation; matrix formulation; physicochemical properties, including those of blended cements; waste-matrix interactions. These studies, essential for developing a verified technology, are not in a highly advanced state. Apart from the contractually-defined relationship with UKAEA, twice-yearly contact is maintained with other CEC contractors.

B. Work Programme.

Basic Property Measurements. Solubility-pH model developed for three-components. Model being extended to include alkalis, etc.

Modified Cement Systems. The constitution of modified cement systems, specially those containing slag, are being explored. Measurements include reaction kinetics, pore fluid composition pH, Eh.

Interactions Between Cements and Waste Systems. Assessment has been performed on the action of several hundred materials on cement.

Ageing, Environmental Studies. The effect of radiation on the physical and chemical properties of cement is being determined.

Cement and Near-field Interactions. Work has thus far been limited to scoping studies.

STATE OF ADVANCEMENT

The state of advancement can be summarized under four main headings.

1. Properties of Cement Matrices.

2. Durability and Environmental Reactions of Cements.

3. Blended Cement Matrices, Especially Those Containing Slags and the Properties of Slag.

4. Behaviour of Selected Radwaste Species in Cement.

PROGRESS AND RESULTS

1. Properties of Cement Matrices

Commercially available cements differ, depending on manufacturer and plant : moreover, temporal variations occur. It is therefore desirable to have a general framework to assess the consequences of these variations to the immobilization potential of cemented radioactive wastes. The behaviour of cemented systems at longer ages, beyond those for which test data can reasonably be expected to be obtained, is also an important area in which modelling studies are needed. No ready-made models exist, largely because the range of problems which require to be addressed have not previously arisen. It has, therefore, been necessary to develop the approach. We adopted three guiding principles for the development of models which should (i) be general, rather than specific to one or at most a few compositions (ii) rest on a foundation of physiochemical data, capable of being subjected to independent verification and in accord with the current state of knowlegde of cement chemistry, and (iii) capable of interfacing with other types of predictive exercises.

At short ages, cements provide conditions which are particularly suitable for the immobilization of many radioactive waste species. The principle chemical feature in their favour is the high alkalinity of their internal environment. Such conditions, i.e., pH>10, are known to precipitate actinides and other waste stream components by the formation of insoluble species. In cements, the phases responsible for this high pH are crystalline $Ca(OH)_2$ and a calcium silicate hydrogel designated C-S-H. Moreover, temporal variations occur. It is therefore desirable to have a general framework to assess the consequences of these variations.

2. Durability and Environmental Reactions

Actions under this heading take a variety of forms. We complete a review of the effect of adding a range of substance, both inorganic and organic, to cement. The actions of several hundred substances are reported. It has been found that interactions between cements and other components can be classified on a time scale; in the short term, chemical effects include (i) alteration of the setting properties, by acting as set accelerators or retarders, and in the medium - to long term, (ii) alteration of the microstructure, strength gain, etc. of matured cements and (iii) attack on mature cement and concrete, leading to disintegration.

Chemical substances which alter the set properties, especially accelerators, are not necessarily harmful, but may affect the rheology properties, especially flow : in extreme cases, false set and premature stiffening may result. Excessive retardation is also to be avoided : in extreme cases, the cement may never set properly.

A wide range of substances affect the general strength development and microstructure. However, little is known about how they affect the immobilization potential of the matrix.

Some substances are aggressive towards set cements. These include principally those which, in aqueous solutions, are acidic and which form strong complexes with Ca.

Progress has, therefore, been made in being able to predict interactions between cement and the constituents of miscellaneous waste streams. The study has also proven useful in highlighting two potential areas in which our knowledge is deficient. The first of these is the extent to which organics may degrade in wet cement, the nature of the degradation products and their potential to act as complexing agents for radwastes, or interact with cements, etc. The second is the effect which trace constituents, either organic or inorganic, have on the corrosion potential of metal in concrete.

Cements exposed to natural environments and, additionally, radioactivity, may also undergo changes in matrix properties. Work undertaken on the Harwell subcontract has concentrated on two areas :

- the effect of radiation on the chemical environment in a cement grout, especially on the redox potential
- the effect of slightly elevated temperature on the stabilities of the metastable hydration products.

When hydrated cement grouts are exposed to radiation, the free water in the pore network is radiolysed. However, it is believed that the solid phases do take part in some of the radiolytic processes. Consequently, the first stage in investigation of the effect of radiation on redox potential has been to develop techniques for its measurement in the presence of all the phases. The preferred method is to use a well-hydrated grout, crushed and slurried with additional water. It has been shown that reproducible Eh measurements can be made with this type of sample using Pt electrodes and Ag/AgCl reference electrodes. Preliminary results for BFS/OPC grouts show a trend towards higher (less negative) redox potentials during irradiation.

Initial work on the effect of elevated temperatures on phase stability has investigated the phases formed in the hydration of BFS/OPC grouts at temperatures in the range 20-70°C, and their subsequent development on ageing. Major changes are observed at temperatures about 40-50°C. In particular, the content of calcium hydroxide is progressively reduced above this temperature.

Blended Cement Matrices

Blended cement matrices comprise an activator, normally Portland cement, and slag, fly ash, etc. The latter eventually participate in the hydration reactions, albeit at a slower rate than Portland cement. This may have certain advantages but from the standpoint of property prediction and assessment, it is disadvantageous because of the length of time taken to react a steady state. In the longer term, the chemistry, mineralogy, porosity, permeability and microstructure of blends increasingly diverge from those of Portland cement. Thus it is practicable to establish many of the features of these systems from short term (1-2 year) tests.

One essential body of information, therefore, concerns the kinetics of hydration of slag, especially in slag-rich Portland cement activated blends.

Methods for determining this are described. One of the more promising methods involves heat treatment (heating to 1000°C) followed by XRD analysis of the resulting product. Under this heat treatment "fresh" blast furnace slag glass partly crystallises to melilite; XRD reflections resulting from this phase form the basis for the quantitative determination of unreacted slag in the sample.

Preliminary trials on slag cements with a high slag content reveal a relatively rapid (<1 month) reaction of BFS with the hydration products of OPC, followed by a period of dormancy, lasting at least 1 to 1.6 years. The degree of reaction also decreases as BFS replaces OPC in the original blend.

These results are yet to be compared with those of selective dissolution. One possible source of error may accrue through crystallisation of some of the hydrated blast furnace slag to melilite along with that from the fresh BFS glass. Electron microscopy may help to elucidate this question. Future work will also include the effect of particle size of BFS and of temperature on the hydration kinetics of BFS.

Some evidence concerning the stability of slags can be obtained from analogues. We have examined slags allowed to weather in outdoor UK conditions for up to 50 years. The slags remain partly glassy, but frequently exhibit hydrated and crystalline reaction rims which penetrate to unequal depths. These reactions occur under near-neutral pH's but the results support our general contention that the glassy slag is thermodynamically unstable under surficial ambient conditions. Moreover, the occurrence as principal crystalline weathering products of "gehlinite hydrate" and calcite show the importance of carbonation, and that gehlenite hydrate, which is also observed to form in slag rich cement composites, is an important product phase. It is, however, not present in hydrated Portland cement. Since hydrated slag cements may develop much gehlenite hydrate, it is important to include it within the scope of predictive excercises, e.g., modelling, as well as in practical experiments, whose aim is for example, to determine its sorption potential.

We also have results of a desk study designed to establish whether cement systems have the potential in the very long term to develop zeolitic phases. If this were to occur, the long-term chemical immobilization might be much enhanced. A survey of the composition, synthesis and occurrence of zeolites has been made. The results show that the potential of ordinary Portland cement systems to form zeolites is virtually non-existent, very slight in the case of slag-containing systems and slight in the case of fly-ash blends. If zeolites were to occur, the types to be expected would likely be amongst the lower-silica representatives, the ion-exchange properties of which are not on the whole well documented.

Behaviour of Selected Radwaste Species in Cement.

Predictive approaches to radwaste immobilization are in many instances limited by the data base. Cement matrices not only furnish hydroxyl ions (OH-) but a host of other cationic and anionic species, many of which are appreciably soluble or present as fine grained, high surface area solids, which are potentially reactive. Therefore, it is essential to determine the behaviour of radwaste species in cement environments. We have data on two : iodine and uranium.

A survey of the literature has been made concerning (i) I sorption in the near-field, and (ii) precipitation and encapsulation of I in mineral phases. From this it is apparent that AFm and AFt phases (found in cement) are capable of incorporating considerable quantities of I (as I^-) into their structure, probably replacing $SO4^{2-}$. The leaching properties of I-AFm analogue encapsulated in OPC were found to be at least as good as those of other leading candidates for I incorporation - $Hg(IO_3)_2$, $Ca(IO_3)_2$ and $Ba(IO_3)_2$.

Analysis of pore fluids from OPC and 85% BFS - 15% OPC show that I^-, present initially in the aqueous phase undergoes a significant decrease in solubility as a result of hydration processes. Iodide is found to be less soluble in pure OPC pore fluid, relative to BFS-rich OPC. No variation of (I^-) content in pore fluid with respect to time could be discovered in aged samples. These pore fluid studies will be extended to include the fate of (IO_3^-) in the same cement systems.

Results on the behaviour of uranium in cements are in accord with its reduction from U^{6+} to U^{4+} in slag cement simulate environments. This reduction does not occur in Portland cements. It is encouraging that this reduction, which can be predicted from pH-Eh diagrams of the U-O-H systems, are in fact observed to occur. Nevertheless, the solubilities in simulates do not seem to be controlled by that of the precipitated simple hydrous oxides or hydroxides. Instead, formation of relatively insoluble calcium and sodium compounds containing uranium have been observed. Since these compounds may not previously have been described in the literature, and their solubilities are unknown in alkaline solutions, it is desirable to continue these studies with a view to providing some overview of the behaviour of U in cement environments.

b) High active and alpha waste forms characterization

LONG TIME BEHAVIOR OF TRU-WASTE BEARING CERAMICS

Contractor : KfK, Karlsruhe, Federal Republic of Germany
Contract No. : FI 1W-0098-D (B)
Working Period : July 1986 - December 1986
Project Leader : A. Loida

A. OBJECTIVES AND SCOPE

Alumosilicate-based ceramics are suitable matrix materials for the immobilization of TRU-waste. The feasibility of this conditioning method has been demonstrated by synthesizing alumosilicate ceramics, loaded with original TRU-waste up to 20 wt.-% on lab-scale. The final products consist of a mixture of mullite ($Al_6Si_2O_{13}$) and corundum (Al_2O_3), as well as actinide oxides and fission product alloys and oxides. The leach rates for actinides show values between 10^{-8} and 10^{-9} g/cm^2d after the ISO-draft.

Aim of the current programme is to get information on the long time behavior of these kind of ceramics with respect to radiation and hydrolytic influences.

Changes in microstructure and hydrolytic stability as a function of long storage time, induced by high α-dosis and thus accelerating mutual interactions, will be recorded.

B. WORK PROGRAMME

B.1 : Synthesis of samples:
- ceramics (type KAB 78), loaded with 30 wt.-% of dissolver residues
- ceramics (type KAB 78), loaded with 20 wt.-% of $Pu(238)O_2$.

B.1.1: Preparation of these samples for ceramographic and leaching investigations.

B.2 : Characterization of these samples as a function of time (α-dosis).

B.3 : Leaching of these samples at elevated temperature in Q-brine.

B.4 : Characterization of these samples after the leaching experiments and after reaching the α-dosis required.

C. PROGRESS OF WORK AND RESULTS OBTAINED

For reaching the aim of this programm it is necessary to perform "time-lapse"-experiments by doping the ceramic matrix with a short-living α-emitters radionuclide, which transmit an accelerated α-dosis on the matrix within a short time. $Plutonium(-238)O_2$ with an amount of 20 wt.-% has been incorporated into the ceramic matrix, which consisted of a mixture of 66 wt.-% reactive corundum, 17 wt.-% kaolinite, and 17 wt.-% bentonite. Another series of specimens for comparing investigations consisting of the same type of matrix, loaded with 30 wt.-% of dissolver residues from the reprocessing of fast breeder reactor fuel has been prepared simultaneoulsy. In both cases, the firing temperature was 1300°C. Density, open porosity and α-activity have been determined as follows:

ceramic KAB 78

Loaded with	20 wt.-% $Pu(-238)O_2$	30 wt.-% dissolver residues
density	3.63 g/cm^3	3.43 g/cm^3
open porosity	< 2 vol%	< 2 vol%
specific α-activity	1.0 E 11 Bq/g (2.733 Ci/g)	1.33 E 9 Bq/g (0.036 Ci/g)

The preparation of these samples for leaching experiments and the ceramographic investigations are finished.

Radiolytic Oxidation

Contractor: UKAEA, Harwell Laboratory, UK
Contract No: FI1W/0029
Working Period: September 1986 - March 1989
Project Leader: F.T. Ewart

A. Objectives and Scope

Preliminary studies in the UK and USA have suggested that alpha and gamma radiation fields can increase the oxidation state of some elements important to radioactive waste management. This programme will establish the significance of these effects as a mechanism for causing enhanced aqueous concentrations in the near field of a repository. Because of the flux of radiation necessary to cause these oxidiation state changes, the effects are only likely to be found in cemented ILW or vitrified HLW; the programme therefore addresses only these waste forms.

The experimental results of this programme will be used in the construction of a model compatible with the geochemical codes that are used for modelling repository behaviour.

B. Work Programme

B.1. Effect of gamma irradiation on neptunium and uranium solubility limits.
B.2. Electrochemical study of the dissolution of oxides of Tc, Np, Pu and Am.
B.3. Effect of enhanced alpha radiation on the solubility of elements selected by studies under B.2.
B.4. Effect of radiolysis on sorption of Tc, Np and Pu.
B.5. Study of overall effects of radiation, waste, matrix and backfill.
B.6. Effect of colloids.
B.7. Modelling studies.

C. Progress or work and obtained results

Summary

The experimental programme commenced during November 1986 and thus is approximately six months delayed from that originally proposed in the technical annex. In the period until the end of 1986 the existing work on the gamma radiolysis of solutions containing precipitated Np(IV) hydroxide has been reviewed and some new experiments have been started. Gamma irradiation to an accumulated dose of 8 x 10^4 Gy under an argon atmosphere results in an enhanced dissolution of neptunium accompanied by oxidation in granite and bentonite equilibrated water; no such effect is observed in concrete water. The presence of metallic iron inhibits the dissolution.

Studies on the solubility of uranium are about to commence following the identification of a suitable route for the reduction of U(VI) to U(IV) prior to irradiation.

The components of the overall effects experiments have been ordered and these experiments will be set up on delivery in the early part of 1987.

The cell has been designed for the electrochemical experiment, and is about to be constructed. The instrumentation for the experiment is being commissioned.

The modelling studies have concentrated on the reactions which occur after the termination of the irradiation. The effects of transient species has been shown to be negligible which has enabled some considerable simplification of the reaction scheme to be achieved.

General work progress has been delayed some six months due to delays in contract negotiations. The present state is as follows:

B.1., B.2, progressing normally
B.3., B.4. delayed until spring 1987
B.5. delayed, will start early 1987
B.6. not programmed to start yet
B.7. progressing normally

Progress and results

1. Gamma Irradiation (B.1.)

Neptunium

Our existing work on the gamma irradiation of solutions in contact with Np(IV) hydroxide solid has been reviewed and some key results are presented in Table I for waters that have equilibrated with bentonite, granite and concrete; these are all possible components of the repository near-field for ILW or HLW. All experiments were irradiated under argon with external ^{60}Co sources and analysed by filtration through an Amicon Centricon-10 filter unit (Molecular Weight Cut off = 10,000) and determination of the ^{237}Np concentration by liquid scintillation counting. Irradiation in concrete water to a dose of 8 x 10^4 Gy results in neptunium concentrations which are at or below the detection limit of 2 x 10^{-8}M. This suggests that no net oxidation of Np(IV) is taking place in this system as the solubility of Np(V) is expected to be well above the detection limit at pH values of around 12. In bentonite and granite water, which are between pH8 and pH9, irradiation to the same dose gives a neptunium concentration of 2 x 10^{-4}M, which would suggest oxidation of Np(IV)and consequent increase in solubility. The addition of iron filings prior to irradiation significantly decreases the measured Np in solution when added at the rate of 1g per 20ml water. Other experiments, not given in the table, have found that addition of sodium dithionite (a soluble reducing agent) will decrease the neptunium concentration below the detection limit in granite water. When solid bentonite or granite is present slightly lower concentrations are recorded than in their absence. This work is continuing and some long term experiments which are being irradiated at a dose rate of approximately $40 Gyhr^{-1}$ have been running for about six months.

Uranium

Work on the uranium system has just started and initial experiments are measuring the solubilities of U(IV) and U(VI) in concrete, granite and bentonite waters in the absence of radiation. These will define the expected concentrations when U(IV) is irradiated. No results are yet ready for reporting.

2. Electrochemical Experiments (B.2.)

A preliminary cell design has been completed for the electrochemical experiments, this is being modified and construction of the cell will follow. The instrumentation for the experiment is available and is being commissioned.

3. Overall Effects (B.5.)

The stainless steel containers for these experiments have been constructed and the individual components of the experiments have been acquired or are ordered.

Table I

Dissolution of Neptunium(IV) hydroxide

Water	Approximate Dose(a)/10^4Gy	Time elapsed /days	Solid(c) present	[Np]/M
Bentonite	1.5	2	-	2E-5
	8.2	9	-	1E-4
	3.2	3	0.01g Fe	2E-5
	4.8	5	1g Fe	≤2E-8
	6.5(b)	7	1g B	5E-6
	-	25	-	2E-5
Concrete	1.4	2	-	≤2E-8
	8.1	9	-	≤2E-8
	3.2	3	0.01g Fe	≤2E-8
	4.8	5	1g Fe	≤2E-8
	6.5(b)	7	1g C	≤2E-8
	-	25	-	≤2E-8
Granite	1.5	2	-	1E-5
	8.2	9	-	1E-4
	3.2	3	0.01g Fe	1E-5
	4.8	5	1g Fe	2E-7
	6.5(b)	7	1g G	5E-6
	-	25	-	1E-5

Notes

a - Dose Rate = 700 Gy/hr unless otherwise stated

b - Dose Rate = 1400 Gy/hr

c - B = Bentonite
C = Concrete
G = Granite

4. Modelling Studies (B.7.)

The calculations which simulate radiolysis in a HLW repository were initially applied to studying effects which might be compared with the results of laboratory experiments. Using a kinetic model for radiolytic oxidation of Pu (based on the Harwell FACSIMILE code), it had been shown that Pu(V) might be expected to be a major product, and that with a "switching off" of the radiation field prior to laboratory measurement, the concentration of Pu(V) would remain relatively constant.

In the past year, this "switched" model has been applied, in both pure water and alkaline, carbonated water cases, to determine whether the inclusion of postulated transient species, such as Pu(II) or Pu(VII) has any effect on the relative concentrations of the other Pu oxidation state. The results have shown that the effect is negligible; therefore it has been possible to simplify the reaction scheme considerably; with Pu(II) and Pu(VII) no longer included.

The application of the model in a manner compatible with other parts of the overall scheme of work requires some means of correlating these results with results calculated from thermodynamic-based codes. Therefore it has been necessary to go back to a re-appraisal of the kinetic data used in the model, and to ensure that it is compatible with a recognised thermodynamic code. In applying essentially equilibrium data to a kinetic model, various simplifying assumptions have to be made, such as diffusionally limited rates on certain reactions involving highly energetic, small, radicals, and some ranking of reactions between charged species on a scale proportional to charge density on the nuclide ion.

The progress in this area has revolved around calculation of equilibrium constants between various Pu complexes without reference to a single, uncomplexed form which seems to be the basis of most thermodynamic codes. This process is both tedious and time consuming; it has not yet been completed nor applied in a simulation.

CHARACTERIZATION OF HLW GLASS SAMPLES

Contractor: HMI, Berlin, FRG
Contract N^{o}: FI1W-0099-D(B)
Working Period: October 1986 - December 1989
Project Leader: G. Malow

A. OBJECTIVES AND SCOPE

In the frame of the two preceding European joint programs on "Testing and Evaluation of the Properties of Various Potential Materials for Immobilizing Highly Radioactive Waste" starting in 1975 a lot of data on the characterization of simulated solidified high level waste forms has been acquired. Thermal, mechanical and radiation stability and the chemical stability under the attack by various aqueous media were tested. The experiments have been performed under waste repository relevant conditions and under simplified laboratory conditions selected to investigate the corrosion mechanism. In the present research program the fully radioactive Cogema glass R7T7 proposed as a reference glass will be investigated in the hot cell facility. The results will be compared with those obtained for non-radioactive glass samples in order to find out whether there are significant differences due to radiation and to the different way of making the glasses.

B. WORK PROGRAMME

B.1. HAW glass R7T7 or SON68.18.17.L1C2A2Z1 will be produced in Valrho, France, and delivered with nominal composition and production conditions.
B.2. Quality control outside the hot cells.
B.2.1. Chemical composition of the bulk glass by EPMA measurements and comparison with nominal composition.
B.2.2. Homogeneity of glass and unsoluble phases in the glass melt by EPMA and SEM.
B.3. Crystallization and devitrification at the temperature of maximum crystallization velocity.
B.4. Preparation of imbedded, polished samples for B.2.1., B.2.2. and B.3.
B.5. Leaching and corrosion behaviour under static conditions at higher temperature.
B.6. Leaching experiments
B.6.1. Experiments in autoclaves between 110° and 190°C in saturated salt brines.
B.6.2. Preparation of samples: chips and possibly powder.
B.6.3. Short and long term leaching experiments, i.e. between <30 d and ~1000 d.
B.7. Analysis of the leachates by ICP optical spectroscopy.
B.8. Investigation of HAW glass.
B.8.1. Mass loss measurements of leached glass samples.
B.8.2. SEM and EPMA investigation of the surface layers and identification of crystalline phases.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Due to a delay in the melting of the highly radioactive glass in Valrho, France, the start of the investigation of the active glass R7T7 has been scheduled for march 1987. Therefore results cannot be reported at this time.

The research programme has been started with new equipment of the hot cell facility. Experimental devices have been constructed and installed to perform the experiments listed in the work programme. Experimental techniques for handling the radioactive samples have been tested.

The quality control of the glass will be performed using scanning electron microscopy for the homogeneity of the glass and unsoluble phases in the glass melt. Electron microprobe will be used for measuring the chemical composition of the glass and the crystal phases formed during the annealing of the glass at the temperature of maximum crystallization velocity.

For these experiments a technique was developed to prepare radioactive samples small enough to be removed from the hot cell for chemical analysis and identification of the phases within the glass. Small pieces will be taken from the glass block. Their weights will be about 15 µg and their total β, γ-activities will be less than 2 µCi. The dose rate at the surface should be about 40 mrem/h. Some of the samples will be cut with a low-speed saw and polished to get tiny low activity thin sections.

The corrosion of the glass will be measured at 110, 150 and 190°C under static conditions in saturated $NaCl-CaSO_4$ and $KCl-MgCl_2-Na_2SO_4$ solutions and with container material present. The leachates will be analysed by ICP for the elements Sr, Zr, Mo, Ba, La, Ce, Nd, Cr, Fe, Mn, Ni and the glass formers Si and B. The surface will be investigated by SEM and EPMA and enrichments and depletions of elements in the surface layer will be measured. From short time (<3 d) and long time (1000 d) experiments the time law for the corrosion will be derived and the results compared with those obtained for non-radioactive glass samples. The question of long-term extrapolation of corrosion rates will be addressed by discussing the leaching mechanism.

Laboratory and in-situ interaction between simulated waste forms and clay

Contractor: S.C.K./C.E.N., Mol, Belgium
Contract N°: FI1W/0100
Working Period: August 1986 - December 1987
Project Leader: P.Ph. Van Iseghem

A. Objectives and Scope

The present programme is a continuation of the research carried out in the framework of the second CEC R&D programme (81-84; covered by contracts no. 302-83-15 WASB and 324-83-55 WASB). A large amount of important indications on the corrosion behaviour of various candidate HLW and TRUW reference waste forms in static conditions, including e.g. the influence of SA/V (surface area to volume), temperature and clay, and on the leaching behaviour of Pu from the TRUW waste form was obtained. In situ experiments in a surface clay quarry were performed. The preparations for the γ irradiation tests and the in situ experiments in the underground laboratory in clay were nearly finished.

The programme aims to elucidate the corrosion mechanisms of some reference HLW and TRUW glasses in clay media. This must enable one to propose a source term for the radionuclide release into the near field, and to model the long term interaction between glass and clay. The study includes both laboratory (inactive and tracered glasses; without and with external γ radiation) and in situ experiments. Four reference high-level waste (the AVH SON68, the Pamela SM513 and 527, and the Italian BEL-15) and alpha waste (WG124) glasses are being studied.

One part of the programme is carried out by ENEA Casaccia (Item B.4).

B. Work Programme

B.1. Corrosion experiments on waste glasses SON68, SM513, SM527 and WG124 in various clay media (without, with different amounts of clay), with attention to the leaching of the matrix components Si, B, Na, Fe, ..., and of the radionuclides Pu, Cs, Sr, Tc, Np, Am. Most experiments are performed at 90°C for periods until two years, in carefully controlled redox conditions.

B.2. Corrosion experiments on waste glasses SON68, SM513 and SM527 in clay media, in an external γ radiation field of 10^5 rad h^{-1}, without and with the simultaneous presence of container material (maximum test duration 1000 h).

B.3. In-situ experiments on various candidate HLW and TRUW reference glasses in direct contact with clay (first samples will be retrieved in 1988), or in the clay derived atmosphere (2 and 6 months results will become available in 1987.

B.4. Laboratory interaction tests on the Italian BEL-15 reference glass with clay media, to determine its quality as compared with other candidate glasses, and to simulate the in-situ experiments.

C. Progress of work and obtained results

Summary

The experimental design and conditions for the inactive laboratory tests (see B.1. and B.4.) have been elaborated, and partly blank tested (B.4.).

The very recent Pamela-HEWC reference glass SM527 has been manufactured. The inactive tests will start beginning of 1987. Special care in these experiments, as well as in the others (see further), is being given to the atmospheric conditions (reducing or oxidizing), to the composition of the clay medium, and to the analysis of the leachates.
The other experiments - the tracer laboratory tests, the tests in an external γ irradiation field and the in-situ experiments - are nearly all operational since mid of 1986. Partial results until one month corrosion for the Pu-Cs-Sr tracered glasses have been obtained. γ irradiation experiments until one month (4.2×10^7 rad) were performed, which indicated non negligible H_2 and CO_2 production in the clay/water solution. The in-situ experiments in clay are operational, and those in the clay derived atmosphere are being installed.

Progress and results

1. Corrosion mechanisms in clay media

The very recently defined reference Pamela-HEWC glass SM527 has been prepared in the S.C.K./C.E.N. laboratories.

The experimental corrosion conditions in laboratory were chosen as close as possible to those encountered in situ. Therefore, the liquid part of the clay to water solutions consists of synthetic interstitial claywater (SIC) and the E_h value of the leaching solutions is about - 200 mV.

1.1. Inactive experiments (glasses SON68, SM513, SM527, WG124)

The following corrosion experiments are in preparation:

* Corrosion in two mixtures of clay with SIC (10 and 500 g l^{-1}) at 90°C, $SA.V^{-1} = 1\ cm^{-1}$, $E_h \cong -200$ mV, test durations between a few days and years.

* Corrosion in one clay/SIC mixture, in similar conditions as above, but with or without removal of the surface layer after various test durations (at 40, 90, 190°C).

Special attention in these experiments will be given to the analysis of the leachates for the glass matrix components, and the glass surface.

Some screening experiments are in operation on glass SON68 in two clay/distilled water mixtures (10 and 500 g l^{-1}), in ambient atmosphere conditions. The data until 80 d indicate a different leaching rate for B and Li between the two clay media.

1.2. Radioactive (tracer) experiments (glasses SON68, SM513, SM527)

Experiments on glasses SON68 and SM513, tracered with Pu-239, Cs-134 and Sr-90 in the 500 g l^{-1} clay/SIC mixture (CCSICM) are underway. The initial E_h was - 100 mV. Test durations until one month were finished. The mass loss data indicate close similarity with previous inactive experiments in a more concentrated clay/water solution. Leachate analysis is underway, with separate analysis of the radionuclide inventory with a size smaller and larger than 10^5 MWU (which can be considered as a conservative limit to migration through the clay host).

2. Influence of an external γ radiation field

Four series of experiments have been carried out, with exposure times of 50, 100, 340 and 670 hours. The temperature was 90°C, and the γ dose 0.63×10^5 rad h^{-1}. The leach solutions were 100 g l^{-1} mixtures of clay with water. In the first two tests only blank solutions were used; in the latter experiments, both blank solutions and solutions together with waste glasses (SON68, SM513 and the SM527 precursor, $SAN602519L_3C_2$) were exposed to the γ-field. The solutions were prepared in either oxidizing or reducing ($E_h \cong -200$ mV) conditions.

In both reducing and oxidizing clay solutions, considerable amounts of CO_2 and H_2 (up to 11 and 18 wt % of the gas phase, respectively) were produced during irradiation, a.o. as a result of the reaction between oxygen and organic compounds. The solution pH decreases in both redox conditions, while the E_h increases (anoxic condition) or decreases (oxic condition). The corrosion of the waste glasses might have increased with a factor between 2 and 3, compared with the test in the absence of radiation.

3. In-situ experiments

All tubes for the experiments in direct contact with clay were installed, and heated to the design temperatures during the first half of 1986. One of the two 90°C test tubes also includes some Pu-Cs-Sr tracered glasses (SON68 and SM513). The temperature at the interface with clay and pH-E_h of the clay are continuously monitored.

The porous filter tubes used for the experiments in the clay atmosphere were installed during the first half of 1986. A steady state water flux of 100 ml m^{-2} d^{-1} was measured. One loop was completely installed by the end of 1986; it is scheduled that the four loops will be in operation by the end of March 1987. Two of them will be heated at 90°C (instead of 90 and 50°C), but either oxygen or helium will be used as carrier gas. The other two loops (clay host temperature and 170°C) will operate with helium as the carrier gas.

Laboratory simulation experiments of the in-situ interaction with the clay host are being performed at 90 and 170°C (at the corresponding saturation pressure). The data until 180 d at 90°C yield dissolution rates between 15 and 120 μm per year. Good conformity is obtained with the results in the more diluted clay media (500, 2000 g l^{-1} instead of 8000 g l^{-1}) studied before. New containers were designed, to implement also the actual in-situ pressure of 4 MPa in the laboratory simulation tests.

4. Compatibility between the Italian BEL-15 glass and clay

4.1. Short term interaction with clay media

The matrix B-MCC1 standard test will be used to investigate the short term interaction (max. test duration 28 d; T_i = 40 and 90°C) with the following clay media: synthetic interstitial claywater, and a 500 g l^{-1} mixture of clay with synthetic interstitial claywater.

Specially designed Teflon corrosion cups of 7 ml inner volume were manufactured by the S.C.K./C.E.N. Mol. The start of the experiments is foreseen for February 1987.

4.2. Clay contact test

This test aims to simulate the in-situ experiments carried out in Mol. Either Mol "Boom" or Italian clay will be brought into contact with a glass sample at 90°C, 4 MPa, for periods of 3, 6, 9 and 12 months. The atmosphere will be inert.

The corrosion container has been designed, constructed and tested during three months for its tightness and pressure performance.

Radionuclide release from solidified high-level waste

Contractor: UKAEA, Harwell UK
Contract No: FI.1W.0097.UK(H)
Working Period: July 1986 - December 1989
Project Leader: J.A.C. Marples

A. Objectives and Scope

The aim of the research is to ensure that the Community reference glasses in general and the UK reference vitrified high-level-waste form MW in particular are suitable for eventual disposal in either hard-rock or clay.

The comparative study of the radiation stability of all four of the Communities reference borosilicate glass waste forms will ensure that problems do not arise in the future from the effect of radiation.

Studies of the release of radioisotopes from the reference waste form under conditions that will or could occur after disposal will provide data for mathematical models of the long-term health effects of radioactive waste repositories.

B. Work Programme

B.1 Leaching behaviour
  B.1.1. Equilibrium leach tests with glass and backfill only
  B.1.2 Simulated repository tests
B.2 Effect of radiation and radiolysis
B.3 Effect of product quality
  B.3.1 Imperfectly incorporated calcine
  B.3.2 Slow cooled samples

C. Progress of the work and results obtained

Summary

Inactive samples of the glass MW which is to be used in the Windscale Vitrification Plant were made with a complete spectrum of inactive isotopes of the fission products. These were then doped separately with Tc, Np, Pu and Am. In order to measure the equilibrium concentrations of these radioactive elements under conditions that may occur in the near-field of a repository, the glass was then crushed and sealed in capsules under a reducing atmosphere with iron, representing the overpack, with various candidate backfill materials and with water. Coupons of glass were included in some of the capsules so that the conventional leach rate could be measured. Capsules have been opened at intervals and Eh measurements showed that conditions were reducing as would be expected in a repository. Leach rates determined by weight loss were lower if a cement-containing backfill was present. The equilibrium concentrations of the radioisotopes were also extremely low particularly in the capsules that contained cement. It is not certain whether this is due to sorption on the cement or to the high pH.

As the number of α-decays per gram increases, the density of MW glass doped with Pu-238 is decreasing at an approximately similar rate to that previously observed for other glasses.

The progress of the work is as follows:

. B.1.1. and B.2. Tests are in progress and preliminary results are reported herein.

. B.1.2. and B.3. These experiments are not yet scheduled to have started.

Progress and results

1. Equilibrium leach-test measurements (B.1.1.)

The experiments used MW glass, made with a full inactive waste simulant but separately doped with Tc-99, Np-237, Pu-239/240 and Am-241. Mixtures of crushed glass, iron powder, a candidate backfill material and water are sealed in tubes under an atmospheres of Ar-5%H_2. Table I lists the components used.

Five tubes of each mixture were prepared and are being held at 60°C. One tube of each batch will be sampled after 1,2,6 and 12 months. One set of tubes contains glass and iron powders and an iron coupon only; the other sets also contain one of the candidate backfills. About half the tubes also contain a solid glass disc which is used to determine the bulk leach rate of the glass. Most of the tubes are made of glass, sealed with a ground glass joint and a sealant compound. However, where bentonite backfill is included, a steel tube, with an o-ring seal is used because of the pressure generated by the swelling of the bentonite when water is added.

The tubes are opened under an argon 5% hydrogen atmosphere and measurements of Eh and pH are made, (Table II). Bulk leach rates are calculated from the weight losses of the glass coupons and the equilibrium concentrations of the isotopes measured by radio-chemical analysis of the water, the latter both after filtering through an 0.45µm filter or a 25,000 molecular weight cut-off membrane. The discs for α-counting are prepared by electrodeposition after spiking the leachate with a Cm-244 calibration solution. Electrodeposition gives greatly improved α-spectra compared to merely evaporating the leachate when the latter contains a lot of dissolved material.

The presence of the isotopes does not appear to affect either the Eh or pH of the leachates. The leach-rates measured by weight loss are also given in Table II. The effect of higher ionic concentrations arising from the backfill in suppressing the dissolution of the glass is clearly seen. This effect apparently overrides any deleterious effect that high pH might have on the glass.

The measured equilibrium concentrations are given in Table III. Americium and plutonium show a large decrease in concentration after filtering through the 25,000 molecular weight cut-off membrane, suggesting that a large fraction of the material is in a colloidal or pseudocolloidal form. In all cases these observed concentrations are extremely low, showing that, under reducing conditions, these isotopes will be well localised in the near field.

2. Radiation stability of glass

A sample of glass MW doped with 2.5wt% Pu-238 has now accumulated as many α-decays per gram ($8.5x10^{17}$) as the real waste will in about 1000 years. The density has decreased by 0.28% in a similar manner to that observed for several other borosilicate glass samples/1/ and extrapolation suggests that, at saturation, the decrease will be 0.37±0.04%.

3. Acknowledgement

This work was carried out with the financial support of the European Commission, British Nuclear Fuels plc and the UK Department of the Environment. In the Department of the Environment context, the results may be used in the formulation of UK Government policy but do not yet represent such policy. Reference to the use of a particular manufacturers product does not necessarily imply a preference for that product.

4. Reference

/1/ LUTZE, W., MANARA, A., MARPLES, J.A.C., OFFERMANN, P., and VAN ISEGHEM, P., European Community Conference on Radioactive Waste Management and Disposal. April 22-26 1985. Proceedings pp 232-251.

Table I

Components of equilibrium leach tests

Component	Weight(g)	Condition
Glass	1.0	Crushed (<200µm)
Iron	5.0	Filings
Backfill (4 tested)	10.0	Crushed (<200µm), precast OPC/BFS 1:3 OPC/PFA 1:3 OPC/limestone 1:6 Sodium bentonite
Water	20ml	Equilibrated with crushed granite at ambient temperature.

OPC = ordinary portland cement.BFS = blast furnace slag.
PFA = pulverised fly ash.

Table II
Eh, pH and mass loss leach rates

	Fe Only	OPC/ BFS	OPC/ PFA	OPC/ limestone	Bentonite
Eh(mV)	-320	-520	-150	-100	-280
pH	9.8	12.7	12.5	12.6	8.3
Mass loss leach rate $kg.m^{-2}.sec^{-1}$	$2.3x10^{-9}$	$8x10^{-10}$	$\sim 1x10^{-10}$		

Table III
Equilibrium concentrations

	Backfill	Iron only		OPC/BFS		OPC/PFA		OPC/ limestone		Bentonite	
	Time/ month	A	B	A	B	A	B	A	B	A	B
$Pu/10^{-12}M$	1	5	0.5	2	0.2	1	0.1		0.2	9	2
	3	2	0.9	2	0.04		0.1				
$Am/10^{-12}M$	1	5	0.6		1	20	1		0.6	73	5
	3	30	8		1	6	0.4				
$Np/10^{-9}M$	1	11	7	0.3	0.6		0.5		0.2	440	210
$Tc/10^{-9}M$	1	120	90	10	12	17	14	320	300		6
	3	90	70	40	30	25	25				

A. Concentration after filtering through 0.45µm filter.
B. Concentration after filtering through 25000 molecular weight cut off membrane.

BASIC MECHANISMS OF AQUEOUS CORROSION OF WASTE GLASSES

Contractor: CEA, CEN-Valrho, SDHA, F
Contract No: FI1W-0030
Working Period: August 1986 - July 1989
Project Leader: N. Jacquet-Francillon

A. OBJECTIVES AND SCOPE

Although a major research effort has been undertaken during the last decade on aqueous corrosion of nuclear glasses |1| |2| our understanding of the basic corrosion mechanisms is essentially phenomenological and many important questions remain unanswered. This understanding is indispensible to ensure that the mechanisms taken into account in corrosion models correspond effectively to those governing the long term release of radionuclides.

The experiments proposed here are parameter studies of simple glass-water systems designed to investigate the effects of saturation, leaching under hydrothermal conditions, corrosion at the interface layer, and the behaviour of technetium and the actinides.

B. WORK PROGRAMME

B1 Investigation of the apparent solubility limit of SON 68 glass for different SA/V values. (Are the steady-state concentrations in solution related to the glass itself, to the gel or to newly formed crystalline phases?)

B2 Hydrothermal leaching and analysis of the crystalline phases formed between 50°C and 250°C.

B3 Examination of the interface or ionization layer between the surface layers and the sound underlying glass.

B4 Determination of the concentration profiles in the surface layers for the principal actinides.

B5 Filtration study of the physicochemical form in which plutonium is found in the leachates.

B6 Investigation of technetium behaviour.

C. PROGRESS OF WORK AND OBTAINED RESULTS

SUMMARY

The first months of this study were mainly devoted to investigating the solubility of SON 68 glass (B1). The most striking result to date has been the appearance of an apparent solubility limit for SON 68 glass that varies considerably with the SA/V ratio.

An X-ray diffraction analysis method on a minute sample gave encouraging results for the identification of the neoformed phases at various temperatures (B2).

Investigation of the actinide concentration profiles in the leached layers has just begun (B4).

Items B3, B5 and B6 have not yet been started.

1. Solubility (B1)

The objective of this study is to determine the apparent solubility limit for SON 68 glass. The steady-state concentrations obtained after static leaching of glass samples at 90°C in "Volvic" water are studied at different SA/V values.

Experimental Protocol

Preliminary experiments were conducted with four SA/V ratios: 5, 10, 20 and 80 cm^{-1}. All of the experiments were carried out at atmospheric pressure in hermetically sealed teflon containers. A specimen of known mass and geometry was placed in a specified volume of "Volvic" water. The containers were placed in an oven at 90°C for 70 days.

Two types of glass specimens were used. For the 5 and 10 cm^{-1} SA/V ratios monolithic glass blocks were sawed into the shape of a comb and a suitable water volume was added to maintain the desired SA/V value. For the 20 and 80 cm^{-1} tests the glass was provided in powder form with a granulometry of 400-500 microns and 100-125 microns, respectively. Two grammes of powder were placed in the container with 5 ml of water; the containers were set on rollers to ensure constant agitation of the powder.

The leachate obtained after each test was checked for pH at room temperature and the solution was submitted to ICP analysis.

Results

The silicon concentrations varied only slightly after 28 days, and maximum concentrations of 50, 65 and 100 ppm may be defined for SA/V ratios of 5, 10 and 20 cm^{-1}, respectively. The number of significant points plotted for the 80 cm^{-1} experiment was insufficient to determine the maximum silicon concentration in the leachate, but suggests a value on the order of 200 ppm. The concentration curves levelled off in the same way for the soluble elements in the glass (boron, sodium, lithium) indicating that corrosion slowed down significantly.

Discussion

The maximum silicon concentration variation according to the SA/V ratio was correlated with pH variations in the leachate: the pH rises with the SA/V ratio. This phenomenon may be explained by differences in the importance of the interdiffusion mechanism according to the SA/V.

2. Hydrothermal Leaching (B2)

SON 68 glass will be leached at temperatures ranging from 50 to 250°C at a pressure of 10 MPa and the neoformed phases at each temperature will be identified.

Experimental Protocol

Comb-shaped monolithic samples with high specific surface areas (SA/V = 3.5 cm^{-1}) are leached in the device shown in Figure 1, made of stainless steel and capable of withstanding temperatures of 300°C and pressures of 50 MPa.

Progress and Results

The experiments at 50°C and 150°C in "Volvic" water have begun, but no results are available. However, preliminary experiments using double distilled water have been carried out with the collaboration of the University of Poitiers: the use of a linear localization detector for X-ray diffraction on very small material quantities gave very promising results for the identification of the neoformed phases. |3|

3. Actinide Concentration Profile (B4)

Four SON 68 glass samples doped with 0.85 wt % of different actinide oxides (corresponding to the industrial glass content) were leached in Soxhlet conditions for 28 days. The samples doped with ^{237}Np, ^{239}Pu and ^{241}Am, as well as the simulated uranium-thorium reference glass are now being examined by electron microprobe analysis. The distribution profile in the leached layer (approx 10 microns thick) will be determined for each actinide.

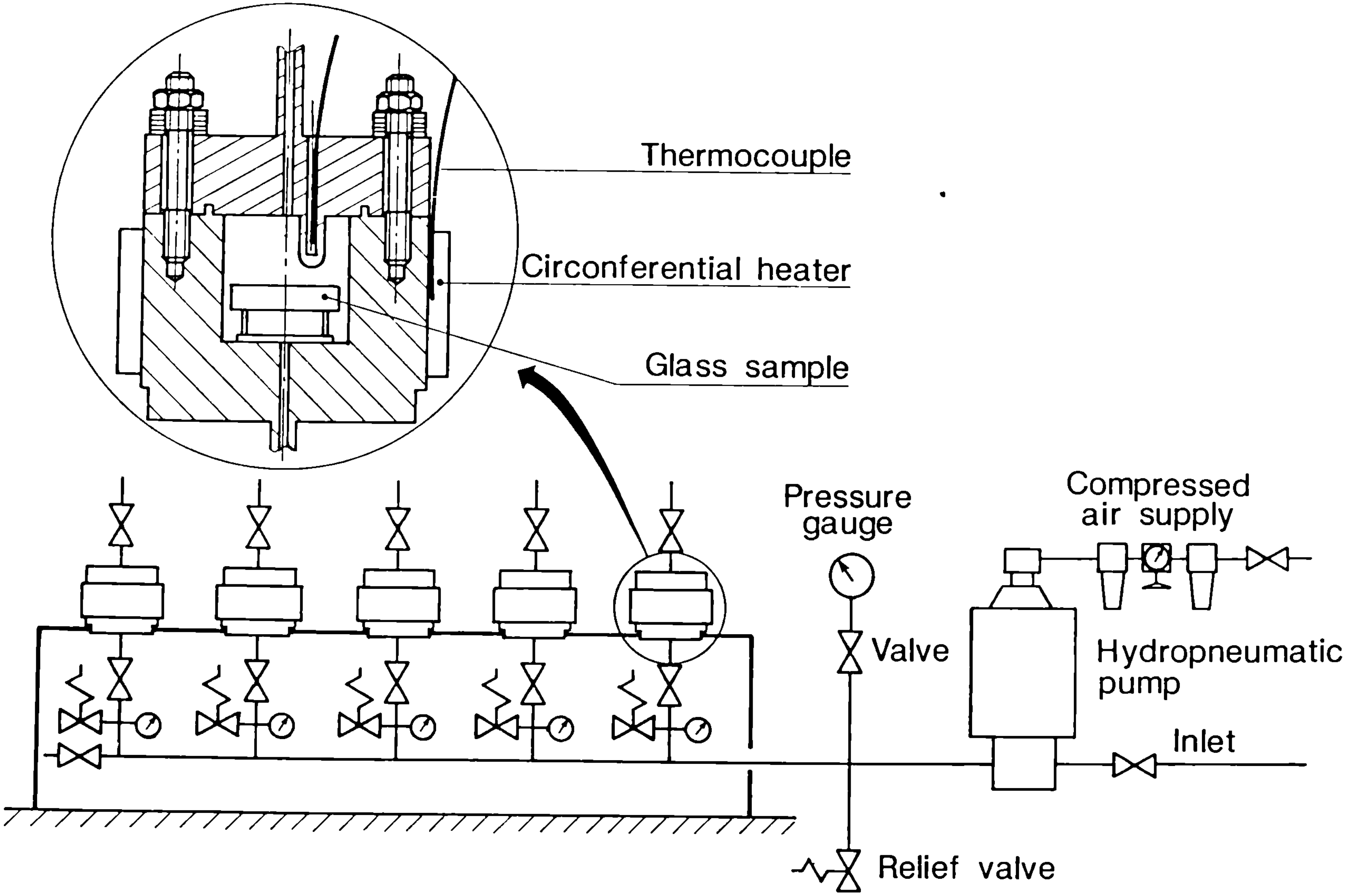
REFERENCES

|1| NOGUES, J.L. et al., Nuclear Glass Corrosion Mechanisms Applied to the French LWR Reference Glass. In: Scientific Basis for Nuclear Waste Management VIII. C.M. Jantzen et al, (eds). MRS, Pittsburgh (1984).

|2| FILLET, S. et al., Corrosion Rate of Nuclear Glass in Saturated Media. Third International Symposium on Nuclear Waste Management. American Ceramic Society. 88th Annual Meeting, Chicago (1986).

|3| RASSINEUX, F., et al., (to be published).

HP 40 LEACHING DEVICE



TESTING OF THE ALTERATION OF WASTE GLASSES UNDER GEOLOGICAL STORAGE CONDITIONS

Contractor: CEA, CEN-Valrho, SDHA, F
Contract No: FI1W-0096
Working Period: September 1986 - August 1988
Project Leader: N. Jacquet-Francillon

A. OBJECTIVES AND SCOPE

A large number of parameters must be taken into account to predict glass alteration behaviour in a geological repository: flow rate, temperature, pressure, pH, Eh, CO_2 content, radiolysis, water composition, nature of the surrounding rock, backfill material, possible corrosion products, etc. Laboratory parameter studies have been conducted for many years and are indispensible to an understanding of the glass alteration mechanisms and the effects of each parameter. However, none of the parameters is independent of the others and although investigating them separately is not sufficient, a systematic study of all possible combinations would be prohibitive. Under these circumstances parameter experiments must be completed by integral tests which simulate all of the parameters of a granitic repository as realistically as possible.

The objective of this programme is to conduct a series of integral leaching experiments meeting this criterion. The programme is expected to provide information in the following areas:

- equilibrium concentrations which tend to occur when all of the environmental materials are present;
- glass alteration rate under steady-state conditions;
- effect of smectite (considered for storage in France) on glass alteration: previous experiments showed the determining effect of the nature of the clay used as a backfill material;
- identification of newly formed compounds under integral test conditions;
- actinide behaviour in a complex geological medium: leaching rate and physicochemical form.

B. WORK PROGRAMME

B1 Two non-radioactive experiments with simulated SON 68 glass using fractured blocks to simulate an industrial glass block.

B2 Four experiments with alpha-doped glasses: the glass samples will be spiked with uranium-thorium, neptunium, plutonium and americium, respectively.

B3 Four mini-experiments with moist clay on non-radioactive glass and on plutonium-doped glass.

C. PROGRESS OF WORK AND OBTAINED RESULTS

SUMMARY

The first months were used to prepare the materials and set up the six integral experiments. No results are available at the present time.

PROGRESS

1. Inactive Experiments (B1)

The device used for the integral experiments is shown in Figure 1. The preconditioning pot contains 815 g of crushed granite (granulometry < 5 mm) and 1100g of a mixture containing 95% sand and 5% smectite. The leaching pot contains 35 rectangular granite blocks with a total surface area of 88 cm^2, approximately 1100 g of the 95%-5% sand and smectite mixture, 38 pieces of NS 24 steel with a total surface area of 131 cm^2 (the steel specimens were oxidized for 1 hour at 1000°C to improve the canister simulation conditions), and the SON 68 18 17 glass block measuring 70 mm in diameter and 80 mm high.

The following technique was used to fracture the glass block: the block was first lined with a fine stainless steel mesh, then fractured by raising its temperature to 520°C and quenching it in water. A calibrated weight was then dropped twice on the block from a height of one meter. The glass specimen was next placed in the leaching pot, which was then packed with the environmental materials. The steel mesh was only removed immediately before closing the pot. This technique allows blocks to be prepared with major fracturing while maintaining a monolithic aspect.

Test Startup

The leachant ("Volvic" water) was preconditioned for 1 month at 90°C under a pressure of 100 bars in the preconditioning pot. The leaching temperature was regulated at 90°C, then the pressure was adjusted to 100 bars. Samples are taken at 2-month intervals, and the quantity drawn off is replaced by leachant preconditioned at the same temperature and pressure for the same length of time as in the leaching pot.

State of Advancement

Two inactive experiments are now in progress, one with a monolithic glass block, the other with a fractured block. Both tests are scheduled to last one year. The long-term (3-year) test on a fractured block which is to be initiated under this programme has not yet begun.

2. Alpha-Doped Glass Experiments (B2)

The experimental device, environmental materials and test protocol are the same as for the inactive experiments.

Uranium/Thorium-Doped Glass and Neptunium-Doped Glass

Both of these tests are set up in a low activity glove box with monolithic samples 70 mm in diameter and 80 mm high; the uranium-thorium sample contains 0.52% UO_2 and 0.33% ThO_2, and the neptunium sample contains 0.85% NpO_2 with a specific alpha activity of 2×10^5 $Bq \cdot g^{-1}$.

Plutonium-Doped Glass and Americium-Doped Glass

These two tests are conducted in another glove box because of their higher specific activity. The monolithic plutonium-doped glass block is 70 mm in diameter and 80 mm high, and contains 0.85 wt % of PuO_2 with a specific activity in the glass of 3.7 x 10^7 $Bq \cdot g^{-1}$.

The americium-doped glass contains 0.85 wt % $^{241}AmO_2$ for a specific activity level of 1.0 x 10^9 $Bq \cdot g^{-1}$. An 800 g block of this glass would have represented a gamma and neutron* dose rate unacceptable in the laboratory, and was therefore replaced by two rods measuring 25 x 25 x 100 mm with a similar total surface area but a much lower mass.

Test Startup

All four active experiments are now in progress. The first leachate samples have been taken, but have not yet been analyzed.

3. Moist Clay Experiments (B3)

At the present time the most probable engineered barrier in France is compacted smectite rather than a clay/sand mixture. The latter material was selected for the preceding experiments to maintain environmental permeability. The moist clay tests are designed to compare the two options, and compare SON 68 glass alteration in French smectite with other types of clays. The experimental programme has not yet begun.

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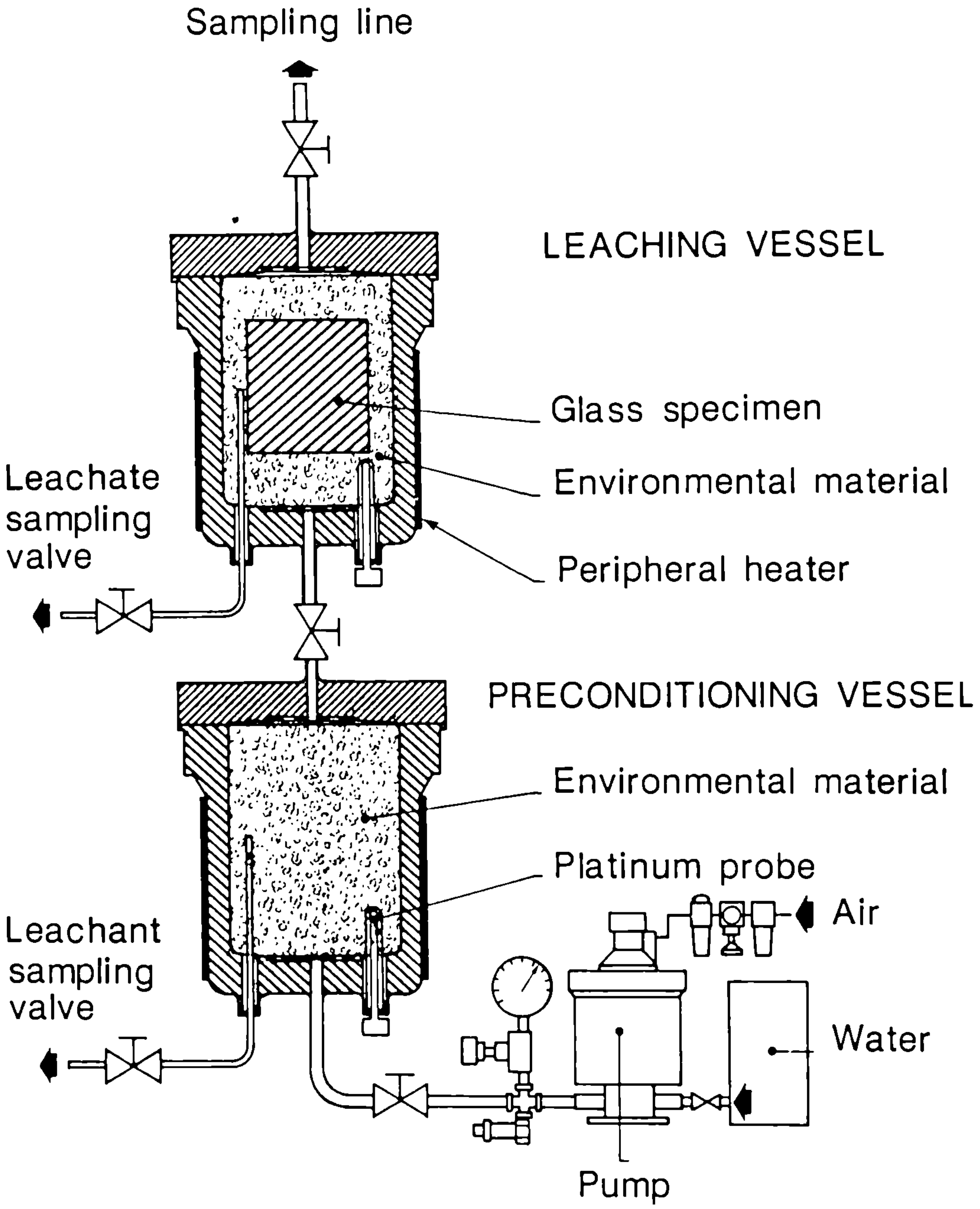
* from (alpha, n) reactions in the glass



Schematic diagram of test mockup

Investigation of the Long Term Behaviour of HLW Glass Under Conditions Relevant to Final Storage

Contractor: Fraunhofer-Institut für Silicatforschung,
Würzburg, F.R.G.
Contract No.: FI1W/0028
Working period: May 1986 - April 1988
Project leader: H. Roggendorf

A. Objectives and Scope

Borosilicate glasses are proposed as waste form for the final disposal of High Level Waste (HLW) by the Federal Republic of Germany. Between 1980 and 1985 extensive studies on the corrosion mechanisms of the inactive HLW glass type SM 58 in a salt brine were performed by the contractor (contract nos. WAS-232-81-53 D (B) and WAS-323-83-53 D (B)). A theoretical study /1/ on reported corrosion data (for different glasses and different corrosion conditions) showed that most HLW glasses corrode according to a very similar pattern. The main mechanisms are:

- network dissolution (responsible for almost the total mass loss of the glass during corrosion),
- formation of layers of reaction products of glass and solution (which in most cases do not act as a diffusion barrier, but as precipitate may control the solubility of glass components in the leachate), and
- ion exchange (altering the composition of the remaining glass surface).

In fresh leachants corrosion starts with an initial rate r_0 linearly depending on t. Due to the accumulation of corrosion products in the leachate, this initial rate slows down, it may even pass a period of zero dissolution, but finally reaches a long term rate r_∞, which again is linearly depending on t. Long term corrosion conditions can be achieved in the laboratory by the variation of the sample surface area to solution volume ratio s. The product s•t is a parameter taking into consideration that in corrosion tests with higher s values saturation with glass corrosion products is reached in a shorter time.

At present the interest is focused on the following open points: The data at high s•t values should be approved by additional experiments. Only a few data could be collected up to now about the composition of leachates, especially salt brines, saturated with glass corrosion products, and the influence of the surface composition of the remaining glass on the corrosion rate is still unknown. The last point is important for high s•t values, because it is expected the depth of the ion exchange zone to be increased when the corrosion rate decreases. The aim of the current contract is to clear the questions indicated above and to investigate the corrosion mechanisms of the new reference HLW glass SON 68. The corrosion tests will be performed in cooperation with the Hahn-Meitner-Institut (HMI), Berlin.

B. Work Programme

B.1. Corrosion pre-tests for the optimization of analytical techniques.
B.2. Supplementary corrosion tests.
B.3. Optimization of analytical techniques (Photoelectron spectroscopy (XPS), acid etching).
B.4. Optimization of preparation methods.
B.5. Preparation and measurement of standard samples with XPS.
B.6. Surface analysis of corroded glass samples.
B.7. Evaluation of test results.

C. Progress of work and obtained results

State of advancement

Since September 1986 the original COGEMA glass SON 68 is available. Before that time, a substitute produced by the HMI, Berlin, was used for pre-tests which showed some encouraging results. The reaction layers, formed on SON 68 glass corroded in salt brines, can be removed easily, so that surface analytical methods can be applied. First results from HF-etching experiments showed that with this technique comparatively thin surface zones (about 50 nm) of the glass can be dissolved per etching step. The techniques for analysing the obtained low concentration solutions need further improvement. A sedimentation method was applied to prepare well-defined size fractions of glass powders for high surface area leaching experiments.

With the original glass SON 68 a set of 12 different corrosion experiments was started. The resulting corroded glass chips will be analysed by photoelectron-spectroscopy (XPS) and the HF-etching technique to establish a correlation between surface composition and corrosion rates determined by HMI.

For XPS a set of 15 standard glasses was prepared and tested. The first results indicated that the homogeneity of the standards has to be improved and that surface preparation methods have to be applied which neither contaminate the glass surface nor change its structure (as normal grinding methods do).

The general work progress is as follows:

- B.1. and B.4.: progressing normally,
- B.2.: delayed because the original SON 68 glass was not available before September 1986,
- B.3. and B.5.: partly delayed due to defects in XPS-equipment.

Progress and results

1. Sample preparation and pre-tests (B.1. and B.4.)

The HLW glass SON is a borosilicate type with the major components (in wt.-%): 45.5 SiO_2, 14.0 B_2O_3, 9.9 Na_2O, 2.0 Li_2O, 4.9 Al_2O_3, 4.0 CaO, 2.9 Fe_2O_3, 2.7 ZrO_2, 2.5 ZnO, and 11.4 rest. From the original COGEMA glass as well as from a substitute prepared by the HMI (and used for pre-tests) glass chips with a size of 12 x 9 x 2 mm^3 were cut and glass powders were prepared. For the powder preparation the Atterberg cylinder sedimentation method was applied, using methanol and iso-propanol as sedimentation liquids. The following particle size fractions were prepared (in µm): 2 to 10, 5 to 10, 10 to 20, 20 to 30, 30 to 40, and 40 to 50. Table I, part a, shows the amounts of certain glass powder fractions used to determine the different s values in pre-tests for the corrosion of glass chips and powder in salt brines. Table II shows the composition of the leachants used. No. I is the so-called Q-solution (consisting of five components, quinary solution), no. II a saturated $MgCl_2$ brine, and no. III a saturated NaCl brine.

Pre-tests were performed with all three solutions. It is of importance that the reaction layers formed during corrosion can be removed easily. Therefore, surface analytical methods such as XPS can be applied to the remaining glass. The samples of the pre-test shall be used for the development of the analytical methods as indicated above.

2. Corrosion tests (B.2.)

To prepare samples for surface analysis a set of 12 corrosion tests has been started. The following test parameters were chosen to provide representative results for the short, medium, and long term range of the corrosion process:

190 °C, 60 d, s = 0,1 cm^{-1} (1 cm^{-1})
190 °C, 120 d, s = 10 cm^{-1} (100 cm^{-1})
150 °C, *, s = 10 cm^{-1} (100 cm^{-1})
110 °C, *, s = 10 cm^{-1} (100 cm^{-1})

The s values in brackets are those for leachant no. III. The asterisk (*) means that no test duration can be indicated yet both for the 150 °C as well as the 110 °C experiments. Analogous to the pre-tests, s values > 0,1 cm^{-1} will be achieved by adding SON 68 powder to the system. The leachant volume is 30 ml and Table I, part b, shows the amounts of powder added to the leachant. These corrosion tests are performed at HMI to achieve results which can be compared with other corrosion tests performed there.

3. Surface analysis (B.3. and B.5.)

A set of 15 standard samples for quantitative XPS analysis of the surface composition of corroded SON 68 glass chips has been used. These standards have a general composition similar to SON 68, but in each of them, the compositions were varied. Therefore the molar ratios were varied within one group of similar components, whereas the molar ratios of the other components were kept constant. Four groups of similar components with respect to their influence on the glass structure were chosen for variation:

1. SiO_2, B_2O_3 (network formers),
2. Al_2O_3, Fe_2O_3, Nd_2O_3 (trivalent network modifiers),
3. ZnO, CaO, BaO (divalent network modifiers), and
4. Li_2O, Na_2O, Cs_2O (alkalies; network modifiers).

The composition of the standards are expected to cover the whole range of compositions of the glass surface built up by the leaching process.

In a first run, the standard samples have been prepared and analysed with XPS. Due to inhomogeneities in the bulk glasses and surface contaminations from preparation new standards have to be prepared to achieve more reliable results.

The chemical etching of SON 68 was applied, too. With diluted HF-HNO_3-$HClO_4$ mixtures (for example 0.1 wt. % HF, 0.2 wt. % HNO_3, and 0.2 wt. % $HClO_4$ in water) it is possible to dissolve glass surface layers of about 50 nm thickness. The chemical analysis of such small quantities of glass is still a problem and has not yet provided reproducible results with respect to B_2O_3 and Na_2O. Other components have not yet been investigated.

/1/ CONRADT, R., ROGGENDORF, H., and OSTERTAG, R., Report of the Commission of the European Communities, Report EUR 10680 EN (1986).

Table I. Realization of different s values in glass powder and chip experiments; chip surface: 3 cm²

s in cm^{-1}	particle size in µm	amount of powder in g
a) leachant volume 90 ml; pre-tests		
0.033	chip only	-
1	30 - 50	0.159
10	20 - 30	1.01
25	10 - 20	1.46
100	2 - 10	1.83
b) leachant volume 30 ml; preparation of samples for surface analysis		
0.1	chip only	-
1	40 - 50	0.061
10	40 - 50	0.613
100	10 - 20	1.95

Table II. Composition of the leachants in wt. % used in the present study

component	no. I	no. II	no. III
H_2O	65.62	64.29	73.50
NaCl	1.45	0.31	25.90
KCl	4.73	0.11	-
$MgCl_2$	26.80	33.03	-
$CaCl_2$	-	2.25	-
K_2SO_4	-	-	0.23
$MgSO_4$	1.40	-	0.16
$CaSO_4$	-	0.005	0.21

3 c) Other engineered barriers

Title : Study of the physico-chemical properties of the transuranian elements necessary to the understanding of the migration/ retardation processes in the near- and far- field

Contractor : CEA-IRDI/DRDD/SESD/SCPCS - Fontenay-aux-Roses - FRANCE
Contrat n° : FI1W-0035 F (CD)
Working Period : June 1986 - January 1989 Project leader : A. BILLON

A. Objectives and Scope

The modelization of the transfer of the transuranian elements through the different barriers to the geosphère implies the knowledge of :

- the exact nature of the species which are able to migrate under the influence of the groundwater ; ions, molecules, colloïds.
- the equilibrium relationship between these species and the surrounding dominant other species either in a mineral or an organic form.

From this point of view it is admitted that carbonate (e.g. the different species CO_2, HCO_3^-, $CO_3^=$) due to his relatively high abundance in the geosphere play a major rôle in this sense that it forms complexes whith almost all the transuranian elements.

Therefore the present work is devoted toward the identification of the different carbonated complexes of the transuranian elements. The determination of their stability constant, their comportment in the geological medium in the vicinity of the source term and in the man-made barriers and finally the elaboration of a model which will describe the migration of these radioelements.

B WORK PROGRAMME

B1 - Basic chemistry :
Measurement of solubility and stability constant of the transuranian elements with the ligand carbonate. Identification of the different species. E_h - pH diagramms.

B2 - Migration ; Experiment of transfer through argileous material. Preliminary assays of diffusion cells whith Cs and Sr. Application to the migration of americium (III).

B3 - Modelization. A model wich take in account the chemical properties of the elements issued from the source term with be elaborated and tested.

C. Progress of work and obtained results

State of avancement

In basic chemistry (B-1),the previous measurement (WAS 83-361-7) were on Neptunium (V) carbonate system. We have delayed during this semester the experimentation on Am(III) and Pu(IV) and have worked intensively on the (+VI) oxydation degree.

The experimental set-up in a glove-box to work at a controlled pCO_2, and the modified glass electrode have been tested with U(VI) and give satisfaction.

Measurement have been made on mixture of U(VI) - M(VI) where M = Np or Pu, and the stability constant of mixed complexes have been determined.

The electrochimical device which is to be used to study redox couples like Pu(VI)/Pu(V) or Pu(III)/Pu(IV) is operational and measurements of standard potential of the U(VI)/U(V) system were made which are in excellent agrement with the published value.

A review of the data on the formal potential of (MO_2^{++}/MO_2^{+}) couples have been made by using the Brönsted-Guggenheim-Scatchard specific ionic interaction theory.

Transfer experiments (B-2)
- choice of methodology
- the french a-4 clay has been chosen and experiments of diffusion in cells have been started with tritiated water, caesium and strontium
- preliminary results are available with tritiated water ; diffusion experiment are still running in with caesium and strontium.

Modelling (B-3). We made the first writing of a code which is intended to solve the Fick equation for an ion alone (Cs) with fixed boundary conditions. The source is supposed to be radial with a given thickness of clay (man-made barrier) around it.

Leaching of the glass is governed by the release of Si which in turn correlate with the flux of Cs.

For an actinide, the flux is supposed to be limited by the solubility products of the existing species.

Progress and results

Study of carbonate/bicarbonate complexes of M(VI) ; all measurements were made in glove boxes at ambiant temperature (22 ± 1°C). Spectrophotometrie measurements were made with a Cary-17 D instrument. The experiments consist of the titration of a given amount of M(VI) in presence of carbonate/bicarbonate by H^+ at a given constant ionic strength ($\mu = 3M$), and at a constant partial pressure of CO_2.

The free-hydrogen ion concentration was measured by potentiometry by using a combined glass electrode (Tacussel TCBC 11/HS/Sm, with a modified reference half-cell). The glass electrode has been calibrated in concentration units.

The emf has been measured by using a Tacussel ISIS 20.000 pH meter.

Absorption spectra are given in fig. (1 and 2). The equilibrium constants for the reactions 3 $MO_2(CO_3)_3^{4-} \rightarrow (MO_2)_3(CO_3)_6^{6-} + 3\ CO_3^{2-}$ are log K(U) = - 11,3 ± 0,1 log K(Np) = - 10,1 log K (Pu) = - 7,4 ± 0,2.

It is demonstrated that one of the cation of the trimer can be echanged with another actinides cation. The equilibrium constants of the reactions 2 $UO_2(CO_3)_3^{4-} + MO_2(CO_3)_3^{4-} \rightleftarrows (UO_2)_2\ MO_2(CO_3)_6^{6-} + 3\ CO_3^{2-}$ are log k = - 11,3 ± 0,1, - 10 ± 0,2 and - 8,8 respectively for M = U, Np, Pu. Polynuclear complexes can be efficient solution "carriers" for other hexavalent actinides in waste disposal.

Potential of M(VI)/M(V) complexes by voltamperometry. The formal potentials of the (UO_2^{2+}/UO_2^+) couple has been determined in medium of varying ionic strength. These data has been interpreted by using the Brönsted-Guggenheim-Scatchard specific ionic interaction theory (S.I.T.) to give the standard potential $E°(UO_2^{2+}/UO_2^+)$ = 0.089 ± 0.002 V/NHE (at I = 0) and the interaction coefficient $\varepsilon(UO_2^+, ClO_4^-$ = + 0,28 ± 0.04. The applicability of the S.I.T. and other types of virial expansion (Debye-Hückel, Davies, Baes and Messmer, Pitzer...) have also been discussed.

The review of published data on the formal potentials of (UO_2^{2+}/UO_2^+), (NpO_2^{2+}/NpO_2^+), (PuO_2^{2+}/PuO_2^+) and $AmO_2^{2+}/AmO_2^+)$ couples have been made by using the S.I.T. We found that all of the existing experimental determinations of formal potentials could be well described by the specific interaction theory with constant interaction coefficients $\varepsilon(MO_2^{2+}, ClO_4^-)$ = 0.46 ± 0.02 and $\varepsilon(MO_2^+, ClO_4^-)$ = 0.28 ± 0.04 for all actinides.

Table 1 give estimated values for the redox systems MO_2^{2+}/MO_2^+ for the actinides from the litterature compared to our experimental work.

Migration studies have been stated with the determination of K_d of Cs, Sr, in batch experiments. Preliminary results with Sr indicate that an equilibrium value is obtained, K_d (Sr) = 2800 $cm^3\ g^{-1}$. The value for Cs is still increasing after 200 h of contact time, even at a concentration of 10^{-6} M, which means that the true value is not attained, as can be seen from table (2) ; measurements are to be continued.

Diffusion of tritiated water leads to the values summarized in the table (4) ; l(cm) is the thickness of the clay layer in the diffusion cell, D_e the effective diffusion coefficient in $cm^2.j^{-1}$.

Some results are given with Cs in the table (5). The influence of the density and of the thickness of the clay layer were first investigated. These preliminary experiments will be completed with more sophisticated measurements.

Experiments with Sr are still going on. Some partial results are given in table (3).

Modelization : The Code CONDIMENT whose aim is to solve the Fick equation, with convection, for a manifold of ions either radioactive or agressing crossing the clay carrier, take in account the diffusion, the convection, the radioactivity and the chemical equilibrium.

In a first time, to compare with known results, we take in ac count only one ion. The method of solving is the finite difference method, following the implicit scheme of LAASONEN. The mesh is bidimensionnal, but we assume that the convection is more weak than the diffusion. Consecutively we have a very rough angular mesh.

We want to be able to couple CONDIMENT to a code computing the migration of ions in geosphere, in preserving the continuity of the concentrations and of their normal derivatives. Consecutively, the boundary conditions considered are CAUCHY conditions :

- a linear combination of the concentration and its normal derivative is fixed.

CONDIMENT may be able to compute the degradation of a waste package. We have assumed in a first step that this degradation is made by dissolving an hydroxyde. This leads us to write a CAUCHY condition on a moving bound. This is the first try to take in account chemical equilibrium. We give the first results with an alone ion.

The Fig. (3) give the progression of the glass gel issued from the dissolution of the glass. The boundary between the glass and the clay moves with a velocity which is proportionnal to the flux of silica supposed to contain soluble element e.g.Cs. with estimated diffusion coefficient of 0.3 $m^2.g^{-1}$ for Cs in the gel and 3.5 10^{-6} $m^2.g^{-1}$ in the clay, the cesium is released as indicated in fig. (4).

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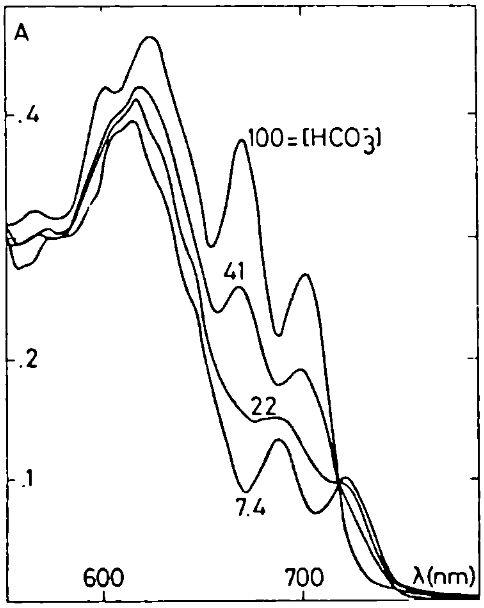

Fig 1 : Absorption spectra of Np(VI) carbonate solutions at varying concentrations of HCO_3^-

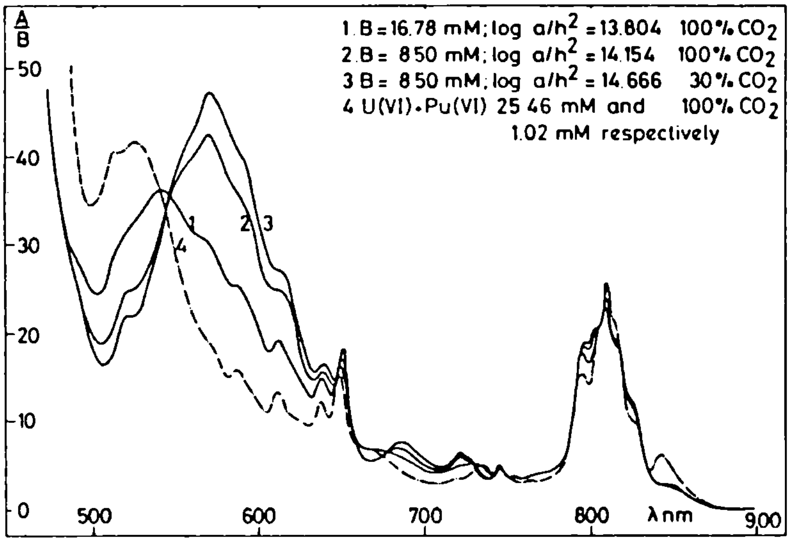

Fig 2 : Absorption spectra of Pu(VI) carbonate solutions and a U(VI)-Pu(VI) carbonate solution, where the predominant Pu species is $(UO_2)_2\ PuO_2(CO_3)_6^{6-}$.

B : total concentrations of M(VI)
A : absorbance
a : pCO_2 partial pressure of CO_2 in the test solutions
h : concentration of H^+

Couple (MO_2^{2+}/MO_2^+)	Formal potential in 1 M ClO_4^- medium		Standard potential (V/NHE)			
	(V/NHE)	Ref.	[1]	[2]	[3]	This work
U	+ 0.065 ± 0.002	This work	+ 0.16 ± 0.05	+ 0.080		+ 0.089 ± 0.002
Np	+ 1.136 ± 0.001	[4] [5]	+ 1.24 ± 0.01	+ 1.153		+ 1.160 ± 0.005
Pu	+ 0.9164 ± 0.0002	[6]	+ 1.02 ± 0.05	+ 0.933		+ 0.940 ± 0.004
Am	+ 1.600 ± 0.005	[2]	+ 1.70 ± 0.05	+ 1.62	+ 1.59 ± 0.06	+ 1.624 ± 0.009

Table 1 : Estimated E° values for the redox systems MO_2^{2+}/MO_2^+ for actinides

Elément	Concentration en élément ($mole.l^{-1}$)	Temps de contact h	K_d ($cm^3.g^{-1}$)
Sr	3.10^{-7}	24 100 200	1200 2671 2837
	10^{-5}	24 100 200	1139 2039 2800
	10^{-3}	24 100 200	1308 1184 928
Cs	$\simeq 10^{-6}$	24 110 200	2280 3290 4591
	10^{-5}	24 110 200	952 1120 1278
	10^{-3}	24 110 200	566 626 940

Table 2

Values of K_d of Sr and Cs for the french clay a - 4

l (cm)	Concentration en élément ($mole.l^{-1}$)	D_e ($cm^2.j^{-1}$)	t_i (j)
0,1	10^{-3} 10^{-5}	$1,4.10^{-4}$ $1,2.10^{-4}$	50 80
0,2	10^{-3} 10^{-5}	$1,0.10^{-5}$ en cours	80
0,4	10^{-3} 10^{-5}	en cours en cours	
0,5	10^{-3} 10^{-5}	en cours en cours	
0,6	10^{-3} 10^{-5}	en cours en cours	

Table 3

Effective diffusion coefficient of Sr in a - 4

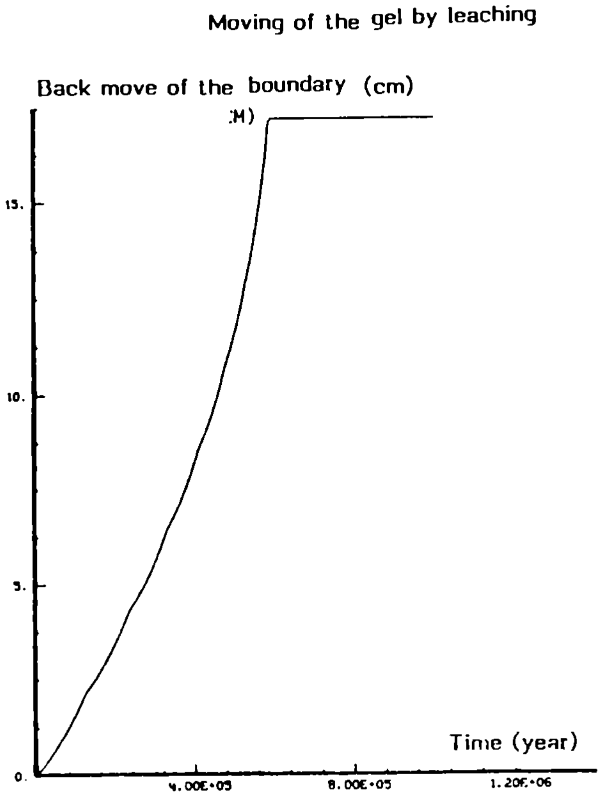

Fig 3

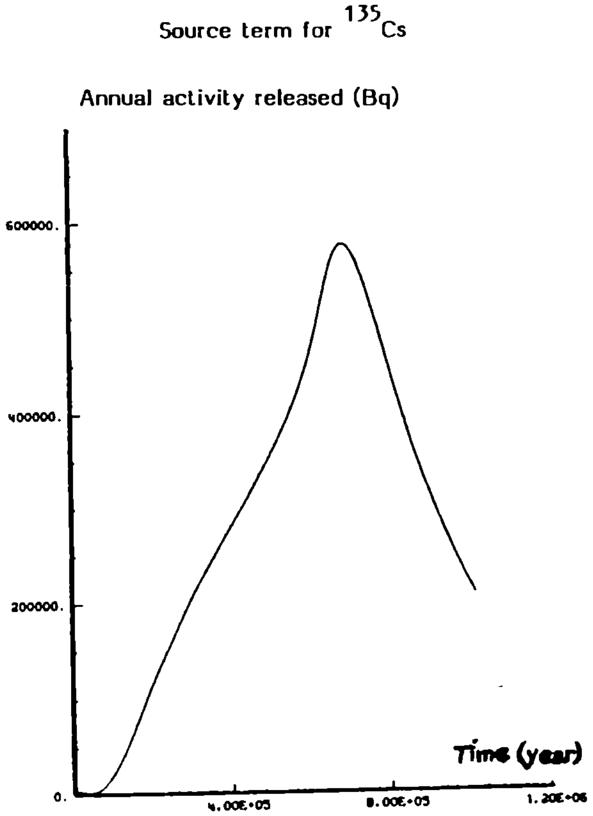

Fig 4

l (cm)	D_e (cm².j^{-1})	t_i (j)
0,1 0,1	$2,7.10^{-3}$ $4,6.10^{-3}$	0,4 0,3
0,2 0,2	$5,1.10^{-3}$ $3,8.10^{-3}$	2 1
0,4 0,4	$1,0.10^{-2}$ $6,0.10^{-3}$	2 2
0,5 0,5	$8,7.10^{-3}$ $8,5.10^{-3}$	3 3
0,6 0,6	$8,0.10^{-3}$ $9,0.10^{-3}$	5 4

Table 4

Diffusion of tritiated waste in a - 4 clay

Nature de l'argile	ρ (g.cm^{-3})	l (cm)	D_e (^{137}Cs) (cm². j^{-1})	t_i (j)
	≈ 2,14 ≈ 1,7 ~ 1,1 ≈ 1,1 ≈ 1,1	0,4 0,4 0,5 1,0 1,5	$\approx 7.10^{-6}$ $\approx 2.10^{-3}$ $\approx 2.10^{-3}$ $\approx 3.10^{-3}$ $\approx 2.10^{-3}$	140 110 15 15 15

Table 5

Effective diffusion coefficients of Cs in a - 4 clay

CORROSION OF CONTAINER AND INFRASTRUCTURE MATERIALS UNDER CLAY REPOSITORY CONDITIONS

Contractor : S.C.K./C.E.N., Mol, Belgium
Contract No : FI 1W-0033-B
Duration of contract : May 1986 - December 1989
Project Leader : W. Debruyn

A. OBJECTIVES AND SCOPE

Objective of the programme is to determine corrosion rates of selected candidate materials under realistic repository conditions over long exposure periods, to determine the in-situ clay agressivity and its evolution after introduction of waste containers, to evaluate the effect of gamma radiation on corrosion rates in a clay environment and finally, based on the combined results of these experiments, to develop mathematical models for the prediction of long term corrosion damage. This approach will enable to qualify materials for use as a barrier between vitrified high level waste and clay as a host medium, and between the underground facilities and clay.

B. WORK PROGRAMME

1. Installation and exploitation of corrosion tubes in the underground laboratory.
    1.1. Interaction of metal alloys with solid clay.
    1.2. Corrosion in a humid clay atmosphere.
2. Instantaneous and integrated corrosion measurements in the underground laboratory.
3. Characterization of the clay environment (solid clay and humid clay atmosphere) by means of pH- and Eh-measurements.
4. Assessment of the influence of an external gamma radiation field on corrosion rate and mechanism.
5. Electrochemical laboratory experiments in a range of conditions resulting from previous actions.
6. Development of a mathematical model for the prediction of long term corrosion damage accumulation.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The main achievement during the contractual period covered in this report is situated in the programme segment of in-situ experiments, B1 and B3. All "direct contact with clay"-tubes, B1.1, have successfully been emplaced and brought to the target operative conditions. Electrochemical sensors have been introduced in the immediate vicinity of the specimens located on the first direct contact tube and the environment is being characterized in terms of Eh and pH, B3. The "contact with clay atmosphere" tubes, B1.2, are on their way to be emplaced and will become operative in the near future.

The RITA gamma irradiation facility, B4, has been loaded with candidate materials in interstitial claywater. A thousand hours experimental exposure has been started.

Action points B2, B5 and B6 have at this point in time not been started yet, which is in accordance with the time schedule foreseen in the contract.

Progress and results

In the underground laboratory at S.C.K./C.E.N. the following experimental work has been accomplished :
An overcoring technique has been developed for removal of corrosion test tubes together with the enclosing clay. This clay layer is needed to determine diffusion rates of corrosion products by analytical techniques. When it was proven that the sample recovery procedure could deliver undisturbed and hence representative samples of both the alloys and the clay environment, it was decided to start implantation of the four, direct contact with clay corrosion tubes. Consequently the steering and measuring instrumentation was connected and the tubes were brought to their target temperatures of 170C, 90C (two tubes) and formation temperature. Data collection has been installed on the mainframe computer. The test tubes to study corrosion under influence of a humid clay atmosphere have been loaded with specimens and are actually being emplaced. They will also function at 170C, 90C (two tubes) and formation temperature. The atmosphere will be kept inert or oxidizing.

To characterize the clay environment in terms of Eh and pH is an easy task as long as a humid clay atmosphere is being investigated.

The characterisation of a solid clay surrounding is far more awkward. To validate the possibility of electrochemical measurement in solid clay, its electrical conductivity has been determined first. A value of $1.46.10^{-5}\ \Omega^{-1}\ m^{-1}$ has been obtained. This value, though low, should permit accurate measurements.

Consequently a number of electrodes has been mounted in the vicinity of the coupons of the contact with clay test tubes : pt and Au-electrodes for Eh measurements and a modified glass-electrode, to withstand the high hydrostatic and lithostatic pressures, for pH measurement. In both cases the reference electrodes are Ag/AgCl electrodes with an acrylic polymer serving as a (salt bridge) contacting medium. The configuration for the electrode implantation is given in figure 1. The ambient temperature corrosion tube has been instrumented at this point in time. The measurements obtained after an emplacement period of one month show a stable pH of 8.3. The redox measurements are, after the same exposure time, still unstable (a firm contact between electrode surfaces and clay is necessary) but they already testify the reductive nature of the medium. This seems to indicate that the effect of e.g. oxygen ingress during the drilling operation would disappear fairly rapidly.

Apart from the in-situ experiments, the RITA gamma irradiation facility of the BR-2 reactor has been loaded with samples of C-steel, Hastelloy C4 and Ti/0.2 Pd under different conditions in interstitial claywater. A 1000 hours experimental run at a 10^3 gray/hour dose is foreseen to evaluate the radiation effect on corrosion rate and mechanism.

NOTE : The laboratory experiments which have preceeded the recently started in-situ experiments, and which were run for screening purposes of materials, continue to yield valuable results. These results are described in the elaborate yearly report, and not in this short overview report.

List of publications

1. Tas H., Debruyn W., Dresselaers J., Compatibility of candidate overpack materials with deep argillaceous HLW disposal environments, IAEA technical committee meeting on materials, Vienna, 2-5 September 1986.
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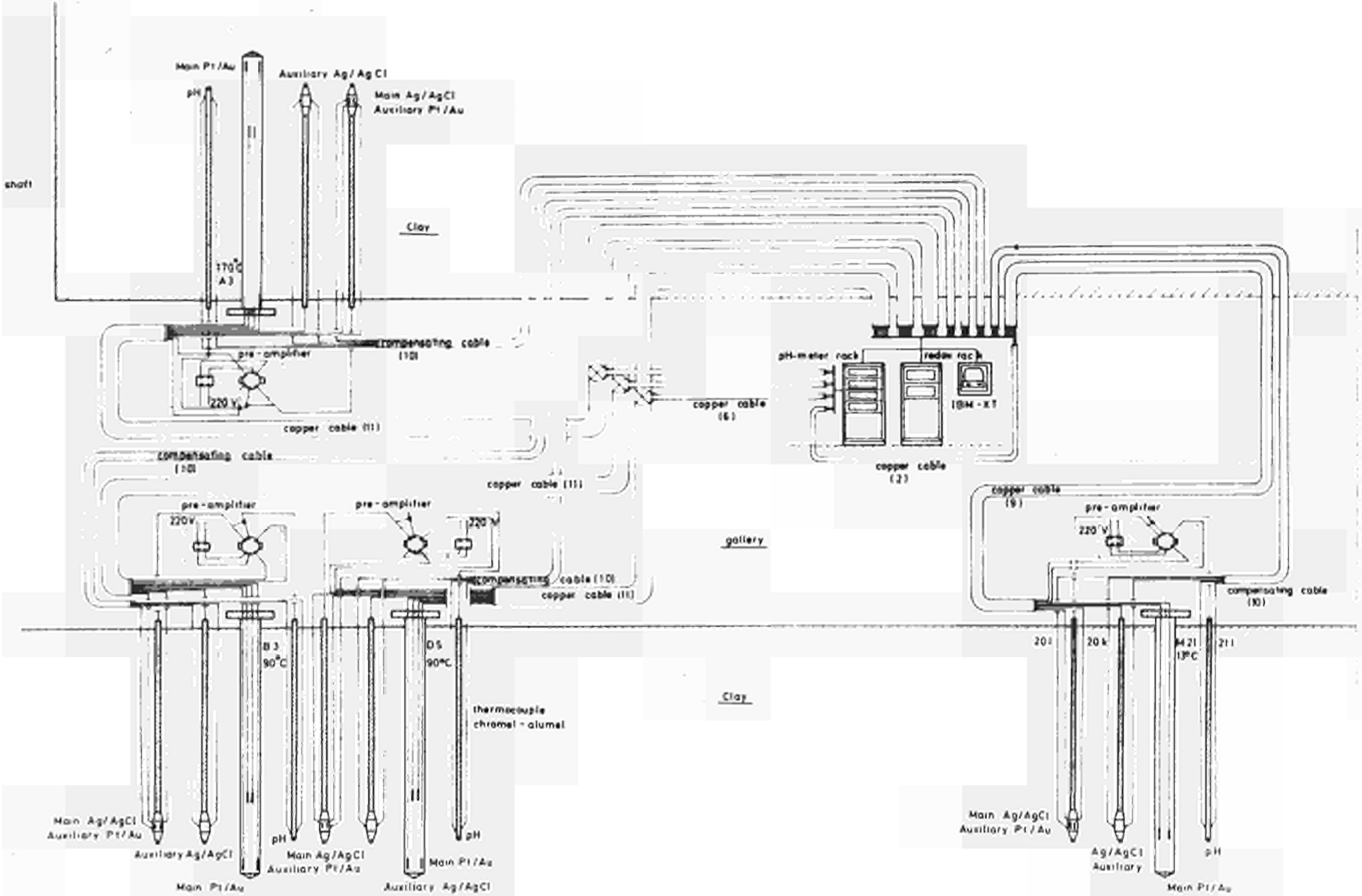
shaft
Main Pt/Au
pH
Auxiliary Ag/Ag Cl
Main Ag/AgCl
Auxiliary Pt/Au
Clay
170°C
A 3
compensating cable
(10)
pre-amplifier
220 V
copper cable (11)
copper cable
(6)
pH-meter rack
redox rack
IBM-XT
copper cable
(2)
compensating cable
(10)
copper cable (11)
pre-amplifier
220V
pre-amplifier
220 V
gallery
compensating cable (10)
copper cable (11)
copper cable
(9)
pre-amplifier
220 V
compensating cable
(10)
B 3
90°C
D 5
90°C
20 i
20 k
M 21
13°C
21 l
Clay
thermocouple
chromel - alumel
Main Ag/AgCl
Auxiliary Pt/Au
Auxiliary Ag/AgCl
Main Pt/Au
pH
Main Ag/AgCl
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Main Pt/Au
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pH
Main Ag/AgCl
Auxiliary Pt/Au
Ag/AgCl
Auxiliary
pH
Main Pt/Au

Near-Field Modelling in Cement Environments

Contractor: Harwell Laboratory, U.K.

Contract No.: FI1W/0090/2

Working Period: July 1986 - December 1986

Project Leader: Dr. P. W. Tasker

A. Objectives and Scope

The primary aim of this work is to develop research models which examine in detail the approximations and assumptions implicit in the assessment models that are used to analyse repository behaviour. The assessments models are necessarily relatively simple. They must make assumptions in many areas including the time evolution of the repository chemistry, the influence of corrosion products on local chemistry etc. The research models use data from experimental programmes to study these points in detail.

The near field has a complex chemistry which determines the solubility of radionuclides. This chemical environment changes both with time and spatially throughout the near-field region. The engineered barriers are very different chemically to the surrounding geology and so will not only degrade with time but may also cause a front of perturbed chemistry to progress into the surrounding regions. All these points involve the space and time evolution of chemistry but where they have been considered previously, the coupling between transport processes and chemistry have largely been neglected. Yet these processes underlie most of the assumptions in the simple near-field models. The conditions of primary interest to our programme concern the waste contained in a steel canister and buried in a concrete environment.

B. Work Programme

B.1 Development of the CHEQMATE computer program which couples chemical equilibria (via. the PHREEQE code) with ionic diffusion and electromigration.

B.2 Incorporation of ionic advection in flowing systems in the CHEQMATE code.

B.3 Incorporation of ionic activities in the transport part of CHEQMATE for applications beyond the dilute solution limit.

B.4 Application of CHEQMATE to coupled chemistry and transport problems relevant to the near field of a repository, for example the time and space distribution of the oxidation potential in the backfill pore water, the time and space distribution of the pH and the influence of intrusion of external chemistry on the near-field components.

C. Progress of Work and Obtained Results

State of Advancement

The first stage in the development of the CHEQMATE code is now complete (B.1). The present version combines one-dimensional ionic diffusion and electromigration with chemical equilibration via the PHREEQE program/1/. It also includes the dissolution and precipitation of minerals, and a facility to include electrochemical reactions. The program has been used to model the evolution of the oxidation potential of the backfill pore water in a repository under the influence of corroding embedded canisters (B.4). Sensitivity tests to the many physical and chemical parameters in this model have been performed.

Progress and Results

1. Development of CHEQMATE Code (B.1)

The computer program CHEQMATE (CHemical EQulibrium with Migration And Transport Equation) has many applications in modelling various changes in chemistry in the near field of a nuclear waste repository. The program combines ionic migration with chemical equilibration via the PHREEQE program/1/. The first stage in the development of CHEQMATE is now complete. The program iteratively couples one-dimensional ionic diffusion and electromigration with PHREEQE so that local chemical equilibrium is maintained as the transport processes evolve. CHEQMATE also includes automatic mineral accounting (solid phases are added or removed from the equilibrium as precipitation or dissolution occurs) and electrochemical reactions (using empirical data for reaction rates).

2. Prediction of Oxidation Potential within Near-Field of a Nuclear Waste Repository (B.4)

We have used CHEQMATE to model the evolution of the oxidation potential (Eh) in the backfill pore water under the influence of the corroding steel canisters. The oxidation potential is one of the most important chemical parameters affecting the release of radionuclides from the near field, for example the solubilities of some nuclides can differ by many orders of magnitude under different redox conditions. The model consists of a one-dimensional section of concrete backfill between two uniformly corroding canisters. The repository is assumed fully saturated and closed to the atmosphere. The section is discretised into 20 equal width cells for the purposes of the mathematical solving method. We assume that the pore water within the concrete section is initially saturated with oxygen and there is no external source, although we note that this assumption may not be valid if there is a significant groundwater flow through the repository. This oxygen is principally consumed by the canister corrosion reactions. In regions of the repository where oxygen is present, the oxidation potential in the pore water is controlled by the oxygen, but in areas where it has become depleted, such as in the vicinity of the canisters, the balance of oxidation states of other species will control the Eh. This model involves many physical and chemical input parameters so we consider a 'base case' set initially, which is the most realistic set we can estimate from available empirical data and from the predictions of other models. We have tested the sensitivity of the results to the parameters of most uncertainty. The main conclusions we may derive from this model are as follows:

1. For our base case, we predict that reducing conditions will be established throughout the repository in a period of approximately 100 years. Sensitivity analysis yields bounds of about 50-150 years. However, in all cases reducing conditions will be established at the canister surface within a very short period. This is extremely important to escaping radionuclides as this is the environment which will determine their solubilities. Corrosion of reinforcement and other oxygen getters in the repository could reduce the deaeration period further.

2. If we assume the system is truly in chemical equilibrium, and in particular that the kinetics of the hydrogen reaction are fast enough, then we predict that the oxidation potential in the repository is controlled by the aqueous hydrogen. The concentration of hydrogen in solution and the Eh will be determined by the partial pressure at which hydrogen gas forms. For the base case of bubbles forming when the partial pressure reaches 2 atmospheres (to account for the depth of the repository, assumed closed to the atmosphere), the Eh near the canisters is buffered at -0.73 V. It is unlikely that such a low oxidation potential would be realised in practice, suggesting the the oxidation kinetics are not fast enough to achieve equilibrium over these timescales. However, even if we artifically remove aqueous hydrogen in the model, thus ensuring that the Eh is dominated by the iron complexes, we still predict a highly reducing environment next to the canisters within a short timescale. Although the concentrations of the iron species near the canisters are maintained at fairly low levels by the solid corrosion products, they should still dominate the Eh over most of the radionuclides which may be released from the canister.

3. The reducing periods for the whole repository and the predicted oxidation potentials are relatively insensitive to the choice of solid corrosion products in our model or the rate of corrosion of the canisters chosen. However, these results are fairly dependent on the diffusion coefficients of the ionic species in the pores of the cement, which vary considerably with different mixes and grades of cement, different amounts of sorption of iron species and different rates of transport of oxygen.

This model not only provides a useful test of the CHEQMATE program but has also yielded much detail regarding the chemical conditions within the pore water and the sensitivity of our predictions to the many physical and chemical parameters of the system. The most important and robust predictions of the model are that reducing conditions are established quickly in the vicinity of the canisters (which will be important in keeping the solubilities of escaping nuclides low) and that aqueous hydrogen has a significant role in determining the precise Eh in the system.

References

/1/ Parkhurst, D. L., Thorstenson, D. C. and Plummer, L. N., U.S. Geological Survey, Water Resources Investigations, 80-96 (1985).

Nearfield behaviour of clay barriers and their interaction with concrete

Contractor : CEA, CEN Fontenay-aux-Roses
Contract n° : FI1W - 0031
Working period : May 1986 - December 1986
Project leader : R. ATABEK

A. Objectives and scope

In order to guarantee the safety of underground disposal, coming from spent fuel reprocessing, engineered barriers will be implemented as backfill materials in galeries and access shafts and as buffer materials between the host medium and the waste packages. One of the first requirements for engineered barriers is to minimize water and chemical species transfer. The materials being considered are essentially swelling clays, in particular calcium smectite clays coming from french deposits.

The long term stability of clay materials, as a function of temperature, water salinity and ionic species in solution, has to be evaluated for the different types of host rock (granite, clay and salt).

The final objective of the programme is to take into account material property modification with time in the choice and design of the engineered barriers used for both vitrified and T.R.U. waste disposal.

B. Work programme

B.1 Material choice and experimental condition definition
B.2 Vitrified waste disposal : definition and characterization of clay barriers
B.3 Vitrified waste disposal : temperature effect on clay material properties
B.4 Vitrified waste disposal : hydrothermal degradation of clay materials
B.5 T.R.U. waste disposal : study of concrete durability

C. Progress of work and obtained results

Summary

Samples coming from french clay deposits are under investigations to select one or two clay materials which may be used as constituents of engineered barriers. The reference scheme is vitrified waste disposal in granite. The criteria for good candidates are mainly : smectite content in the clay materials, carbonate and organic carbon content and bulk density of the material, compacted under a pressure of 100 MPa. Additional mineralogical analyses are now performed on two of the six selected materials to get a better knowledge of the layer homogeneity and of measurement dispersion. Preliminary results are obtained on compacted materials for permeability and diffusion coefficient determinations and swelling pressure measurements.

. B.1., B.2. are progressing normally

. B.3., B.4. samples and experimental devices are under preparation

. B.5. will start in 1988, as planed in the contract.

Progress and results

1. Material choice (B.1.)

Eighteen samples coming from fourteen french clay deposits, different in age and origine as reported on Figure 1, are involved in this work. These samples, of an average weight of 200 kg, are chosen in places where the average thickness and layer homogeneity allow industrial winning. In order to select two deposits for more precise investigations, careful analyses are undertaken which are mainly :

- Semi-quantative mineralogical analyses

  The amount of the three main components is obtained (a) by counting technique on smear slides for free silica (accuracy = 10%), (b) through a Bernard's calcimeter for carbonates and (c) X-ray diffraction for the clay fraction. In case (c), three diffractograms are made to get a quantitative evaluation of the different types of clay mineral (respectively on natural samples, glycolated samples and on samples heated during two hours at 490°C). As clear on Table I, the studied clay sediments are mainly constituted with smectites excepted samples 11 and 15 for which illite and palygorskite are the main constituents respectively. The total amount of clay minerals is always higher than 60%.
- Titration of organic carbon

  Carbon dioxide is titrated after organic carbon of the clay material is burnt under pure oxygen. The organic carbon content of the samples does not exceed 0.7% in weight.
- Exchange properties

  The exchange properties of clay materials are displayed through cation exchange capacity (C.E.C.) any specific area (S) measurements. The C.E.C. is determined on the entire material (a) by Metson's method which uses ammonium as saturation cation and sodium as extraction cation, (b) by using cobaltihexamine ion as saturation ion. This last technique when compared on Table II with Metson's method leads to larger C.E.C's as no extraction of fixed ions is necessary. Specific area obtained by measuring the amount of methylen blue absorbed by one gram of clay material is given in Table II. C.E.C. and specific area are correlated through the following linear relationship : $S = 6.96\ C.E.C + 70.9$.

- Atterberg's and shrinkage limits

  According to its water content (% in weight), the three states of a clay material are separated by the liquidity limit (w_L) and the plasticity limit(wp). The plasticity index (Ip) is defined by the relation : Ip = w_L - wp. The results of Table II show that the studied materials are very plastic (Ip > 17, following Atterberg's classification). The shrinkage limit (w_R) is also reported in Table II and corresponds to the water content under which the sample during drying undergoes only very small size variations.
- Compaction ability of clay materials

  The previous materials at their natural water content (20°C, air humidity = 60%) are then reduced to powder of various bulk density or of various granulometry distribution. Several mixtures of clay powders are compacted under isostatic or uniaxial pressure. It is observed that, for high pressure (> 60 MPa), the powder density has only a slight influence on the compacted material density ; but at low pressure, the powder density has to be optimized. For most of the samples, the bulk density of the pressed material is greater than 2.0, excepted for samples 5, 6, 7 and 2.

Parameters leading to the classification of Table III are (a) bulk density of the material under a pressure of 100 MPa (>2.0 Mg/m^3), (b) smectite content in the clay material (> 60%), (c) calcite content (< 10%) and (d) organic carbon content in the material (< 0.5%). Additional mineralogical analyses are now performed on two of the six selected materials, i.e. references 4 and 13.

2. Definition and characterization of clay barriers (B.2)

In the case of vitrified waste disposal in granite medium which is the french reference scheme, the buffer material being considered is highly compacted clay materials. The properties of the prepared material have to be determined as a function of parameters such as dry density (ρd) and water content of the material, pressure, temperature and salinity of water. The main properties to be measured are : hydration kinetic, permeability, water diffusion coefficient and swelling pressure. Preliminary results obtained at 20°C for reference 4a, using a permeameter, are :

- permeability coefficient (K in m/s) : K is between 10^{-15} and 10^{-14} m/s for a dry density of 2.0 and a hydraulic gradient of 10^5.
- water effective diffusion coefficient (De in m^2/s) : using tritiated water, a value of $2.10^{-11} m^2/s$ is found for the previous experimental conditions. It can be noticed that diffusion process leads to higher water flow than convection process.
- Swelling pressure : is given as a function of dry density (reference state : 105°C, 24 h in an oven) in Figures 2 and 3, for distilled and granitic water respectively. The highly compacted sample (see point 1 on the curves) is loosened to decrease its density. It can be noticed that a small decrease in material density induces a strong decrease of swelling pressure (by a factor of ~ 4). The swelling pressure measured with granitic water (32 MPa for ρd = 1.9) seems to be fairly the same as in the case of pure water (36 MPa).

Table I : Semi-quantitative mineralogical analyses
Percent of minerals based upon counting technique (silica), calcimetry ($CaCO_3$) and X-ray diffraction

(REF = references ; sm. = smectite ; Ill. = illite ; Kaol. = kaolinite ; I.S. = indiferenciated mixed-layers ; Paly. = Palygorskite ; tr = traces ; Goet. = goethite ; Felds. = Feldspars).

REF	FREE SILICA (%)	$CaCO_3$ (%)	CLAY MINERALS (%)					CLAY SUM. (%)	ASS. MINERALS
			Sm.	Ill.	Kaol.	I.S.	Paly.		
1	24	2	71	3	-	-	-	74	-
2	37	2	55	6	-	-	-	61	-
3	23	12	62	3	-	tr	-	65	-
4	28	2	70	-	tr	-	-	70	Goet.
5	38	1	55	6	-	tr	-	61	Felds.
6	18	1	73	4	4	tr	-	81	Opale
7	15	2	75	8	tr	tr	-	83	Felds.
8	7	2	87	4	-	-	-	91	-
9	22	2	68	4	4	-	-	76	-
10	20	7	55	10	4	4	-	73	-
11	7	1	-	69	18	5	-	92	Felds
12	16	2	62	16	4	tr	-	82	Felds
13	9	4	66	21	-	tr	-	87	Felds
14	23	17	45	9	tr	6	-	60	-
15	10	6	tr	tr	-	-	84	84	-
16	19	2	79	tr	-	-	-	79	-
17	13	13	37	18	15	4	-	74	Felds
18	25	10	44	10	10	tr	-	64	Felds

Table II : Exchange properties (C.E.C and Specific Area). Atterberg and shrinkage limits (% weight of water)

REF	C.E.C NH4/Na meq/100g *	C.E.C. $Co(NH3)_2$ meq/100g*	S m^2/g*	w_L %	wp %	Ip %	wR %
1	39	-	360	106	39	67	32
2	28	-	277	97	38	59	30
3	33	44	264	97	36	60	30
4	37	-	306	88	33	55	30
5	22	-	226	95	46	49	28
6	36	-	369	127	34	93	43
7	20	-	344	120	34	86	31
8	48	50	427	112	41	71	28
9	26	-	237	75	39	36	26
10	23	-	258	86	29	57	25
11	21	24	195	71	36	35	28
12	33	-	292	105	47	58	25
13	36	45	400	125	47	78	23
14	29	36	276	89	43	46	23
15	23	28	207	100	70	30	42
16	43	52	361	108	63	45	42
17	33	-	325	90	32	58	24
18	35	-	171	98	32	66	27

* Reference State : 105°C, 24 h in an oven

Table III: Choice of good candidates for engineered barriers (X meaning yes)

Ref.	Bulk density > 2.0 t/m³	Smectite content > 60%	Calcite content < 10%	Organic C content < 0.5%
14	X			
17	X			X
18	X			
3	X	X		X
5			X	X
2			X	
9	X	X	X	
10	X		X	
7	•	X	X	X
6		X	X	X
1	X	X	X	X
12	X	X	X	X
13	X	X	X	X
8	X	X	X	X
16	X	X	X	X
4	X	X	X	X

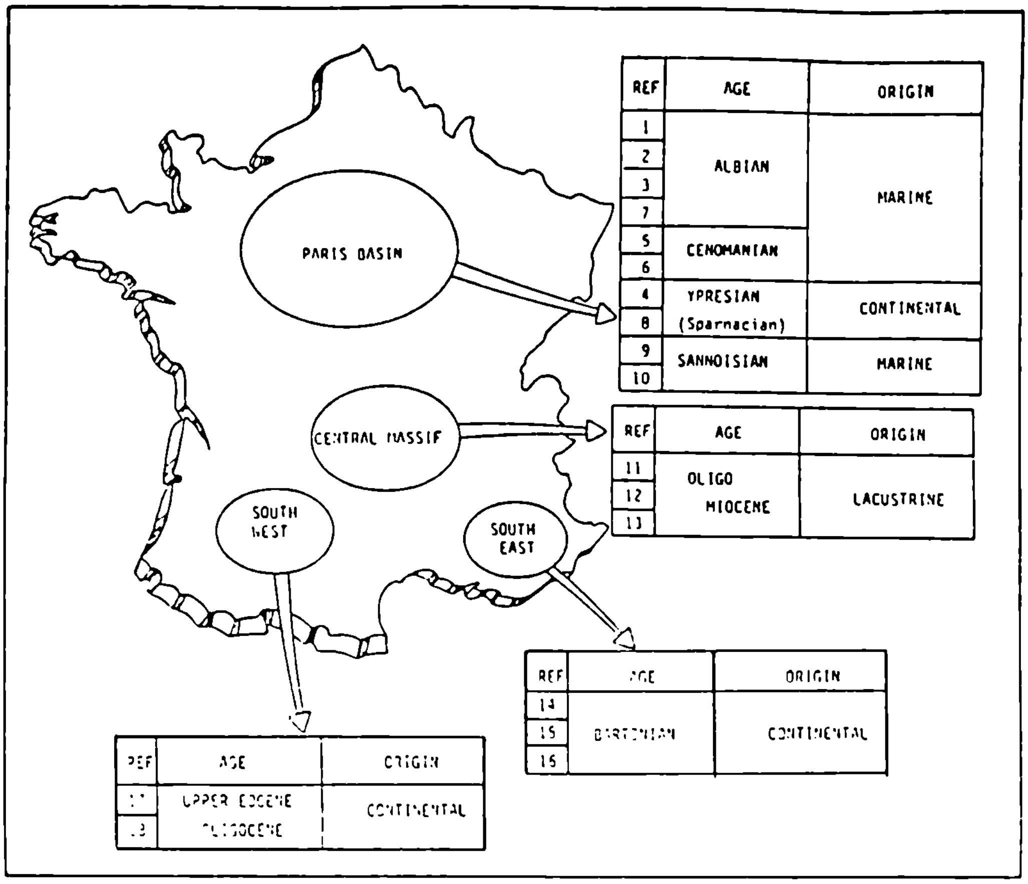


Figure 1 : Geographical and stratigraphical locations of clay deposits

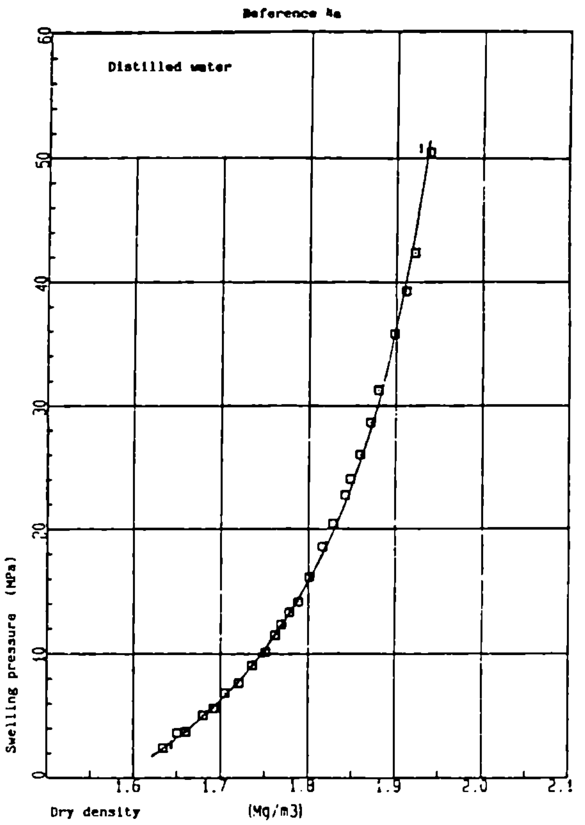


Figure 2 : Swelling pressure as a function of dry density (pure water)

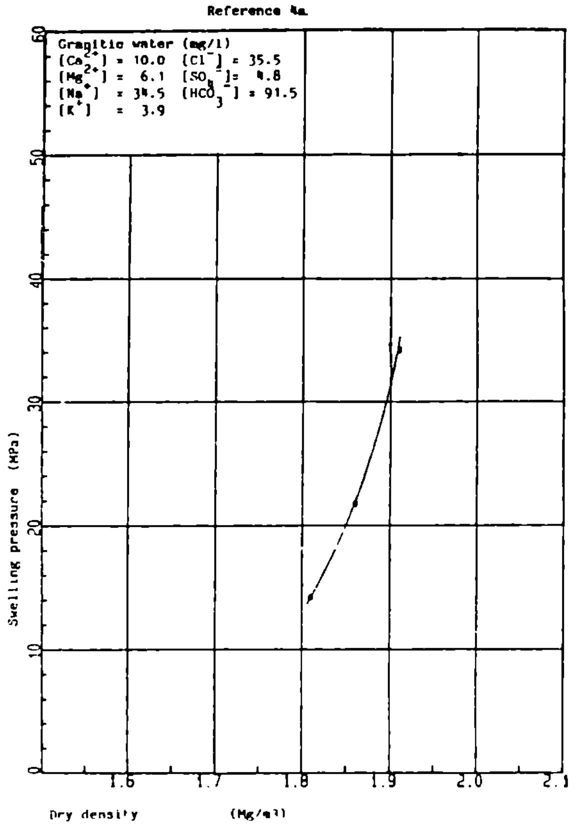


Figure 3 : Swelling pressure as a function of dry density (Granitic water)

CORROSION TESTING OF SELECTED CONTAINER MATERIALS FOR DISPOSAL OF HLW GLASS

Contractor: KfK, Karlsruhe, Federal Republic of Germany
Contract No.: FI1W/0032
Duration of contract: May 1986 - December 1989
Project leaders: E. Smailos, R. Köster

A. OBJECTIVES AND SCOPE

In order to quality corrosion resistant packaging materials for disposal of high-level waste forms in rock-salt formations, the corrosion behaviour of a number of materials has been investigated in salt brines (postulated accident conditions) under the preceding EC research task. The results of these studies have shown that unalloyed steels are a promising packaging material because they have exhibited so far a long-term corrosion behaviour (general corrosion, no pitting, crevice or stess-corrosion cracking) that can be calculated; moreover, it can be expected from their corrosion rates obtained so far in salt brines that the container wall-thickness will be acceptable under a corrosion allowance concept.

These are the goals of the project:

- Definition of the better suited steel (reference steel) for fabrication of a long-term resistant HLW packaging and the detailed description of the time and temperature behaviour of its corrosion in disposal relevant corrosion media with and without gamma radiation.
- Determination of the corrosion behaviour of Hastelloy C4 subjected to high gamma dose rates and under the in-situ conditions prevailing in the Asse salt mine. These are investigations performed in order to complete the results available now.

B. WORK PROGRAMME

2.1 Selective laboratory-scale corrosion studies on the three preselected steels, namely fine-grained steel, low-carbon steel, cast steel, with a view to selecting a reference steel.

2.1.1 Without gamma irradiation in moist rock salt (rock salt/rock salt brine and rock salt/Q-brine) at 90 °C and 170 °C.

2.1.2 With gamma irradiation (10^3 rad/h) at 90 °C in Q-brine.

2.2 More detailed laboratory-scale corrosion studies on reference steel subjected to various gamma dose rates (10^2 to 10^4 rad/h) in all three corrosion media enumerated under items 2.1.1 and 2.1.2.

2.3 Post-test examination of the steels stored in situ (material specimens, welded tube sections) for corrosion attacks at T = 35 °C and 200 °C, rock pressure and high gamma radiation (about 3×10^4 rad/h).

2.4.1 Laboratory-scale examinations of the influence of the gamma dose rate (10^2, 10^3, 10^4 rad/h) on corrosion of Hastelloy C4 in Q-brine at 90 °C.

2.4.2 Post-test examination of the material specimens and welded Hastelloy C4 tube sections stored in Asse for corrosion attacks. The testing conditions are similar to those under item 2.3.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The time and temperature behaviour of corrosion of the preselected steels fine-grained steel, low-carbon steel and cast steel was determined in moist rock salt at 90 °C and 170 °C. The corrosion media used were Asse rock salt/Asse rock-salt brine (almost exclusively NaCl) and Asse rock salt/Q-brine (rich in $MgCl_2$). The maximum testing period was 12 months. Besides, the irradiation experiments started on the influence exerted by various gamma dose rates (10^2 to 10^4 rad/h) on the corrosion behaviour of the steels mentioned before and of Hastelloy C4 in moist rock salt and in Q-brine at 90 °C. These experiments are performed in the fuel element storage pond of KFA Jülich. In addition to the laboratory- scale corrosion tests the in-situ corrosion experiments have been carried on with material specimens and welded tube sections made from unalloyed steels and Hastelloy C4 at two temperature levels (35 °C, 200 °C), rock pressure and high gamma dose rate (3×10^4 rad/h).

PROGRESS AND RESULTS

2.1.1 Corrosion studies on unalloyed steels in moist salt environments

The steels investigated had the following compositions (wt.%):

- Fine-grained steel: 0.17 C; 0.44 Si; 1.49 Mn; rest Fe.
- Low-carbon steel: 0.1 C; 0.27 Si; 0.66 Mn; rest Fe.
- Cast steel: 0.16 C; 0.61 Si; 1.51 Mn; rest Fe.

The corrosion media were the two-phase systems Asse rock salt/Asse rock-salt brine (almost only NaCl) and Asse rock salt/Q-brine (rich in $MgCl_2$). The most important constituents of the salt brines (g/l) were:

- Asse rock-salt brine: 136.7 Na^+; 1.48 K^+; 0.34 Mg^{2+}; 1.4 Ca^{2+}; 201.9 Cl^-; 5.19 SO_4^{2-}.
- Q-brine: 7.1 Na^+; 31.8 K^+; 91.9 Mg^{2+}; 297.3 Cl^-; 14.4 SO_4^{2-}.

The test temperatures were 90 °C and 170 °C; the test period was one year at the maximum. The ratio of specimen surface to volume of the brines was chosen to be $S/V = 100\ m^{-1}$ and the mass ratio of rock salt to solution 10:1 in each case. The latter gave an H_2O-content of the rock salt of about 6.4 wt.%.

The corrosion results obtained on the three steels after the maximum test period in the media have been indicated in Tables 1 and 2. They can be summarised as follows:

- In the two-phase corrosion media Asse rock salt/Asse rock-salt brine and Asse rock salt/Q-brine the steels exhibited non-uniform general corrosion with shallow pit formation. Deep pitting corrosion or crevice corrosion in the sense of an active/passive corrosion element which would put in doubt using steels as a container material have not been found in these studies. This means that the long-term corrosion behaviour of the steels in these media as well as in salt brines can be estimated.
- The corrosion rates of steels in Asse rock salt/Asse rock-salt brine and in Asse rock salt/Q-brine differed from each other by not more than about 40%, except for the corrosion rate of cast steel in Asse rock salt/Q-brine at 170 °C. In the latter case the corrosion rate was approximately twice that for the two hot-rolled steels, fine-grained steel and low-carbon steel.
- As had been expected, additions of $MgCl_2$-rich Q-brine in rock salt increased the corrosion rate of steels compared with NaCl brine. Under

the selected testing conditions the maximum penetration rates of shallow pit formation in Asse rock salt/Q-brine (60 to 70 µm/a at 90 °C and 170 to 300 µm/a at 170 °C, respectively) were higher by about the factor 1.5 to 2.0 than in the Asse rock-salt/Asse rock salt brine (40 to 50 µm/a at 90 °C and 120 to 150 µm/a at 170 °C, respectively).

- Compared with the corrosion rates determined in earlier investigations for the steels in NaCl-brine and Q-brine at 170 °C the corresponding values in Asse rock-salt/Asse rock-salt brine and in Asse rock-salt/Q-brine are higher by about the factor 2 at the maximum.

  For comparable corrosion rates of the steels in salt brines and in rock salt/salt brines, respectively, the fine-grained steel was selected as the reference material for an HLW packaging on account of its better weldability and higher strength. According to the results available the corrosion rates of this steel in Q-brine (most aggressive salt brine) and in rock salt/salt brines of about 40 to 70 µm/a at 90 °C and 120 to 170 µm/a at 170 °C, respectively, lead for container service lives of, e.g., 300 years to corrosion allowances on the order of 25 to 50 mm. These values are relatively low compared to the estimated container wall-thickness of about 100 mm as a mechanical protection against the rock pressure of 40 MPa at the maximum at 800 m depth.

2.1.2, 2.2, 2.4.1 INVESTIGATIONS INTO THE INFLUENCE OF GAMMA RADIATION ON THE CORROSION BEHAVIOUR OF UNALLOYED STEELS AND HASTELLOY C4

In the irradiation experiments the corrosion behaviour is studied of welded (TIG-welding, EB-welding) and unwelded specimens made of fine-grained steel, low-carbon steel, cast steel and Hastelloy C4 in moist rock salt and in Q-brine at 90 °C and exposed to gamma dose rates of 10^2, 10^3 and 10^4 rad/h. All material specimens are examined for general corrosion, local corrosion and stress-corrosion cracking; the maximum testing period is 12 months. The irradiation experiments are performed in the fuel-element storage facility of KFA Jülich; the radiation source are irradiated fuel elements. During the period of reporting the necessary test equipment was installed and the first specimens are presently subjected to post-examinations for possible corrosion attacks after a period of two months.

2.3, 2.4.2 IN SITU CORROSION EXPERIMENTS ON UNALLOYED STEELS AND HASTELLOY C4 IN THE ASSE SALT MINE

In the in-situ experiments conducted in the Asse salt-mine the corrosion behaviour of base material as well as of welded specimens and tubes is investigated under the conditions prevailing in the rock salt. Within the framework of the in-situ corrosion tests the following investigations are being performed:

- Investigation of base material and welded specimens (sheets) in loose rock salt (salt drilling dust) at rock temperature of about 35 °C (reference experiment). The testing period is one to three years.
- Investigation of specimens in the German/US Brine Migration Test Field in 5 m deep boreholes at 210 °C, at an anticipated rock pressure of about 30 MN/m^2, and a gamma dose rate (Co-60 source) of 3.4×10^4 rad/h. In this experiment brine migration as well as the formation of gas due to corrosion and radiolysis are being measured continuously.
- Examination of tubes with a simulated container closing technique by electron beam welding in 2 m deep boreholes drilled into rock salt at 170 °C and at the rock pressure resulting from convergence. The testing period is one to three years.

During the period of reporting the specimens stored in the Brine Migration Test Field have been withdrawn after two years of storing and the post-test examination for possible corrosion attacks has started.

TABLE I: GENERAL CORROSION RATES AND PENETRATION RATES OF SHALLOW PIT FORMATION OF UNALLOYED STEELS IN ASSE ROCK SALT/ASSE ROCK SALT BRINE

MATERIAL	TEMPERATURE (°C)	TIME (d)	GENERAL CORROSION RATE[1] (µm/a)	MAXIMUM PENETRATION RATE[2] (µm/a)
FINE GRAINED STEEL	90	370	13	40
	170	370	33	120
LOW CARBON STEEL	90	370	10	40
	170	370	23	140
CAST STEEL	90	370	13	30
	170	370	26	150

[1] average values of 3-6 specimens; calculated from weight losses.

[2] calculated from measured pit depths.

TABLE II: GENERAL CORROSION RATES AND PENETRATION RATES OF SHALLOW PIT FORMATION OF UNALLOYED STEELS IN ASSE ROCK SALT/Q-BRINE

MATERIAL	TEMPERATURE (°C)	TIME (d)	GENERAL CORROSION RATE[1] (µm/a)	MAXIMUM PENETRATION RATE[2] (µm/a)
FINE GRAINED STEEL	90	183	50	70
	170	370	150	170
LOW CARBON STEEL	90	370	45	70
	170	370	100	200
CAST STEEL	90	183	40	60
	170	370	240	300

[1] average values of 3-6 specimens; calculated from weight losses.

[2] calculated from measured pit depths.

CORROSION OF CARBON STEEL OVERPACKS FOR THE GEOLOGICAL DISPOSAL OF RADIOACTIVE WASTE

Contractor:	UKAEA, Harwell, UK
Contract No:	FI 1W/0034
Working Period:	September 1986 - December 1986
Project Leader:	Dr G P Marsh

A. Objectives and Scope

The programme is aimed at completing the assessment of the long term corrosion of carbon steel overpacks in granite or clay type formations. It is intended to complete the development of a model for localised corrosion and to test the validity of this model together with a previously developed model for general corrosion, through long term immersion tests.

The programme will yield generic models for general and localised corrosion which may be applied to evaluate overpack life, or the metal thickness needed to achieve a specific life, in granitic or clay disposal sites.

B. Work Programme

B.1. Continuation of existing long term tests to evaluate the previously developed model of general corrosion.

B.2. The continuation and extension of long term tests to evaluate the localised corrosion model.

B.3. Completion of the development of a mathematical model for localised corrosion.

C. Progress of Work and Obtained Results

State of Advancement

Long term tests to measure general and localised corrosion in carbon steel, and to evaluate the predictions of mathematical models developed for both forms of corrosion, are continuing. Additional tests are being set up using specimens prepared from the reference 0.1% carbon steel supplied by the Commission. These include long term immersion tests, in synthetic granitic groundwater under granite and bentonite backfills, as well as pit growth measurements using small and large area specimens. Development of an improved mathematical model for localised corrosion is continuing and will be supported in due course by further experimental work to generate relevant electrochemical kinetic data.

B.1., B.2. and B.3. are progressing normally.

Progress and Results

1. Long Term Tests (B.1.)

A series of long term immersion tests with carbon steel specimens embedded in granite and bentonite saturated with granite groundwater have been in progress for about 3½ to 4 years. Rest potentials of selected coupons are being measured continuously, and their corrosion rates monitored periodically by the polarisation resistance (R_p) method. It is planned to continue the tests for a further 12-18 months before dismantling and evaluating the corrosion by weight loss and visual examination, and measuring the migration distance of corrosion products into the backfill. These data will be used to check the validity of the mathematical model for predicting long term general corrosion.

Additional tests are in process of being set up with specimens prepared from the Commission's reference carbon steel.

2. Pit Growth Measurements (B.2.)

Measurements of pit growth rates had reached test periods up to 10,000 hours when the 1980-84 programme ended. These tests are now being extended to longer exposure periods so that a more accurate empirical relationship can be established relating maximum pit depth with exposure time. One group of tests has been underway for 19 months and will be dismantled in May 1987 after 2 years exposure. Another similar group will be examined after a total exposure time of 3 years. Similar tests have been started with the Commission's reference steel using specimens with the same surface area as before and also with larger area (x30) specimens to test the validity of the extreme value statistical method for extrapolating the results of small specimen tests to much larger area containers.

3. Localised Corrosion Model (B.3.)

The development of a mathematical model for the propagation of localised corrosion also was begun in the previous DoE/CEC programme. This "steady state" model gave reasonable predictions of the solution chemistry within localised corrosion sites but over-estimated the rate of propagation. This problem is considered to be due to inadequacies in the electrochemical input data, because the model considered steady rather than moving boundary conditions and because blocking by corrosion products was neglected by the model. The new programme is aimed at developing an improved model by addressing these uncertainties. This will be supported by experimental work designed to generate relevant electrochemical kinetic data.

List of Publications

"An assessment of carbon steel overpacks for radioactive waste disposal" was given by K J Taylor to the Sixth AECL/EURATOM meeting, Brussels, October 9-10, 1986.

d) Development of tests for quality control and quality inspection purposes

Quality assurance : procedures - standardization

Contractor : CEA - CEN-CADARACHE - FR
Contract N° : F 11 W/0095/1 Task 3
Working period : December 86 - December 90
Project leader : A. SAAS
Executant : A. SAAS

A. Objective and scope

Three objectives are carried out :

- définition of general principles for initial radioactivity measurements,
- etablishment of procedures for homogeneous wastes,
- examination of differents possibilities for measurement the isotopes diffusion in heterogeneous wastes.

B. Work programme

B1. General principles for measurement of initial activity.

B2. Procedures for measurement of initial activity in embedded wastes (polymers, cement, bitument).

B3. Procedures for heterogeneous wastes.

C. Progress of work and obtained results

Summary

General principles for measurement initial radioactivity and homogeneity of this activity in embedded wastes are undertaken.

Generaly, two different specifications exist :

- limit of acceptability (for α emitters),
- maximum permissible activity (for β-γ emitters).

In the case of the homogeneity, this caracteristic is needed for homogeneous wastes. Normaly, the safety authority edict the specifications for this parameter.

The results concerning the cases are :

- procedures for each matrix are necessary,
- list of parameters must defined.

The part B1 is finished.

List of publications :

General principles for determination of initial radioactivity for embedded wastes (project for CEC contrat - progress report).

Evaluation of non-destructive methods for quality-checking of vitrified HLW

Contractor:	UKAEA - Harwell Laboratory
Contract No:	FI1W/0036
Duration of contract:	2 years
Project Leader:	J. Farren

A. OBJECTIVES AND SCOPE

The aim of the programme will be to evaluate the use of on-line non-destructive methods, based on x-ray absorptiometry and γ-spectroscopy coupled with advanced data processing techniques, for the quality checking and/or characterisation of vitrified HLW. Particular emphasis will be placed on developing and demonstrating techniques that will be applicable to fully active glass samples. A cylindrical container of active vitrified waste produced by the Fingal process is available for this work.

Resulting from the proposed programme, we intend to demonstrate firstly the use of γ-emission measurements for determining the content and distribution of γ-emitting isotopes within a highly active sample container and secondly the use of X-ray absorptiometry for measuring the loading of active glass. On completion we aim to have sufficient information to enable the design of a plant instrument to be undertaken.

It is intended that Harwell collaborates with BAM in the exchange of data processing expertise and hardware developments, particularly with respect to detection systems.

B. WORK PROGRAMME

Task 1	Construction of the facility to enable γ-emission and x-ray absorption measurements to be carried out on highly radioactive samples, particularly the Fingal glass container.
Task 2	Adaption and improvement of computer algorithms required for the application of γ-emission tomography to the sample.
Task 3	Construction of an inactive simulant sample containing cavities to permit the introduction of sealed γ-sources.
Task 4	Use the inactive simulant sample to test the mechanical handling aspects of the equipment.
Task 5	With the inactive sample loaded with sealed sources; test the measurement and data processing parts of the γ-emission system.
Task 6	Carry out x-ray absorptiometry on the inactive sample.
Tasks 7/8	Repeat the emission and absorption measurements, respectively, on the active glass.
Task 9	Apply the equipment development for Fingal glass sample to small (1 litre) samples of cemented intermediate level waste available at Harwell.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Statement of advancement

Measurement of the highly radioactive waste glass sample has required the design of a specific item of apparatus to allow the measurements required for tomography to be undertaken safely. The design of the mechanical apparatus is complete and has been given provisional safety clearance. Approval for manufacture is being obtained, and construction is expected to commence early in the New Year. In preparation for the availability of the apparatus, software simulations have been undertaken. These confirm that cracks of 0.5 mm should be readily detectable and voids of 1 mm detected. Preparation of the inactive specimen has commenced.

Tasks 1, 2 and 3 are progressing satisfactorily. The other tasks are mainly dependant on these.

However, the opportunity has been taken to make x-ray absorption measurements on some samples of fully active vitrified waste that became available as a result of another project.

Progress and results

Task 1 - Construction of facility

The concept of the measuring device is that the glass cylinder is lowered from its transport flask, through a measurement collar, into a storage hole. The mechanism for this task has been designed and is shown schematically in Figure 1. It consists of the transport flask support frame with two tracks. The tracks can either hold detectors for emission tomography, or a source and detector for transmission tomography. The apparatus is heavily shielded. The system is interlocked to prevent exposure of the active sample inadvertently and it has been assessed by Safety Secretariat and Health Physics staff at Harwell. An additional framework, not shown in Figure 1, allows the system to be used for inactive samples without the need for the transport flask. Production of the apparatus is being arranged.

Task 2 - Computer algorithms

Simulation of the experimental arrangements is being undertaken to determine the most suitable conditions for data acquisition. So far the work has only been with transmission measurements on the simulation of cracks and voids. Reconstructions over 45, 60, 90 and 180 degrees on cracks and voids of 0.5, 1, 2 and 4 mm show that cracks and voids can be determined in all cases, but it is unlikely that the smallest voids will be discernible with real data. The images produced do contain artifacts and some studies on anti-aliasing techniques are being undertaken to try and eliminate these effects, as they may hinder the interpretation of results.

Task 3 - Inactive glass simulant

An existing inactive sample of the Fingal glass exists and currently is undergoing some minor engineering to make the fittings equivalent to the active specimen to allow it to be used as a test piece for the apparatus. Once this sample has been used to test the storage hole contamination shield, it will be modified to allow the inclusion of sealed sources.

Task 8 - X-ray absorptiometry of active glass

Vitrified waste samples with compositions identical to that typical of MAGNOX and THORP high-level waste became available for measurement. Three types of glass had been made, all based on the same precursor glass (designated MW):

Type 1 - MW + MAGNOX H.L. WASTE
Type 2 - MW + THORP H.L. WASTE
Type 3 - MW + THORP H.L. WASTE + ALUMINIUM OXIDE

Each type contains approximately 25 wt. % of calcine (including the Al_2O_3 in Type 3 glass).

The THORP calcine contains gadolinium, as a result of its use as a poison in the dissolver. The gadolinium concentration in the glass corresponds to a concentration of 3 g/l in the dissolver solution. For each of the three types of glass, two rectangular blocks with square cross-section, dimensions approximately 10 x 4 x 4 mm and 3 x 4 x 4 mm, were cut and welded into close fitting cylindrical stainless steel containers so as to give path lengths of 10 and 3 mm along the cylindrical axes. Measurements were carried out with the samples placed in a specially designed containment pot that minimised the external radiation.

To summarise, the main points learned from this exercise were:

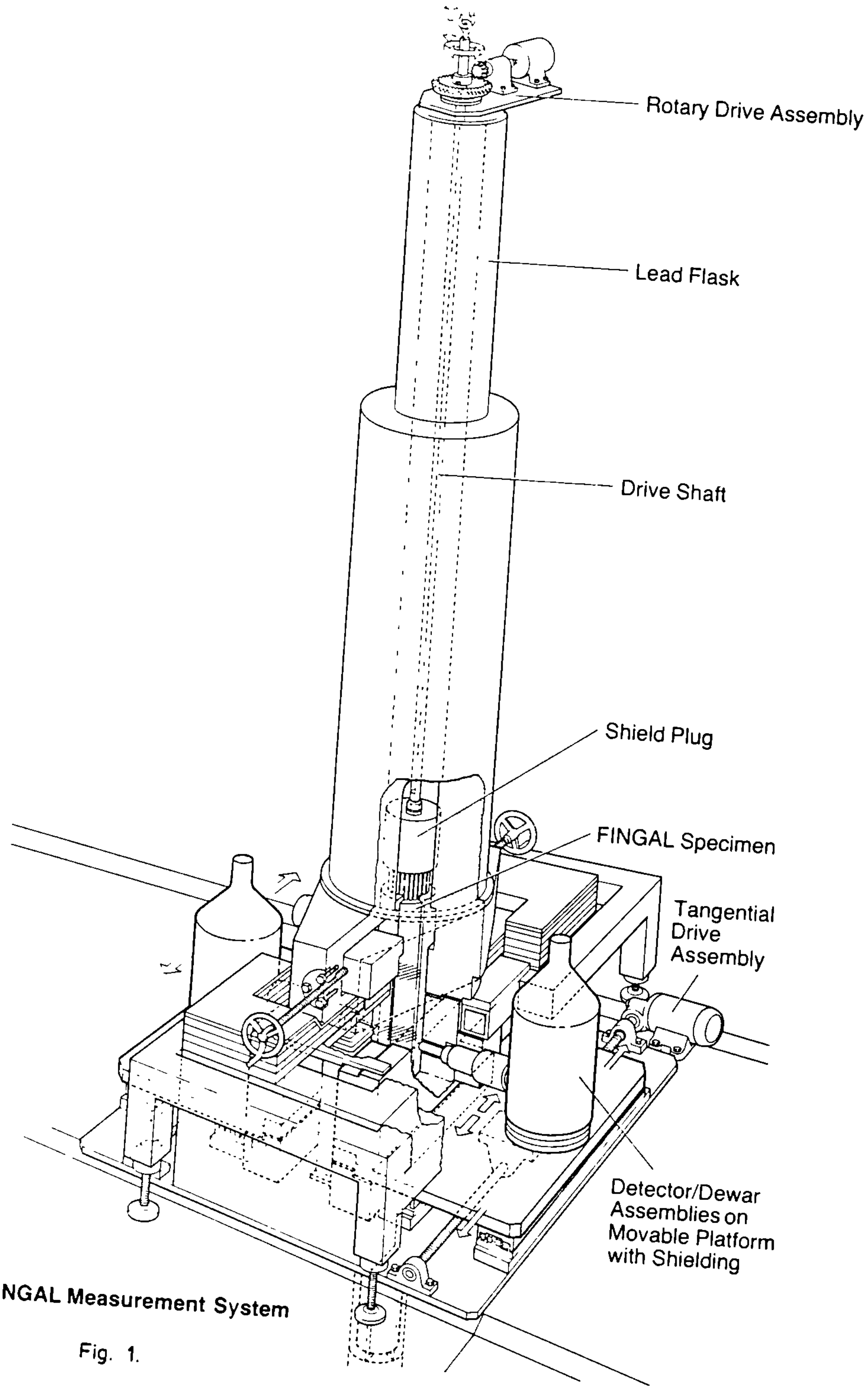
(1) In all cases the sample activity had a negligible effect on the x-ray absorptiometric measurements.

(2) The mass absorption coefficient of the MAGNOX specimens agrees well with that calculated from the known loading.

(3) The mass absorption coefficients of the THORP glass containing gadolinium is approximately 2.3 times greater than that of the MAGNOX glasses.

(4) For the shorter pathlength samples (~ 3 mm) the K-absorption edge of gadolinium was clearly visible, thus permitting a quantitative estimation of this element if required.

Arrangements are in hand for Dr. A. Kettschau of BAM to work at Harwell over the Summer of 1987. This will greatly advance the collaboration between Harwell and BAM.



FINGAL Measurement System

Fig. 1.

STUDY OF A NON DESTRUCTIVE TESTING METHOD FOR PACKED RADIOACTIVE WASTE CONTAINERS

Contractor : CEA, CEN-Cadarache, France
Contract N° FI 1W/0038
Duration of contract : from 1 May, 1986 to 30 April, 1988
Project leader : J.F. MONTIGON

A. Objectives and scope

A high energy computerized tomodensitometer is developed in order to test the physical homogeneity of radwaste packages, in a range spreading from 200 liter drums to 2 m³ concrete shells.

Special studies are required to design such a machine ; in 1985, a feasibility study gave the preliminary design of the system.

Further development of components is then needed and the realization of the machine will be split in two steps, the first leading to an intermediate configuration (Figures 1 and 2).

The objective of this programme is to start operation on intermediate system's configuration by the end of 1988.

B. Work programme

B.1. Optimization of the X ray source : beam energy, dose rate, pulses frequency.
B.2. Design of the detector system : optimization of the BGO crystals dimensions.
B.3. Design of the mechanics.
B.4. Chosing the mechanics controller and writing its dedicated software.
B.5. Interfacing the data acquisition precessor and writing its software.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The new series of experiments on a 10 MV accelerator, needed to achieve B1 and B2, has been delayed from October 1986 to March 1987.

The other items (B3 , B4 and B5) are progressing as scheduled.

Progress and results

1. Experiments on high energy detection (B1 - B2)

The experiments made in 1985 showed that the X ray source had to be and accelerator with a beam energy of about 12 MeV (electrons), and that an optimum had to be found about both the energy of the beam , the dose rate and the frequency of the pulses (B1).

On the other hand, the detector material had been chosen in 1985 (BGO) but it remained to test several BGO crystals to determine the influence of their shape on detection efficiency. (B2)

Further experiments were then planned but their preparation took a very long time and some essential equipment was delivered late, so they are now scheduled in March 1987.

Fully automatic sequences of data acquisition for computerized tomography will be performed on a 200 liter drum filled with concrete (600 mm thick) with a 10 Mev - accelerator. The tomogram will be computed afterwards by a VAX 780.

2. System mechanics (B3 - B4)

The mechanics design is completed (B3). The mechanics controller's type has been chosen and its software is being currently written.

3. Data acquisition precessor (B5)

The acquisition controller that had been previously chosen (a DEC "LSI 11") has been replaced by a mini computer (a DEC "Micro VAX 2") in order to give more calculation power to this item.

This "Micro VAX 2" had then to be turned into an acquisition controller through fitting it with special interfaces for the measurement channels. These interfaces are being currently designed and the acquisition software will be written in 1987.

FIGURE 1 :
FINAL CONFIGURATION
OF TOMODENSITOMETER

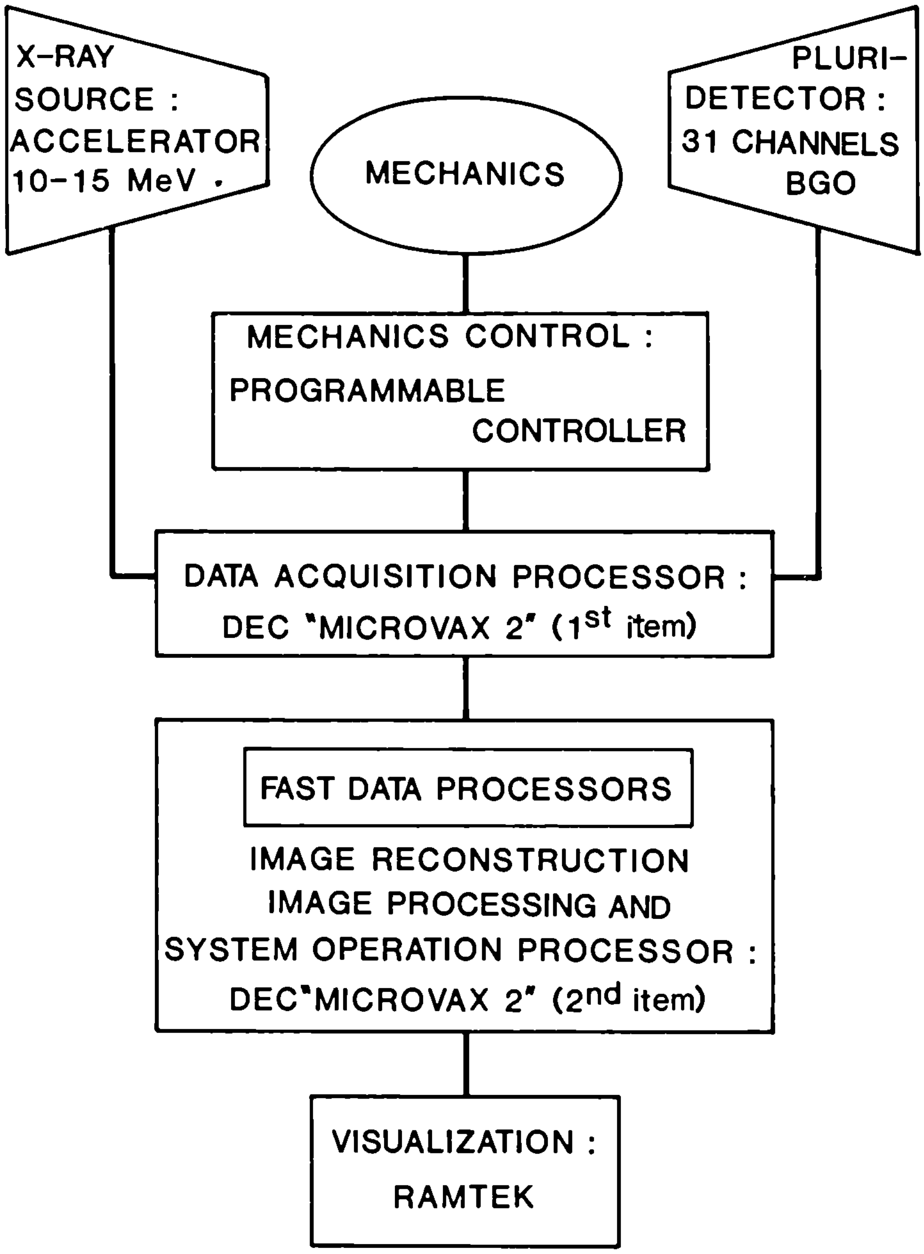
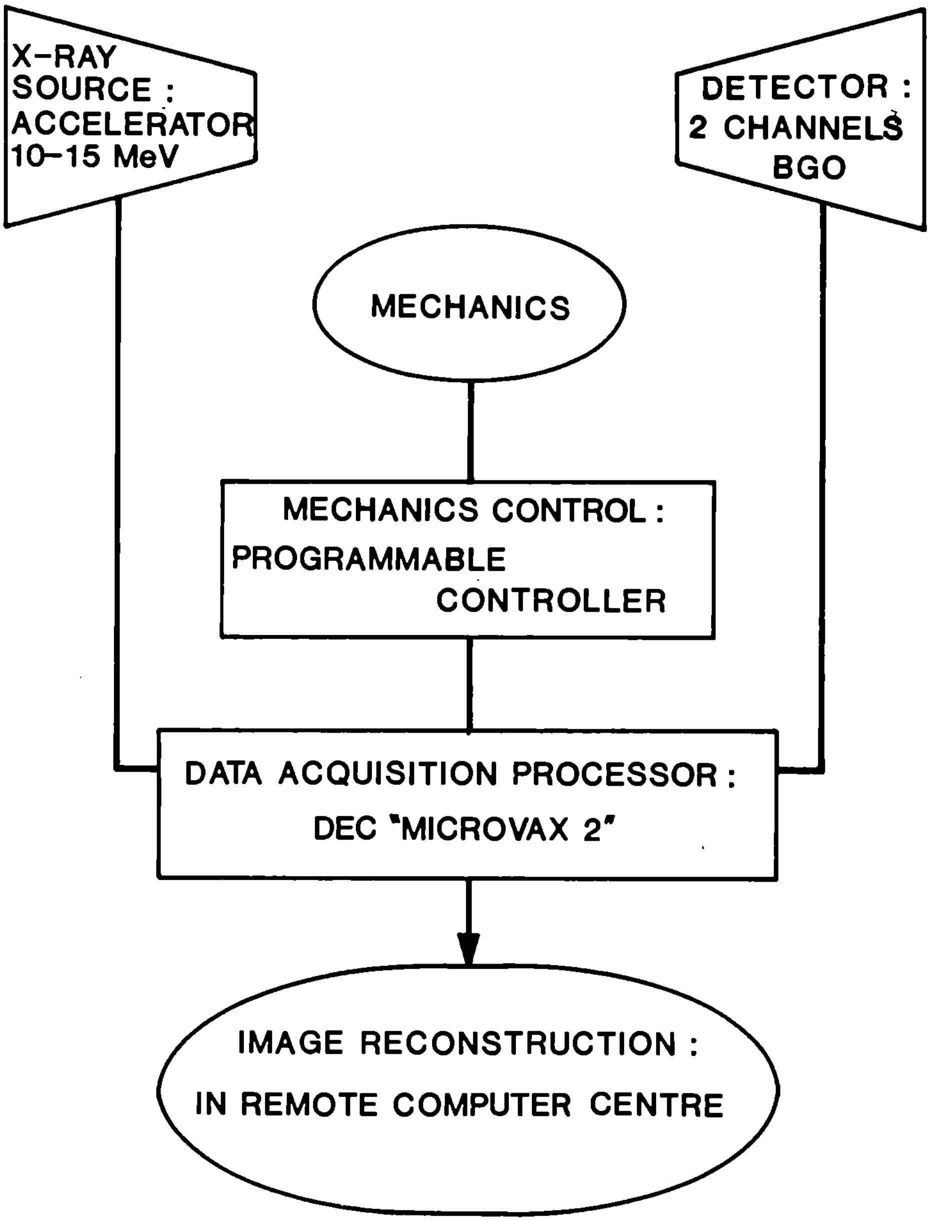


FIGURE 2 :
INTERMEDIATE CONFIGURATION
OF TOMODENSITOMETER



Quality Assurance of Radioactive Waste Packages by Computerized Tomography

Contractor: BAM, Berlin, Germany
Contract No: FI1W/0037
Working Period: August 1986 - July 1988
Project Leader: P. Reimers

A. Objectives and scope

According to task 3 "Testing and Evaluation of Conditioned Waste and Technical Barriers" quality assurance is a main scope of research concerned with the handling of radioactive waste. It'is provided to characterize medium and high active waste by standard test methods which are to be developed and experienced in this contract. Quality evaluation of radioactive waste packages is preferentially done by nondestructive testing methods.

Our proposal is mainly concerned with the elaboration of specific testing methods for ready conditioned waste packages as well as the matrix materials themthelves (e.g. bitumen, concrete, ceramics and glass). CT with X-rays is one of the best methods for the comprehensive nondestructive characterization of the physical and technical properties of the above described test objects. The method is especially suitable for the nondestructive evaluation of the absolute density value, of the density distribution, of the gamma activity distribution, of the localization of voids, cracks and inclusions, of the visiualization of swelling, shrinking and phase precipitations, as well as the detection of liquid phases in bentonite and cemented waste. Also the corrosion attack of metallic waste containers can be studied which is particularly important for the quality assurance of waste packages during the unavoidable intermediate storage period of some decenniums.

During the last years not only technical problems had to be solved but also social ones like the acceptance of nuclear technology by the public became more and more severe. Therefore public agencies as well as nuclear industry must work steadily to assure citizens and state officials that forthcoming operations at any new nuclear facility including the transport, delivery and intermediate or permanent storage of nuclear waste will be carried out with public safety and environmental preservation in mind.

The proposed inspection system allows the advance screening of a wide variety of radioactive waste packages. Until now, much of the waste material mainly of the LLW and MLW type has been produced without precise inventory documentation. In West Germany alone about 100.000 200 l drums must be screened before sending them to the final burial ground "Zeche Konrad".

The internal concrete shielding of such 200 l drums has been revealed as inhomogeneous and cracky (Fig. 1) by early CT investigations./1/

A test system like the proposed one is not only very suitable for the study of the macro structure (> 0,2 mm) of the waste matrix and the tightness of the containment but might also be able to put all anxieties to rest which arise from increased transport risk or unknown radioactive content of closed waste packages.

B. Work programme

B.1 Literature survey for high energy radiography and CT applications for waste assay
B.2 Specification of a suitable detector system for Linac radiation
B.3 Development, construction and test of a single detector
B.4 Acquisition and test of a multidetector system
B.5 Simulationprogram for ECT
B.6 Choice and collection of real waste packages
B.7 Preliminary investigations on those packages

C. Progress of work and obtained results
Summary

C. Progress and results

1. Literature survey (B.1)

The aim of the literature survey was to find out other CT-applications for radioactive waste inspection and the most effective detection method of the shortly pulsed Linac radiation. In most of the high-energy-radiography applications reported until now image detection was performed by film. The problem is to find a detector with a dynamic range of better than 1 : 10^4 as is necessary when examining concrete with a thickness of more than 100 cm and a good efficiency for µsec - pulses of high-energy radiation (1 - 25 MeV).

The following publications were guessed to be most important for our work:

1.1) In December 1985 Nuclear News reports /2/ on a mobile system to assay LLW - 208 litre drums. The system was ordered by DOE for advance screening of LLW-waste containers and was developed by LANL. It is a mobile waste assay unit made up of two self-contained transportable rooms able to fit on flat bed trailers. The system is specifically aimed at wastes stored in metallic 208-litre drums. One of the two rooms includes a rotatable platform where a drum is placed and equipment can scan the drum three-dimensionally with X-rays. So, potential hazards-deteriorations in the packaging, contents that may be caustic or volatile - are brought to light so that corrective actions or precautions can be taken before the drum is sent to the final burial ground or put into a multi-drum container as will be demanded in Germany. Each image (= digital radiograph) can be preserved on a video recorder, so a permanent record can be kept of each scanned drum. Additionally the radioactive gamma emitting isotopes in the drum can be identified and their concentrations determined. The potential benefit of the new system goes beyond identifying and securing shipments of radioactive waste packages. In the past instruments did not exist for the detailed assay of LLW-waste and sometimes it was simpler just to assume that all waste from a particular job or facility was radioactiv. The new system could be used to reexamine the drums and determine if some of them can in fact be disposed as non-radioactive waste with special precautions. In this short report no technical details on the X-ray source, detector system etc. are given. However, it must be concluded that the general idea of the contractors is identical to the BAM-CT-system which works since 1983 and is now to be extended to higher penetration depths (= X-raying concrete packages up to 1 m thick).

1.2 As early as 1982 American Science and Engineering Inc. (AS & E) designed and built a breadboard system as a capability demonstration model for high-energy-CT (HECT)/3/. The key components of the system are: a precision turn table that rests on a precision translation stage being the sample support for a maximum sample diameter of 2 m. The X-ray source, a Varian Linatron L 6000, is located on one side of the motion system. The detectors gather data on the other side. Pre- and post-collimators minimize extraneous X-ray flux that does not contribute to the signal. A detector array is located at the end of the post-collimator. The prototype system uses five detectors. The detector design is reported to be crucial to the quality of the final image: each detector consists of a low afterglow scintillator crystal that is optically coupled to a photosensitive diode. The output current of each diode is routed to an amplifier that is sampled once for each Linac pulse and immediately stored in a computer memory. Crystal width is determined by the geometric resolution required. The limit of crystal height and length is governed by consideration of cross talk between adjacent detectors, although this can be mitigated by judicious use of interdetector shielding. Pre- and post-collimators are reported to be essential to reject scattered radiation an important contributor to image degradation. No technical details are given about scintillator material or amplifier design. The detectability of cracks, separations and delaminations was at least as good as predicted. In a CT-reconstruction of a phantom with a 1024 x 1024 pixel matrix cracks as small as 0,08 mm were visible. The density resolution was better than 1 % over volumens as small as 3.1 cm^3.

1.3) In March 1986 a feasibility study on high energy tomography for radioactive waste examination was finished by CEA SEDFMA - Cadarache, which was supported by CEC D/DG. XII under contract No. 468-85-15-WAS-F /4/. After describing the scope of the research undertaken - radiation source, detector system, data processing, stationary mechanics - the final report deals with the following main points:
The detector material was investigated very carefully.
The conclusion is that the best choice would be BGO.
The transmission of gamma-rays through up to 1625 mm thickness has been measured at different energies (6, 10, 16 MeV) and the calculation code of the attenuation coefficient has been validated.
The radiation source must be an electron accelerator whose energy has to be carefully optimized.
The system configuration has been determined and the data processors have been chosen.
The algorithms for CT-image reconstruction have been validated through taking a tomogram of a concrete sample with four iron reinforcement bars in it.

2. Choice and collection of real waste packages (B. 6)

The following points of view were decisive for the choice of waste packages. The selected waste containers should be

- representative for the various kinds of containers, e. g. 200 and 400 l drums with concrete shielding, steel containers (30 and 43 cm diameter) for HAW-waste
- filled with different waste (radioacitve or simulate), e. g. bituminized waste, LLW immobilized in concrete, inactive glass with HLW-simulate
- able for the simulation of different kinds of defects and activity levels.

Table 1 contains the most important data of the selected waste packages.

a) LLW 200 l-barrel

First experiments with CT on a 200 l LLW waste container were performed at BAM in 1984. The drum contained several steel parts and a plastic bottle with a fixated fluid. All materials were fixated with cement. The container had a prevosiously manufactured shell (thickness 6 cm) of concrete to insure radiation protection.

Using Co-60 as radiation source the maximum absorption through this container (60 cm of concrete) corresponds to an attenuation up to 1 : 10^4. The tomograms revealed many details like a cracked shell, areas not filled with cement, the boundary between the prefabricated shell and the refilled cement /1/. The total (β,γ) activity of this waste was less than 555 MBq (15 mCi).

b) 50 l bituminized waste

A MLW waste drum (Origin COGEMA) containing 50 l bituminized waste was received from EIR Würenlingen. Fig. 2 shows the transport container (7 t, type A) and the 200 l barrel which contains the 50 l waste drum.

A cross-section of these containers shows Fig. 3.

The total (β,γ) activity of this active bitumen waste was less than 0,37 TBq (10 Ci). The main radioactive components are listed in table 2.

c) In collaboration with CEA-Cadarache it is planned to investigate a sample drum containing LLW immobilized in concrete with a diameter of 1 m.

For these experiments the use of the LINAC will be necessary because the maximum thickness of concrete which can be transmitted by Co-60 radiation is about 60 cm.

d) <u>200 l iron-hoop drums</u>

Two 200 l barrels, one of ordinary-concrete the other of high-densitiy-concrete, with a concrete shielding of about 6 cm were fabricated. Inside there are several holes embedded in concrete for simulation and combination of different kinds of defects like holes, fluids, radioactive sources. Fig. 4 shows a cross section of these drums.

e) <u>Container for high level radioactive waste of the Pamela-type</u>

In connection with KfK-Karlsruhe (INE, Dr. Kahl) several steel containers (diameter 30 cm and 43 cm) filled with inactive glass-simulate of the Pamela-type are investigated. The tomograms showing cracks, voids, areas with small bubbles and some pieces of a more absorbing material e. g. metallic precipitations /1/.

f) In connection with CEA-Cadarache a steel container (diameter 43 cm) filled with glass of the la Hague-type was received. Fig. 5 shows a cross-section.

References:

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Possibilities of Quality Assurance on Radioactive Waste Packages by Computertomography and other Radio metric Techniques
Proceedings of the International Seminar on Radio active Waste Products
Jülich, 10 - 13 June 1985, pp. 483 - 491

/2/ Mobile system to assay potential WIPP shipments
Nucl. News Vol. 28, No. 15, Dec. (1985) pp. 81 - 82

/3/ Burstein, P., Mastronardi, R., Kirchner, T.:

Computerized tomography inspection of Trident rocket motors: a compability demonstration
Materials Eval. 40 (1982) pp. 1280 - 1284

/4/ Montigon, J. I.:

Etude de faisabilité d'un appareil de tomographie pour l'examen des dechéts radioactives
Rapport final pour CCE IDG XII, 90 p.
Contract No. 468-85-15-WAS-F/TT/, Mai 1986

Drum type	Origin	Shielding	Total (β, γ)activity	Contents
a) 200-l iron hoop drum	HMI	6 cm concrete	555 MBq (15 mCi)	LLW-waste embedded in cement
b) 50-l iron hoop drum	EIR (COGEMA)		0,37 TBq (10 Ci)	Bituminized waste
c) 870-l drum	CEA Cadarache	concrete		
d) Two 200-l iron hoop drums	BAM	ordinary concrete high density concrete	---- ----	For simulation of defects, liquids and active sources
e) steel container (30 cm + 43 cm diameter)	KfK	steel	----	Inactive glass of PAMELA-type
f) steel container (43 cm diameter)	CEA-Cadarache	steel	----	Inactive glass of La Hague-type

Table 1 Selected waste containers

137 Cs	89	GBq	(2,4 Ci)
134 Cs	30	"	(0,8 Ci)
106 Ru + Rh	113	"	(3,05 Ci)
144 Ce	80	"	(2,15 Ci)
60 Co	16	"	(0,45 Ci)
90 Sr + Y	26	"	(0,7 Ci)
Total $\beta\gamma$	342	"	(9,25 Ci)
Total α	1,8	"	(0,05 Ci)

Table 2: Main radioactive components of the 50 l barrel with bituminized waste (b)

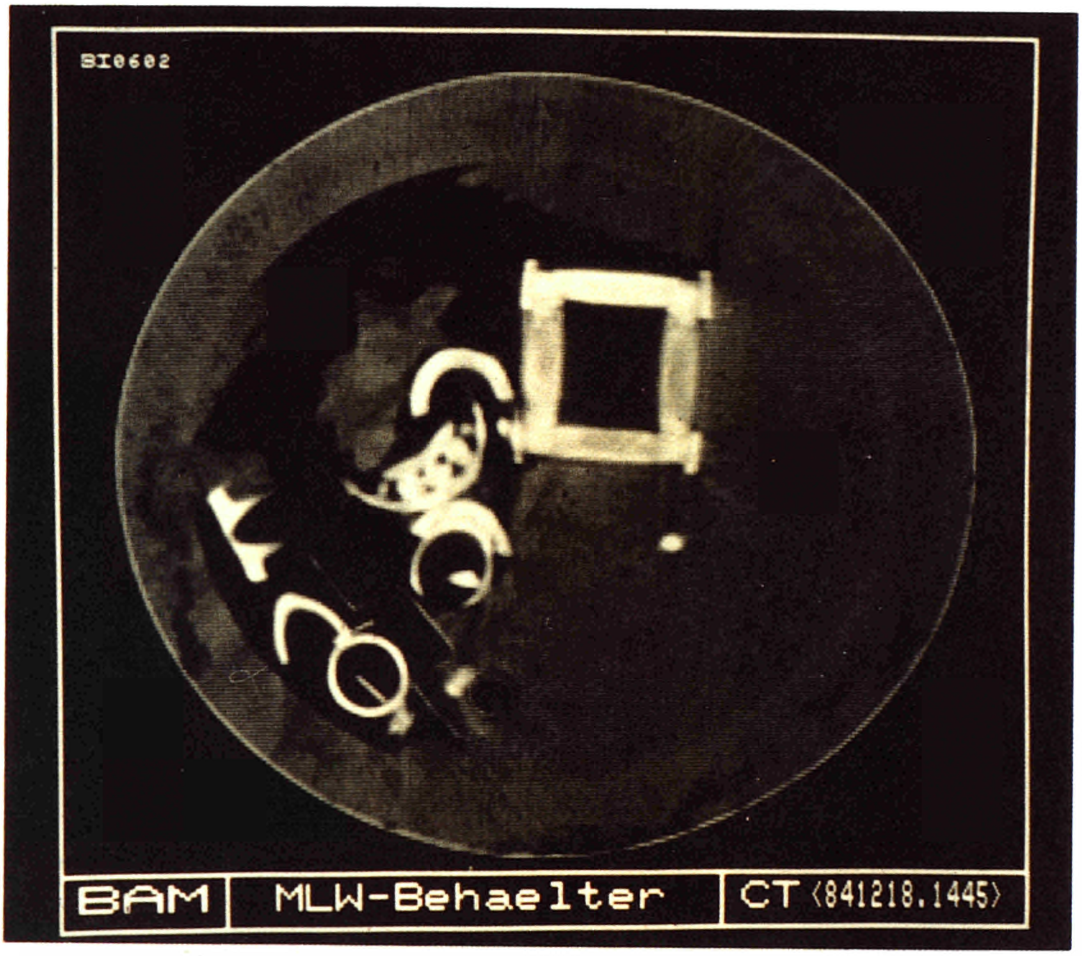


Fig. 1: Tomogram of the LLW 200 l barrel (a)

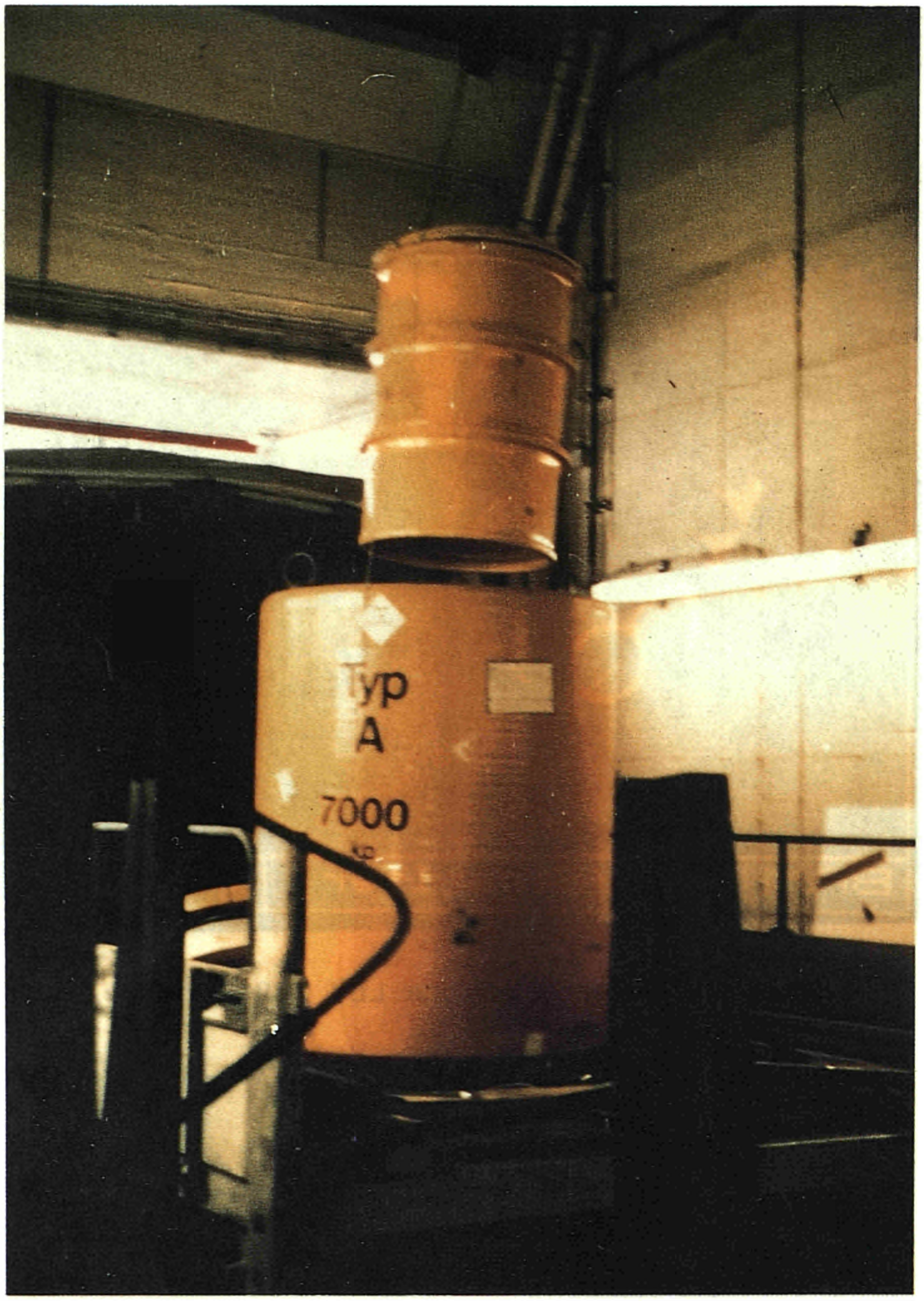


Fig. 2: Delivery of the 50 l barrel with bituminized waste (b)

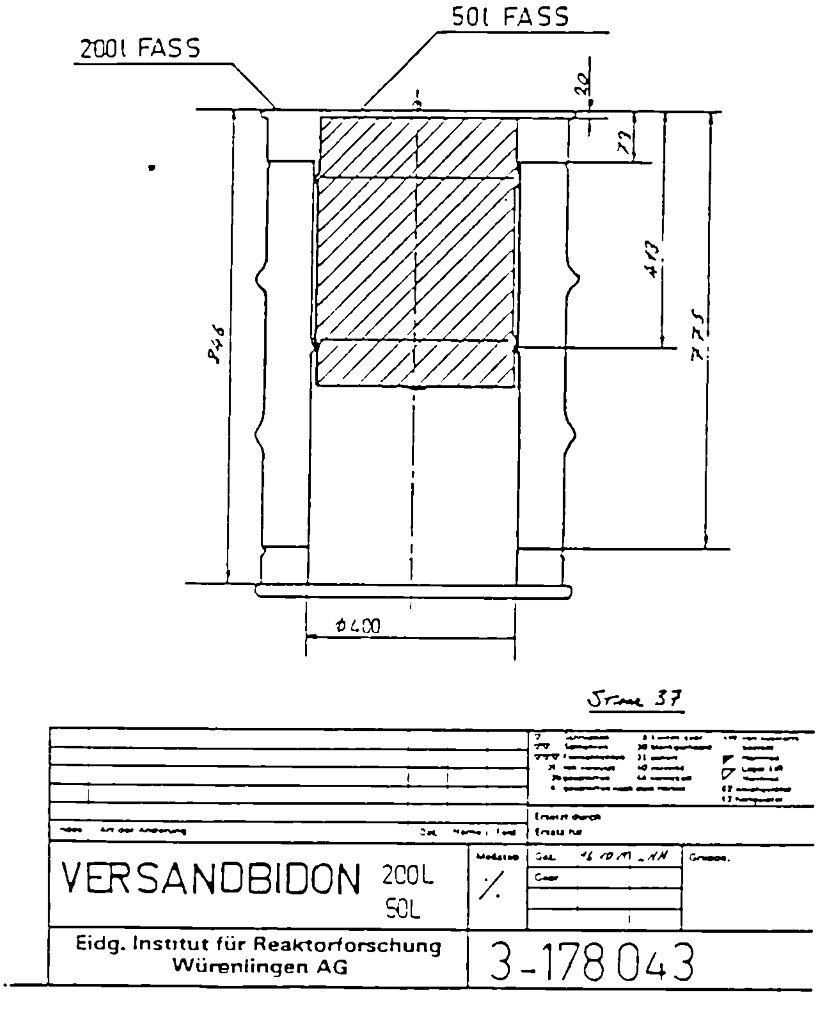


Fig. 3: Cross section of the 50 l barrel with bituminized waste (b)

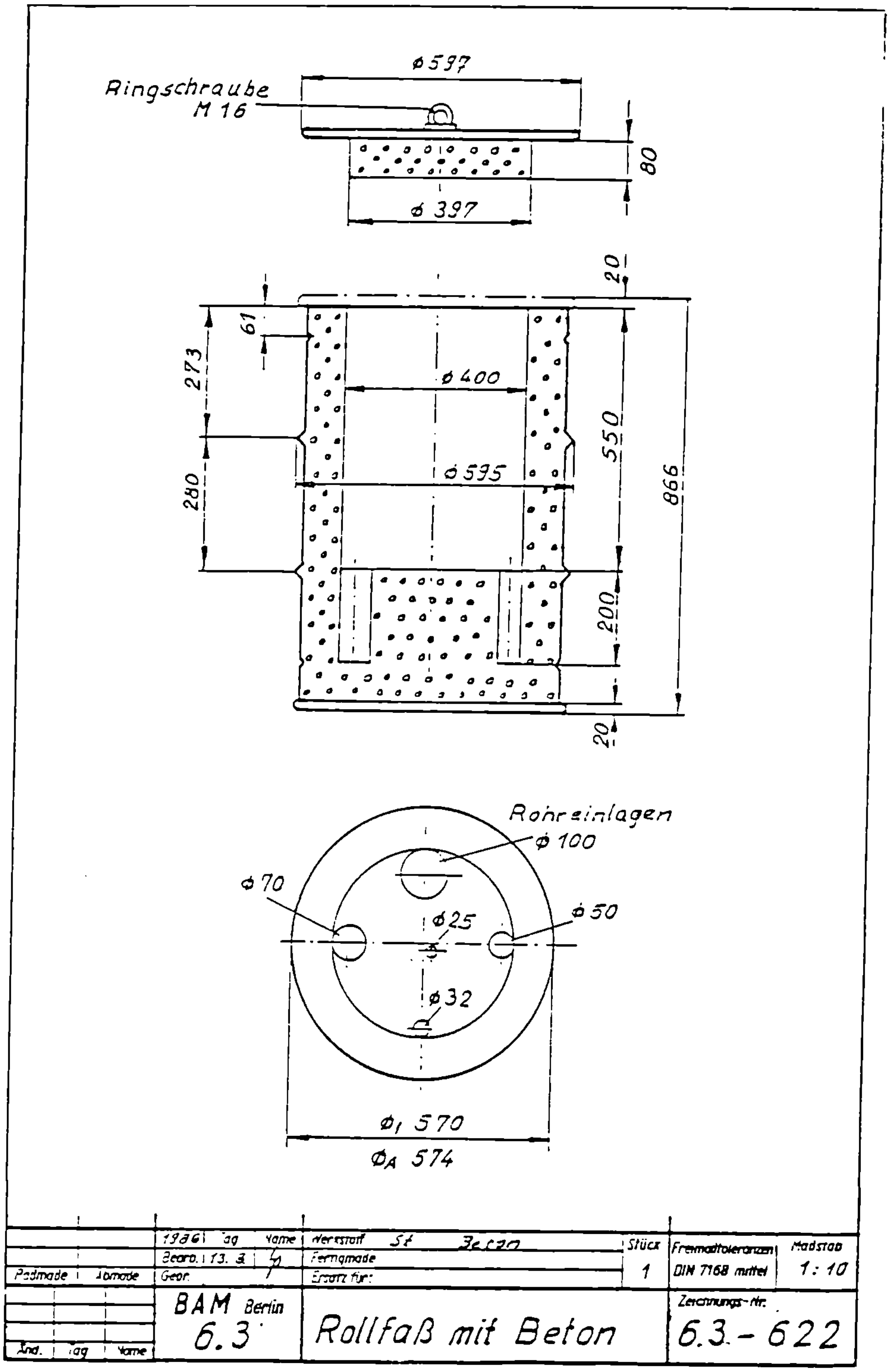
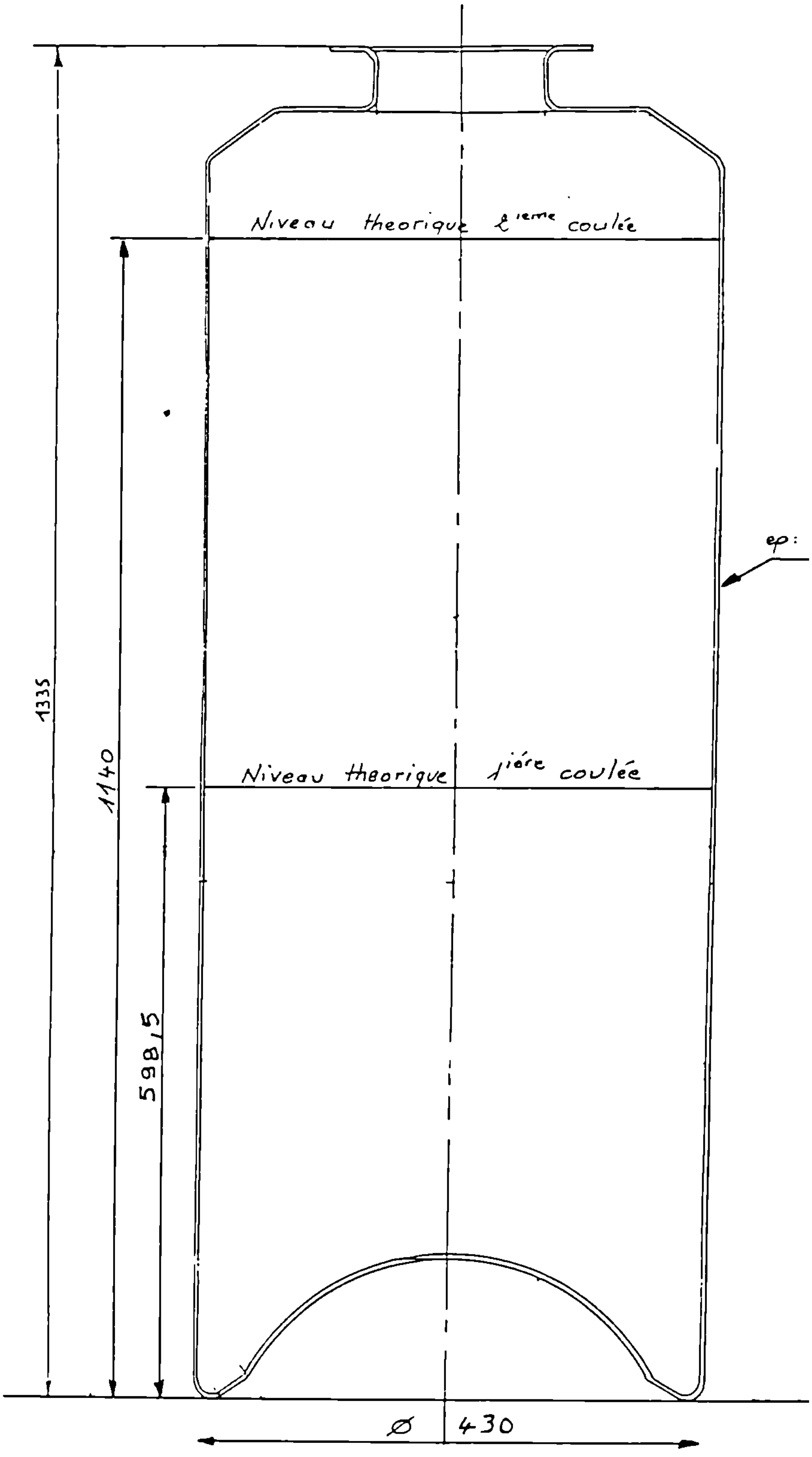


Fig. 4: Cross section of the 200 l iron-hoop drums (d)



SCHEMA D UN CONTENEUR PLEIN DE VERRE

Fig. 5: Cross section of the steel container (f)

CHAPTER 4

TASK No. 4 : RESEARCH IN SUPPORT OF THE DEVELOPMENT OF DISPOSAL FACILITIES; SHALLOW LAND BURIAL AND GEOLOGICAL DISPOSAL STUDIES

CHAPTER 4

TASK No. 4 : RESEARCH IN SUPPORT OF THE DEVELOPMENT OF DISPOSAL FACILITIES; SHALLOW LAND BURIAL AND GEOLOGICAL DISPOSAL STUDIES

A. Objective

Evaluation and modelling of the long-term behaviour of the geological barrier

Development of disposal facilities.

B. Research topics dealt with under the 1980-1984 programme

a) Work related to sites and their characterization

- General survey of geological formations and development of measuring techniques with a view to develop large scale in-situ characterization of the geological formations by direct or indirect methods

- Geoprospective studies : development of an operational method for the prospective analysis of the characteristics of geological containment

- Rock mechanics studies.

b) Work related to geological repositories and barriers

- Improvement of the designs and technologies required for the setting up of repositories in geological formations (salt, granite, clay)

- Development of long-lived containers for vitrified waste and of methods for the backfilling sealing of openings in geological repositories.

c) Work on radionuclide migration in the geosphere

- The work mainly comprised integral experiments on migration simulation, laboratory studies concerning the properties of materials from specific sites, hydrogeological investigations, research on natural geological migration systems and the role of micro-organisms, and, finally, the development of calculation tools and the intercomparison of codes regarding transport and geochemistry.

d) Shallow land burial

- Studies dealt with migration phenomena, improvement of barriers and radiological assessments.

C. 1985-1989 programme

The work will be mainly a continuation of the research started during the 1980-1984 programme; however, special emphasis will be put on calculation tools and their intercomparison, on investigations attached to specific sites as opposed to laboratory work of general nature, on the role of colloïds and complexes in radionuclide migration, on studies of natural analogues, and on the development and assessment of various backfilling materials and concepts.
Co-ordination is ensured by a structure of projects or working groups :

GEOPROS : Geoprospective Studies

ROCMEC : Rock Mechanics

COSA : Comparison of Rock Mechanics Codes for Salt

B & S : Backfilling and Sealing

MIRAGE : Migration of Radionuclides in the Geosphere

COCO : Colloïds and Complexes

CHEMVAL : Geochemical Benchmark for Mirage

NAWG : Natural Analogue Working Group

D. Programme implementation

23 contracts have been signed and the available information is listed thereafter.

a) Work related to sites and their characterization

Development of the methodology
of
Geoprospective study of a repository site

Contractor :	Bureau de Recherches Géologiques et Minières B.P. 6009 45060 ORLEANS CEDEX - FRANCE
Contract n° :	FI IW/0048
Working period	August 1986 - December 1986
Project Leader	P. PEAUDECERF - J. FOURNIGUET

A. Objectives and scope

Since 1981, the BRGM has been working on the development of a method for systematically studying all the factors which might influence the evolution of a waste storage site and their interactions. One of the work phases consisted in a relative quantifying of the links between the factors and in modelling them so as to complete realistic scenarios. These operations are carried out with a simulator called CASTOR ("Construction automatique de scénarios d'évolution d'un site de stockage de radionucléides" Automatic design of scenarios evolution of a radionuclide storage site).

The first simulations showed that a few main mechanisms governing site evolution should be represented more realistically.

They are essentially those concerning climate variations, weathering and erosion processes and relationships between stress and hydraulic parameters. The simulation programme will have to be modified accordingly to take these mechanisms and their interrelationships into account simultaneously.

This work should make the CASTOR code operational when applying the methodology to specific sites.

B. Work programme for 1986

The whole study must revolve around two main aspects:

- increasing knowledge of mechanisms which appeared essential in earlier work:
  - climatology
  - weathering-erosion
  - relationships between stress and hydraulic parameters.
- improving the modelling of the phenomena and the representation of results obtained.

Considering the date at which the contract was signed, it was decided that the first work would be concerned with the complex mechanisms and with the noless complicated mechanisms of erosion.

C. Progress of work and obtained results

At the contract was signed in August 1986, only a few months of the second half year could be given over to the study.

During this period, two of the numerous selected themes were worked upon:

Mechanisms of Erosion and Mechanisms of Climatic Variations.

This work is done on a shared-cost contract with the European Atomic Energy Community as part of its research and development programme on the management and storing of radioactive waste (related studies only).

C.1 - Erosion mechanisms

The climatic conditions envisaged are those between the Mediterranean and temperate types on the one hand, and periglacial conditions on the other.

The first research concerned the catchment basins in the southern subalpine ranges about 10 km NNW of Sisteron.

Sediments liable to erosion are produced in the following successive stages:

- disaggregation of a thin surficial film, producing a friable layer, 15 to 20 cm, thick,
- washing down or mass-movement of this loose layer to gully bottoms by rain-drop impact,
- transportation of this material by traction or in suspension, by water flowing in the gullies and channels.

The main parameters to be considered are:

valley slopes
exposure to direct sunlight
dip of sediments
nature of vegetation cover.

Among the first results, two important points must be emphasized:

- the exponential variation of erosion with rain intensity,
- the discontinuous nature of erosion phenomena; various types of threshold effects exist and it can be reckoned that only 25% of annual rainfall is erosive.

C.2 - Climatic mechanisms

Climatic variations are of considerable importance as they have varied consequences. Several aspects had therefore to be considered:

a. Mathematical formulation of past and future climatic fluctuations checked by astronomic parameters, calculation and plotting of forecast curves.

b. Search for present-day climatic equivalents to compare with the Quaternary climates reconstituted by conventional geological methods. These comparisons enable quick and empirical access to the temperature and rainfall conditions to be used for calibrating the calculated climatic curves.

c. Phenomena induced by the existence of inlandsis: under the ice or on its edges.

During the second quarter of 1986, only points b and c were treated.

Climatic equivalents: a thorougly reference search enabled the collection of data on temperatures (average and extreme values) and rainfall (total, distribution) over Europe. These data resulted in quantification of present climates using indices and zonation maps. Past successive climates will next have to be identified with present synchronous but juxtaposed climates.

Induced phenomena

Among the phenomena induced by the presence of inlandsis, three seem to bring about large scale mechanical modifications:

- the contorted structures in the sediments deposited by ice,
- glaci-tectonics affecting both the glacial sediments and their substratum,
- tunnel valleys, capable of excavating trenches several hundred metres deep.

Long-Term Rheological and Transport Properties of Dry and Wet Salt Rock

Contractor: University of Utrecht, Netherlands
Contract N°: FI1W-0051-NL
Duration of Contract: 01/07/86 - 30/06/87
Project Leaders: C.J. Spiers (author), H.J. Zwart

A. Objectives and Scope

Previous work at Utrecht has shown that small amounts of inherent or added brine can strongly influence the long-term rheological and transport properties of salt rock via processes such as fluid-assisted diffusional creep and recrystallization /1, 2/. Fluid-assisted recrystallization has also been shown to be capable of strongly reducing ("annealing out") radiation damage in salt /3/. The objectives of the present programme are as follows:

1) Characterisation of the long-term constitutive behaviour of salt rock, taking into account such parameters as fluid content, fluid pressure, grain size, and confining pressure.
2) Further characterisation of the dependence of creep-induced dilatancy and permeability in salt rock on parameters such as pressure, temperature, fluid pressure, and deviatoric stress.
3) Determination of the time-dependent compaction creep and permeability characteristics of dilated salt rock, granular salt (backfill), and anhydrite rock, under dry and wet conditions. Special attention will be given to the determination of an optimal (i.e. fast compaction/recrystallizing/sealing) "recipe" for granular salt backfill.
4) Preliminary determination of the rate of recrystallization (hence stored energy reduction) of γ-irradiated salt rock as a function of parameters such as specific stored energy, temperature, brine content, and brine impurity (Fe^{3+}) content.

B. Work Programme

B.1. Rheological experiments (triaxial testing of coarse and fine-grained salt rock).
B.2. Creep-induced dilatancy/permeability tests.
B.3. Compaction creep/permeability tests.
B.4. Radiation damage/recrystallization studies.

C. Progress of Work and Obtained Results

Summary

During 1986, investigations were directed at the compaction creep behaviour of wet granular salt (backfill recipe), at the long term deviatoric creep behaviour of Asse salt rock under steady-state conditions, at deviatoric creep in artificially prepared fine-grained salt rock, and at the influence of temperature and brine content on recrystallization in irradiated salt rock. The compaction work on wet granular salt has proceeded encouragingly, the experimental results showing excellent agreement with theory. Preliminary compaction creep laws have been developed and a preliminary backfill recipe proposed. The deviatoric creep work has resulted in a "best estimate" constitutive law for creep of salt rock under in situ conditions. The recrystallization studies have suffered delays but clearly indicate that provided trace brine is present, recrystallization leads to much more efficient annealing of radiation damage in salt than the well-known solid state reactions. The general status of the work programme is as follows:

- B1 - progressing encouragingly, but slightly behind schedule.
- B2 - delayed.
- B3 - excellent progress with granular salt, anhydrite work delayed.
- B4 - experimental programme complete, analysis of results still in progress.

Progress and Results

1. Rheological Experiments on Salt Rock

Deviatoric creep experiments have been performed on natural Asse salt rock under conditions of constant strain rate and without added brine. These tests have confirmed that results obtained from our previous stress relaxation tests (1, 2), i.e. that fluid assisted effects become important in natural salt when the confining pressure is sufficiently high to suppress dilatancy. Long-term creep experiments have also been performed on artificially prepared, fine-grained salt rock ($\sim$ 1% brine), using the stress stepping technique. Once again, the results are closely consistent with our earlier data (1, 2) and confirm that the low-stress creep of brine-bearing salt occurs by fluid-assisted diffusional transfer (FADT). Analysis of our entire data set has yielded the following "best estimate" constitutive law for creep of brine-bearing salt by this mechanism

$$\text{Diffusional creep rate } \dot{\varepsilon}(DC) = (1.25\text{x}10^{-9})\left[(8.25)T-2350\right]\sigma/Td^3 \ (s^{-1})$$

where σ is the applied differential stress (MPa), T is absolute temperature (K), d is grainsize, and where $\dot{\varepsilon}(DC)$ is thought to be insensitive to actual brine content provided trace brine is present. To a first approximation, this low stress creep law can be added to the well-known BGR creep law (high stress, dislocation mechanism) to obtain the general constitutive equation $\dot{\varepsilon}(net) = \dot{\varepsilon}(BGR) + \dot{\varepsilon}(DC)$ for natural salt (non dilatant conditions).

2. Creep-Induced Dilatancy/Permeability Tests

As a "by-product" of the experiments reported above, data regarding the dependence of creep-induced dilatancy on pressure, temperature and deviatoric stress was slowly accumulated during 1986. However, this data has not been analysed. No specific dilatancy/permeability tests have yet been performed.

3. Compaction Creep/Permeability Work

Compaction creep experiments have been performed on wet granular salt to determine the constitutive compaction behaviour and to test theoretical models. The results show that under backfill/cement-relevant conditions, compaction creep occurs by diffusion controlled FADT (see C.1.) and can be described by a constitutive law of the form

$$\text{Volumetric compaction creep rate } R = A.P^a/d^b.e^c$$

where A is a temperature dependent term, P is the applied effective pressure, d is grainsize, e is volumetric strain, $a = 1$, $b = 3$, $c = 2$. This law applies for $P < 3\text{-}4$ MPa, $d < \sim 5$ mm, $e > 15\%$, brine contents down to a few percent, and for initial porosities in the range 35-45%. At volumetric strains $e > 15\%$, c increases rapidly reaching a value of ~ 5 at $e = 20\%$. Over the entire range of conditions investigated so far ($e \leqq 30\%$, $P < 4.5$ MPa), the experimental data are best described by an empirical relation of the same form as the above but with $a \cong 1.5$, $b \cong 3$, $c \cong 3$. The data have been used to help develop a preliminary "fast compacting" backfill recipe - see Table 1.

4. Radiation Damage/Recrystallization Studies

Hydrostatic annealing experiments have been performed on pre-irradiated salt rock samples (Dose = 1-10 Grad) at T = 70-120°C, P = 10-30 MPa using added brine contents in the range 0-0.5 wt%. Stored energies have been measured using solution calorimetry and DSC methods. Recrystallization rates have been determined by image analysis of sectioned material.

Most samples annealed with brine contents > 0.1% exhibit relatively rapid recrystallization and reduction of stored energy. However, the data analysed so far show a wide scatter, making determination of the dependence of recrystallization rate on stored energy, temperature and brine content difficult. Nonetheless, it can be inferred that provided brine remains present (> 0.1%), recrystallization is a much more rapid annealing mechanism, under the conditions of interest, than purely solid state reactions.

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Table I. Preliminary "fast compacting" salt backfill recipe (d = grain-size).

Material	Mass fraction (%)
Matrix of finely powdered salt ($d < 0.5$ mm)	∿ 75
Coarse-grained salt filter ($1 \leq d \leq 5$ cm)	15-20
Geochemical Barriers: clay/anhydrite/Fe_2O_3 ($d < 0.5$ mm)	∿ 2
Brine	∿ 5

COMPARISON OF COMPUTER CODES FOR SALT FOR GEOLOGICAL DISPOSAL OF HIGH-LEVEL WASTE
PROJECT COSA PHASE II

Contractor : Atkins Research and Development, Epsom, UK.
Contract No : FI1W/0054/UK
Duration of Contract : 1 November 1986 - 31 October 1988
Project Leader : N.C. Knowles

A. OBJECTIVES AND SCOPE

Research into geomechanical aspects of RAW repositories in salt formations has been active in the European Community for nearly two decades, with particular interest being placed on problems of heat producing waste. Central to this work is the prediction of stresses and deformations in the host strata, for which a number of computer codes have been developed /1/. A preliminary exercise ("COSA 1") to compare the ability of the different codes has recently been completed /2/ and has provided a limited "snapshot" of the current European capability to predict the behaviour of rock-salt under well defined conditions. The purpose of the present contract is to extend the comparison to more complex but realistic situations.

Comparison problems in the first phase were relatively simple, and a number of difficulties to do with modelling of the in-situ behaviour of rock salt were deliberately avoided. The present exercise is directed at comparisons of realistic in-situ behaviour. Emphasis will be placed on the characterisation of material behaviour by individual participants. Other modelling topics to be addressed include the representation of 3-D behaviour by 2-D models, algorithms for treating the thermal and geomechanical discontinuity at the moment of encapsulation of the waste canister, the influence of non-homogeneities within the strata and far-field boundary conditions.

There are 9 participants in the exercise, each acting as a sub-contractor to the co-ordinator. In addition an independent expert will provide advice as necessary on aspects of salt rheology (Table 1).

B. WORK PROGRAMME

B.1 To agree, at plenary meetings, suitable in-situ benchmark problem(s) to be solved by participants.
B.2 Co-ordinator to prepare discussion documents and circulate to participants as necessary.
B.3 Co-ordinator to prepare and circulate detailed specifications of agreed problem(s).
B.4 Participants to solve agreed benchmark problem(s) to the best of their ability using appropriate codes, according to the specifications produced by the co-ordinator.
B.5 Co-ordinator to collect and compile results and other data from participants.
B.6 Co-ordinator to prepare draft reports for discussion at plenary meetings to be held approximately every six months.
B.7 Co-ordinator to prepare and issue final reports taking account of participants' comments.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Statement of advancement

As indicated above, the project is still very much in its infancy : A plenary meeting has been held at which an in-situ benchmark problem was selected. A specification is being prepared, prior to solution of the first part of the problem. Hence, B1 is completed and B2 is progressing normally.

Progress and Results

A plenary meeting, held on November 26-27, 1986 in Brussels, agreed that a selection of the experiments performed by ECN in the 300m dry drilled borehole in the Asse mine in W Germany would be the basis for the exercise ('Benchmark 3').

This decision followed extensive discussion about suitable "problems" which in practice are very limited. The attributes of the ideal problem were listed as :

i) in-situ test
ii) realistic timescale
iii) adequate thermal loading
iv) well established behaviour
v) well posed problem in terms of the availability of data describing geometry, loading and material behaviour
vi) unfamiliar to participants
vii) relevant to European needs

Because the field is so specialist it is apparent that conflict between the latter two attributes is inevitable. Thus some participants have already performed calculations for the Dutch experiments. Moreover they are familiar with the difficulties inherent in characterising the in-situ material behaviour in a form suitable for predictive modelling. Nevertheless it is felt that the experiment has many positive aspects and particular care will be taken to try to ensure that the objectivity of the exercise is not compromised by the prior experience of some participants.

The first stage consists of modelling the isothermal free convergence of the borehole, over a period in excess of 800 days. A draft specification is being prepared which will be circulated to participants for comment by the end of January, 1987. It is hoped that the results of the isothermal free convergence calculation will be discussed at the next plenary meeting, set for the end of June 1987.

Table 1 : List of organisations involved in COSA II

ATKINS R&D - Epsom (UK)	Co-ordinator
FORAKY & LGC - Brussels (B)	Calculation Team
GSF - Braunschweig (D)	Calculation Team
KfK - Karlsruhe (D)	Calculation Team
RWTH - Aachen (D)	Calculation Team
CEA-DEMT - Saclay (F)	Calculation Team
EMP - Ecole des Mines - Fontainebleau (F)	Calculation Team
LMS - Ecole Polytechnique - Palaiseau (F)	Calculation Team
ISMES - Bergamo (I)	Calculation Team
ECN - Petten (NL)	Calculation Team
Technical University Delft (NL)	Salt Expert

List of Publications

PIPER D., LOWE M.J.S.L., KNOWLES N.C.,
Atkins Research & Development EAD Report 29.09.86 (1986)

KNOWLES N.C,
Workshop on Mathematical Modelling for Radioactive Waste Repositories, Madrid (Spain) Dec 10-12 1986, Proceedings in press.

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The 600 m bore hole project:
"Development of a surveillance method during dry-drilling of a 600 m deep bore hole in salt and performance of geotechnical measurements in the 600 m hole"

Contractor: Netherlands Energy Research Foundation (ECN)
Petten, The Netherlands
Contract No.: FI-1W1/0084
Working Period: August 1986 - December 1986
Project Leader: T.C. de Boer

A. OBJECTIVES AND SCOPE

During the dry-drilling experiment performed under contract with the Commission of the European Communities in the framework of its previous R&D programme (1980-1984), it was obvious that the applied techniques were limited with respect to the maximum diameter and depth. In fact, a hole with a diameter of 30 cm and a depth of 300 m was succesfully drilled. Since then, a dry-drilling technique was developed for larger diameters and depths.

This technique will be tested by drilling a bore hole with a diameter of 60 cm, typical for a disposal hole, and a depth of 600 m. As there is a need for an alternative for the reconnaissance drilling of each individual bore hole in a HLW repository, a surveillance method during the dry-drilling will be developed in cooperation with GSF. In the 300 m hole of the previous programme, several experiments concerning the creep behaviour of the salt were performed at ambient and elevated temperatures. The convergence measurements of the diameter as a function of the depth of the hole gave insufficient results, i.e. the convergence as a function of the lithostatic pressure could not be checked. As this parameter is important, lithostatic pressure tests will be performed (see figure 1).

The project is funded by the Ministry of Economic Affairs, ECN, BMFT, GSF and CEC and carried out in close cooperation with GSF-Institut für Tieflagerung Braunschweig, FRG. In a first phase, free convergence measurements over the length of the hole and a non-isothermal lithostatic measurement will be carried out. In a subsequent phase of the current five year programme, not covered by the present contract, additional non-isothermal lithostatic measurements at two other levels and isothermal lithostatic measurements will be performed; all these results will be used for the validation of analytical techniques and computer codes such as GOLIA.

B. WORKING PROGRAMME

B.1. Design, construction and testing of a surveillance method.
B.2. Exploration and experiments.
B.2.1. Geochemical exploration.
B.2.2. Isothermal convergence measurement.
B.2.3. Non-isothermal lithostatic pressure measurements.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The present concept of the licensing authorities is to have a reconnaissance drilling for bore holes with large diameters. With a working surveillance method these reconnaissance drillings may be reduced. Therefore there is a need to develop a surveillance method during dry-drilling.

The present database for thermo-mechanical computer code validation, consisting of the ECN 300 bore hole experimental data, needs to be complemented with free convergence and lithostatic pressure data from a 600 m deep bore hole to be drilled in a relative undisturbed environment.

1. Development of a surveillance method (N. Jockwer, GSF)

Laboratory and in-situ investigations have shown that rock salt contains different gas components trapped within small inclusions and pores or adsorbed to the crystal boundaries. Calculations on the liberation of these gases indicated that it is possible to determine them within the flushing air and to determine layers with higher porosity and gas content. Technical concepts have been developed and analytical systems for the gas determination are now in selection.

2. Exploration and experiments

2.2. Isothermal convergence measurements.

"Prediction of the isothermal free convergence of the 600 m deep bore hole" (J. Prij et al.).

Due to the time dependent constitutive behaviour of rock salt, a bore hole in a salt formation will show a time dependent deformation behaviour. The driving force for this deformation is the difference between the stress state at the bore hole wall (where the radial stress is zero) and in the salt at large radial distance from the bore hole where the state of stress is equal to the lithostatic state of stress.

The deformation process is governed by a set of differential equations consisting out of the equilibrium equation, the compatibility equations and the constitutive equations. In the case of a deep bore hole in a large salt formation the geometry is rather simple which makes the equilibrium and compatibility equations relatively simple.

If the constitutive behaviour of the salt can be described with a combination of elastic and secondary creep behaviour, than an analytical treatment of the bore hole deformation behaviour is possible. For a more complex constitutive behaviour, however numerical methods are needed, several authors have stated that the material behaviour of salt can be approximated accurately with the secondary creep /1-5/.

In this report an analytical treatment of the convergence will be used to obtain a prediction of the behaviour of the 600 m hole, based on an extrapolation of the measured convergence in the 300 m bore hole /6/.

Some numerical results are given in table I and figure 2. Here the time to reach some discrete convergences is given for the depths considered. It is clear from the results that there is an enormous difference in the convergence at the various depths. From the analyses it can be seen that the relatively small gradient in rock pressure is mainly responsible for these differences. The geothermal gradient has a smaller influence.

In this report, predictions have been given for the convergence of the 600 m bore hole. For the prediction the concept of a normalized convergence and normalized time is used. This concept could be extended in such a way that a prediction of the convergence can be made with a minimum number of material properties. The basis for the prediction is the measured isothermal convergence in the 300 m bore hole in the Asse [6].

The prediction shows that the rock pressure has a very large influence on the convergence while the geothermal gradient has a smaller influence. The prediction of the convergence will be used for the design of the measuring devices.

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Table I. Time in days to reach the radial convergence u_h at several depths in the 600 m bore hole

DEPTH (m)	RADIAL CONVERGENCE u_h (mm)						
	2,5	5	10	20*)	30	50	100
100	238	785	2557	7101	11704	20909	43923
200	87	280	978	2691	4515	8164	17284
300	36	112	367	1118	1911	3499	7467
400	16	49	160	499	870	1614	3472
500	8	22	74	235	420	790	1714
600	4	11	37	117	213	406	889

*) The convergences at the right side of this line are based on an extrapolation of the measured data.

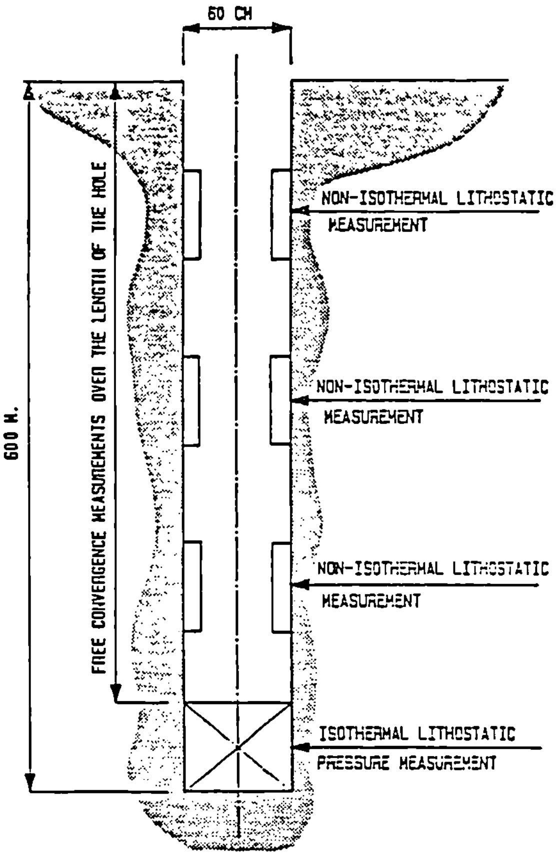


Figure 1: Sketch of the 600 m bore hole measurement set-up

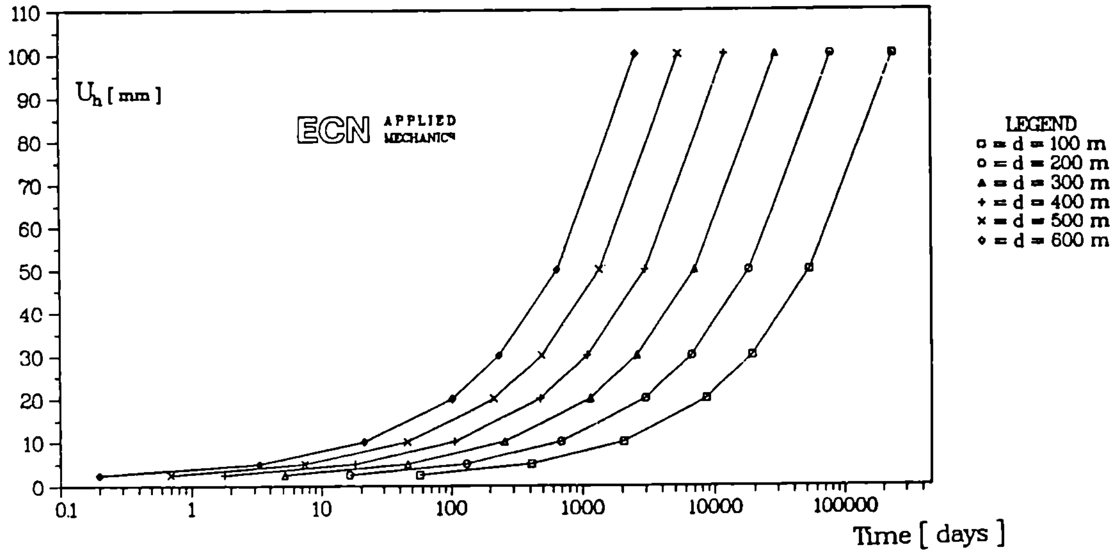


Figure 2: Predictions of the convergence vs. time of the 600 m hole at different depths

Faults in clays: their detection and properties

Contractor: BGS, Keyworth, Nottingham, UK
Contract No.: FI1W/0085/UK
Contract Period: April 1986-March 1989
Project Leader: N.A.Chapman

A. Objectives and Scope

Faults occur in most mixed sedimentary environments but their effects on regional groundwater flow patterns are poorly understood. The hydrogeological significance of faulted clay layers is of particular relevance where mudrocks are potential host formations for radioactive waste repositories.

In cooperation with ISMES of Italy two faults through clay layers will be studied (one site in the UK and one in Italy). The project has three objectives :-

1. To develop suitable geophysical techniques to detect water bearing faults in clays. These techniques will aim to differentiate between hydraulically active faults and those which are either sealed or non-water bearing.
2. To measure the hydrogeological properties of faults in sequences of mudrocks and aquifers. This will be achieved by measuring the hydraulic and chemical properties of the fault directly and by measuring the effect of the fault on the underlying aquifers.
3. To define suitable techniques for use in site investigations and methods for assimilating faulted boundaries into flow and transport models in clays and mixed sediments.

B. Work Programme

B.1. Desk study to evaluate a number of potential UK study sites; selection of two preliminary sites.

B.2. Initial geological and geophysical investigations of the preliminary UK sites; selection of the final study site.

B.3. Development of geophysical techniques for fault identification.

B.4. Detailed geophysical survey of the study site.

B.5. Borehole drilling.

B.6. Wireline geophysical logging of the boreholes.

B.7. Hydrogeological testing of the boreholes.

B.8. Synthesis of the results to evaluate the significance of the fault.

C. Progress of work and obtained results

State of advance

A desk study has been completed which identified 10 potential UK sites from which two preliminary sites have been selected. Plans for the intial evaluation of these two sites are well advanced. A review of single borehole geophysical logging has been carried out to determine which of the techniques might yield useful results within the project.

B.1. is completed,

B.2. and B.3. are progressing.

Progress and results

1. Site selection (B.1.,B.2.)

Desk studies of Mesozoic sedimentary basins within the UK have been carried out to identify potentially suitable locations for field sites. The sites had to broadly meet a pre-determined set of criteria which fall into three groups :-

1. Geological criteria
   a. Shallow overburden above the mudrock
   b. Faulted mudrock between 30-60m thick
   c. Aquifer underlying the mudrock
   d. Throw of fault to be greater than 50% but less than 100% of the mudrock thickness
2. Hydrogeological criteria
   a. Suitable hydraulic conductivity contrast between the mudrock, aquifer and fault
   b. Identifiable flow boundary conditions and driving potentials
   c. Potential for hydrogeochemical assessment
3. Geophysical criteria
   a. Suitable seismic reflectors in the mudrock and velocity contrast between the lithologies
   b. Remote from built up areas to avoid interference effects

In addition to these criteria the site should have no major topographic features in the immediate vicinity. Sites were initially selected on the basis of the limited geological information that was readily available and a list of ten potential sites was drawn up. None of the sites met all the criteria exactly, and it is clear an ideal site will not be found and that some compromises are inevitable. The two most promising sites, Wombleton airfield in the Vale of Pickering, Yorkshire and Down Ampney near Swindon, Wiltshire were chosen for further investigation. Summaries of the information which has been collected for these two sites are given below. These sites have been visited and negotiations with landowners for access to carry out preliminary geophysical surveys have been completed.

Wombleton airfield

The geology predicted at the site is :-

Formation	Lithology	Thicknes (m)
Kimmeridge Clay	clay	} 35-120 combined
Ampthill Clay	clay	} thickness
Corallian	sandstone + limestone	18-36
Oxford Clay	clay	> 20

A number of faults have been located in the region by seismic surveys and the fault throw at the site is likely to be about 50m. Yorkshire Water Authority investigations identified hydrogeological anomolies in this area which may be associated with the faulting. The nearest water abstraction borehole is approximately 4km distant and the frequency of faulting probably means the aquifer is isolated from major pumping influences. If the fault density around Wombleton airfield is as great as that identified by nearby seismic surveys then care may be required to choose the most hydrogeologically significant fault.

Down Ampney

The geology predicted at the site is :-

Formation	Lithology	Thickness (m)
Oxford Clay	clay	20-80
Kellaways Beds	sands + clays	9-24
Cornbrash	sandy limestone	5-10
Forest Marble	limestone, clay + marl	12-24
Great Oolite	oolitic limestone	15-50

Geophysics and field mapping indicate a fault density of about 1 every kilometre and the fault throw at the site is likely to be about 20m. A Thames Water Authority groundwater development scheme initially identified the faults and resulted in detailed geological mapping and geophysics. The site is most likely located within the region of influence of local water supply boreholes.

2. Single hole geophysics (B.3.)

The single hole geophysical logging has two main aims :-

1.Provide calibration data for the detailed surface and cross-hole geophysical surveys which will consist chiefly of seismic and resistivity techniques.

2.Characterise the differences in geophysical properties between the faulted zone and the unfaulted formation and consequently make interpretations of porosity, strength and mineralogy differences.

Support for the surface geophysics requires resistivity and sonic logging to obtain in-situ resistivity and p- and s-wave velocity profiles. This logging cannot be effectively performed through cemented or uncemented plastic casing and thus the logging will have to be performed in the open borehole. Experience at the Harwell Research Site has shown that it is not possible to readily measure the s-wave velocity of mudstones from single borehole geophysics and therefore it is proposed that the standard borehole compensated log should be run to obtain simply p-wave velocities. It is proposed that resistivity should be measured by a focussed tool with a range of depths of investigation so that correction can be made for any borehole effects. It is also necessary to measure the spatial position of the boreholes in order that reliable results may be obtained from cross-hole seismic experiments and if plastic casing is used this could be carried out in the completed boreholes

Differences in geophysical properties between the faulted zone and the unfaulted rock mass may be determined by conventional logs which, in addition to the resistivity and sonic measurements outlined above. This implies that natural gamma, neutron porosity and density logs should be carried out. It should be possible to identify variations in lithology and porosity across the fault zone by the interpretation of this suite of logs.

It seems likely that the fault zone may also be characterised by an increased density of fracturing and therefore performing logs which identify fractures, such as the borehole televiewer, the fracture identification log or the formation micro scanner, has been considered. However the limited chance of explicitly identifying fractures in sedimentary rocks from a mud filled borehole by these methods, and the high cost of such techniques does not justify their use on this project.

The proposed suite of single hole geophysical logs, which was chosen on technical grounds, is :-

Microlaterolog
Dual laterolog
Borehole compensated sonic
Natural gamma
Density
Neutron porosity
Caliper

These logs should be performed in at least one vertical borehole penetrating the aquifer and one inclined cross-fault borehole. It is also proposed that deviation surveys should be carried out in each of the boreholes after being completed with plastic casing.

Cost estimates have been obtained for performing the above programme of logging which suggest that it can be carried out in the UK within the proposed budget. In order to obtain consistent logging results throughout the project the cost of carrying out the Italian logging using a British contractor was investigated but was found to be prohibitive. A document was submitted to ISMES for discussion proposing that the above suite of logs be performed in the UK and that ISMES should find a suitable Italian contractor to carry out a similar logging programme. These proposals have been accepted by ISMES.

METHODOLOGY FOR APPLICATION OF ELECTRIC AND ELECTROMAGNETIC BOREHOLE TECHNIQUES FOR DETAILED EXPLORATION OF FRACTURED ROCKS

Contractor : BRGM, Geophysics department, Orléans, France.
Contract n° : FI1W/0086/F.
Duration of contract : July 1986 - June 1988.
Project leader : P. VALLA.

A. OBJECTIVES AND SCOPE

The aim of the research work is first to complete the technical developments of three borehole geophysical methods for which prototypes have been built, and second to develop a methodology for these tools applied to detailed investigation of fractures.

These tools are :

- ELIAS, an electrical imaging technique to investigate the borehole wall and determine the depth, strike and dip of conductive or resistive fractures,
- ROMULUS-ERIC, a set of induction transmitter-receiver probes to point out conductive fractures and measure their conductance with a one to a ten meters radius of investigation,
- ARLETT, a three axis induction receiver used together with a surface electromagnetic transmitter, to help assess the geometry of the more conductive fractures in a ten to one hundred meters range.

The first and third systems are still in the technical development stage while the second is now operationnal. Numerical modelling of the methods is needed to fully assess their capabilities.

B. WORK PROGRAMME

1. Technical and theoretical development of electric and electromagnetic probes.
1.1. ELIAS
1.1.1. Final step of prototype development
1.1.2. Design of data acquisition and processing software
1.2. ROMULUS-ERIC
1.2.1. Design of modelling software for thin sheet conductors
1.2.2. Set up of a catalog of theoretical response curves
1.2.3. Study of complex geometry of thin conductors
1.3. ARLETT
1.3.1. Study of improvements to be made in the probe design
1.3.2. Development of a new prototype
1.3.3. Numerical modelling

2. Field tests and methodological studies
2.1. Technical field tests of ELIAS and ARLETT
2.2. Methodology for detailed exploration of fractured rocks
2.2.1. Data acquisition on available test sites
2.2.2. Data processing and interpretation
2.2.3. Analysis of results and methodology assessment

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The work done during this first semester of the programme has dealt with technical development of ELIAS and ARLETT probes (steps 1.1.1. and 1.3.1.) and with numerical modelling of ROMULUS and ERIC probes (step 1.2.1.).

For the former, most of the work has been focused on the development of an orientation module to be included in both ELIAS and ARLETT probes. Testing of components has shown that temperature drift might be a problem. First tests of the integrated module are planned for 87 first quarter. A one-axis auxiliary probe named REMI has also been assembled to help design the ARLETT probe. The first field test has been made and has shown the need for a better phase precision. The technical development of probes is a few months behind of schedule and increased work is planned for 87 first semester.

As for numerical modelling of ROMULUS and ERIC, the basic equations of the modelling scheme for modelling induction tools in the low induction number range has been established. A computer programme has been written based on these equations to obtain theoretical curves for thin sheet conductors.

Progress and results

1. Orientation module for ELIAS and ARLETT probes (step 1.1.1.)

Based on previous studies, the orientation module design includes two servo-inclinometers and three fluxgate magnetometers. Individual components testing has shown a temperature drift. For magnetometers the drift is similar for each sensor so it should be of no consequence. However, for inclinometers the drift is different for each sensor and problems might occur. Further testing of the assembled sensors has also pointed out a few misalignment problems which have been solved, except for the inclinometers for which the supplier is to be questionned.

An electronic board has been designed for digital data transmission and dynamic tests are to be made.

2. Numerical modelling for ROMULUS and ERIC probes (step 1.2.1.)

Starting from Maxwell equations and using a generalized reciprocity theorem scheme, the basic equations have been established to describe induction electromagnetic systems in the low induction number range (or "near-zone"). An algorithm has been implemented on a HP-9000 microcomputer, which, up to now, is dealing with a thin conductive plane or half-plane. A set of theoretical curves, such as the one shown in figure 1, has thus been computed as a tool for the interpretation of ROMULUS and ERIC logs.

3. Preliminary study of ARLETT probe (step 1.3.1.)

While the orientation module is being developped, a simplified version of the ARLETT probe has been designed and built. It is the REMI probe which is an one-axis (axial) induction receiver, to be used with the MELIS frequency domain electromagnetic surface receiver. The measurements are performed one depth and one frequency at a time on both the probe output signal and a reference signal from the transmitter, in order to obtain the transfer function (in-phase and out-of-phase). A stacking process is used to improve the signal-to-noise ratio, which can be checked with the standard deviations.

A first field test has been made for the REMI probe in order to check the complete system particularly in term of sensitivity. The test hole was the Echassières GPF borehole (Deep Geology Programme) which has been drilled through 1000 metres of cristalline rocks, micashists and granite. However the hole is now blocked at 400 metres and no major fractured zone occurs in the open zone. This step was thus a technical one. A borehole EM transmitter, named EMMA, has also been used to make reciprocity checks.

The results show that the amplitude measurements agree with theoretical free-air computations (due to high resistivities the secondary signal is small) but that the phase is not measured with an appropriate accuracy (cf. figure 2). The problem might come from the reference link from the transmitter and further tests are needed to analyse and hopefully solve the problem.

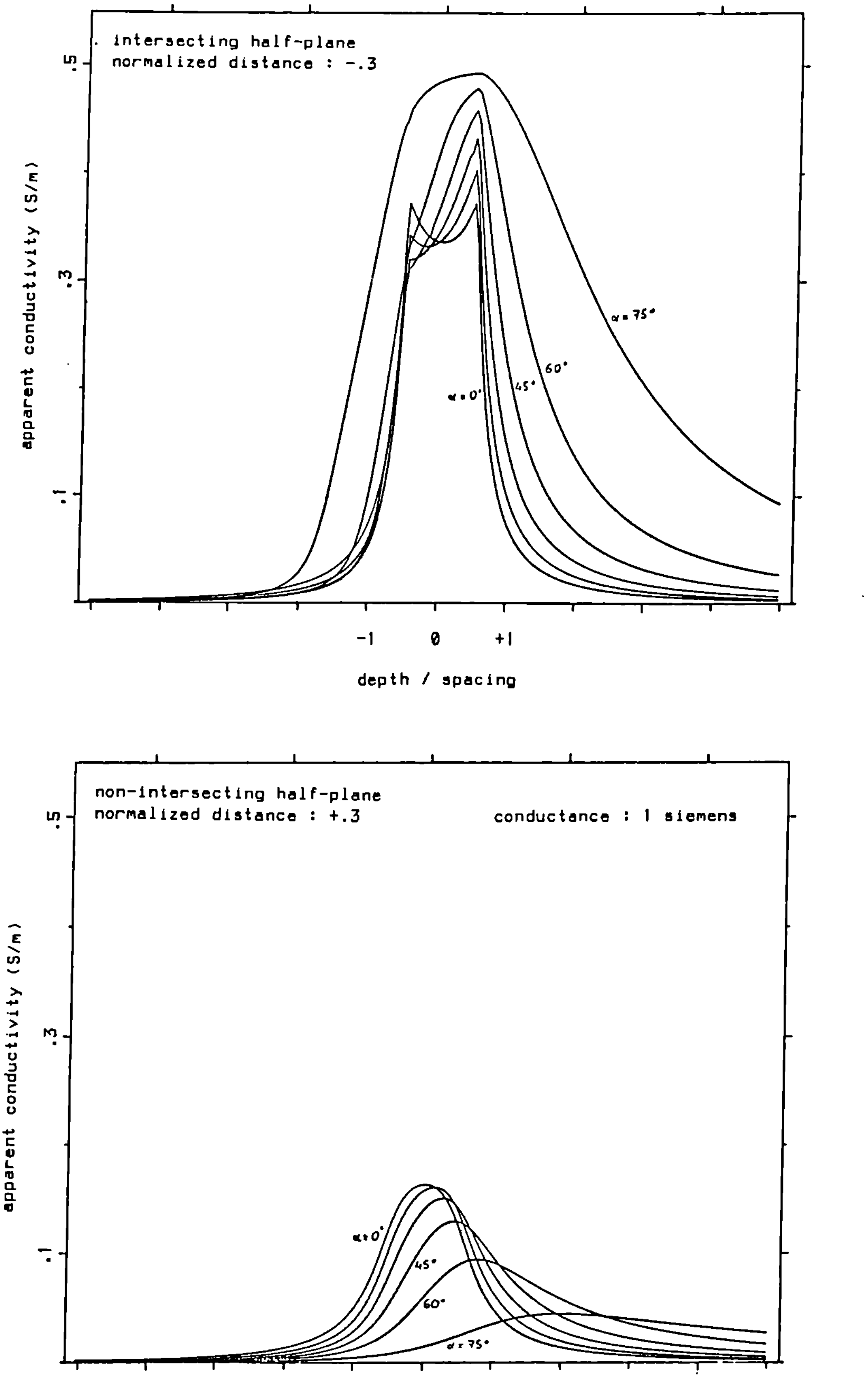


Figure 1 : Theoretical response of induction logging tools (ROMULUS-ERIC) for a thin conductive dipping half-space.

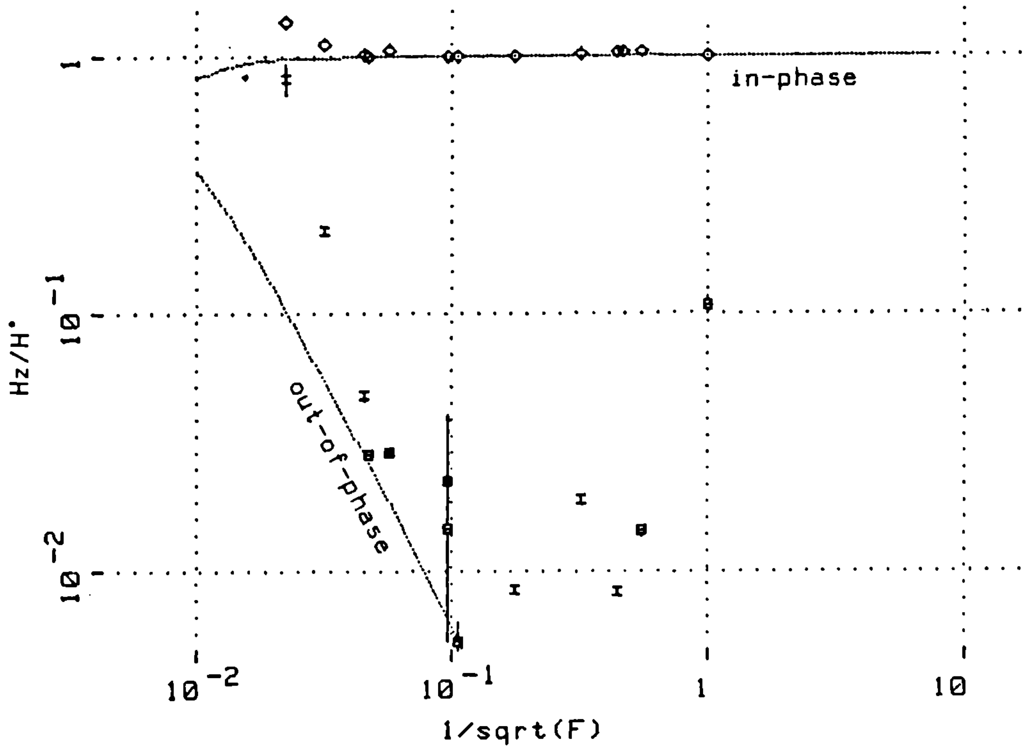


Figure 2 : Comparison of REMI field data measurements with theoretical response for a 2000 ohm.meter half-space at 150 m depth.

Development of a self-contained drill-hole chromatographic probe

Contractor : CEA - CEN CADARACHE F 13108 Saint Paul lez Durance
Contract N° : FI1W/0087
Working period : 36 months
Project Leader : J.M. Vinson

A. Objectives and Scopes

The study of the transuranian nuclide migration from radioactive waste storage places is based on the knowledge of the natural environment and, in particular, of the chemical composition of the water : the transfer vector.

In addition to major elements, the water also contains trace elements which play a prominent part not only on the general equilibrium, but also on the radionuclide migration possibility.

This is in particular the case of the Lanthanides, present in the granitic and argillaceous environments, whose role of sorption competitors with respect to the Actinides has been exhibited throughout numerous experiments.

The scope of this contract is to manufacture and operate a chromatographic probe to be used in a deep drill-hole, so designed as to acquire a representative sample under conditions of equilibrium of the natural environment, to preconcentrate it by elimination of the saline content and to store it for ulterior analysis at the surface.

B. Work Program

B.1. Process Development

B.1.1. Principle laying-down and delineation. In-laboratory model.

B.1.2. Definition of final probe design after study on model. Realization and adjustment on CADARACHE site.

B.2. Probe Qualification in the Deep Drill-hole of AURIAT

B.3. Application to 3 reference sites

C. Work Progress and Results Obtained

Summary

The preconcentration, Lanthanide separation and analysis processes have been studied.

According to the results obtained, the probe design has to be slightly modified to allow for a future coverage of other trace elements by the system, and also to restrict to laboratory execution only the most critical separation operations.

The displacement pump which is the most critical component of the probe has been studied and is now under test.

Progress and results

1. Laboratory model

The purpose of the first stage is to implement, in the laboratory, all the processes required for realizing the experiment.

1.1. Preconcentration

The natural Lanthanide concentrations are too low for being determined by titration.

Two possibilities have been studied according to the versions contemplated for the probe design (Fig. 1) :

- concentration on pre-column
- direct concentration on separation column head.

The average yield figures obtained for concentration factors of 10^3 are listed in the following table.

Table 1 - Results of the preconcentration on column head

Metal. ion	Average area (for 3 analyses)	(Max. deviation) %	Area for each 10µl injected δ_r	Yield (δ/δ_r)
Lu	395883	6.4	515112	77
Yb	465282	10.9	597046	78
Tm	547046	8.9	696641	78.5
Er	610212	8.5	776648	78.5
Ao	775534	0 (1	820304	94.5
Dy	718235	13.9	751218	96
Tb	662403	5.0	869949	76
Gd	797569	3.8	1004488	79
Eu	861667	8.6	1009821	85
Sm	684880	24.1	651452	105
Nd	710217	23.3	704062	101
Pr	626303	23.6	624574	100
Ce	717149	12.6	796388	90
La	728448	14.9	807849	90

The study is being carried on to improve those results.

1.2. Elution gradient (Fig. 2)

The separation column, several types of which were studied, includes grafted silice with sulphonate functions (Nucleosil S.A. or Pertisil SX).

The mobile phases are solutions of hydroxyisobutyric acid (HIBA) and de-ionized water.

. Phase A : distilled de-ionized water.

. Phase B : 0.2 M HIBA with pH = 4.6.

The gradient is accomplished in two linear sections :

1) from 0 to 35 % of B in 15 mm.
2) from 35 to 100 % of B in 15 mm.

The following table shows the reproducibility of the measurements, and Figure 3 shows the Lanthanide separation.

Table 2 - Reproducibility of measurements

Metal. ion	Area average (over 4 analyses) a	Height average h	Max. deviation % a	Max. deviation % h
Lu	584434	49107	1.9	5.3
Yb	664080	50602	5.4	4.05
Tm	787232	60849	1.3	6.0
Er	895730	68477	0.35	4.9
Ao	958745	71018	7.3	5.9
Dy	925465	67673	4.0	5.7
Tb	990864	65250	4.5	5.1
Gd	1162719	67896	7.3	4.9
Eu	1139068	61856	5.5	6.8
Sm	764207	39410	6.6	1.2
Nd	776750	42228	1.7	1.1
Pr	677446	34731	6.8	2.3
Ce	889534	46908	4.0	3.5
La	909784	46225	1.5	2.7

1.3. Analyses

After complexation through Arsenazd I, the Lanthanides are analysed in 585 mm spectrophotommetry.

The limits of sensitivity are in the range of 10^{-10} moles for each ion. They may be improved either through realignment of the system or by employment of spectrophotommetry as an analytical technique.

Both possibilities are being investigated.

2. Study and realization of the probe

2.1. Design

The results gained from the laboratory study led us to redesign the drill-hole-incorporated tool.

From the prospects offered by chromatography, regarding both cations and anions, it may be inferred that the in-laboratory application of several gradients would allow a more complete analysis of the trace elements.

The high carefulness required for achieving the gradient makes it more relevant to proceed in laboratory. It is then possible to design a probe which, in lieu of a fractions collector, is made up of banks of chromatographic columns (cationic and anionic) used both for collecting and for preconcentrating purposes.

It would also be possible to multiply the spots for a more complete analysis.

A pumping system coupled to a permanent elution system would avoid the fixation of monovalent cations (the most numerous), permitting the saline load separation.

The process is under study.

2.2. Pumping system

The first probe realization stage consisted of studying such modifications of a chromatography pump as were necessary to meet drill-hole conditions.

Conventional chromatography pumps are designed for horizontal operation, whereas the drill-hole requisite is verticality.

The mechanical changes made necessary have been studied.

The tests for flowrate reproducibility in connection with the modifications of the dead volumes are in progress.

In the second stage, the electronics had to be modified commensurate to the limited electric power supplied via the conductor cable.

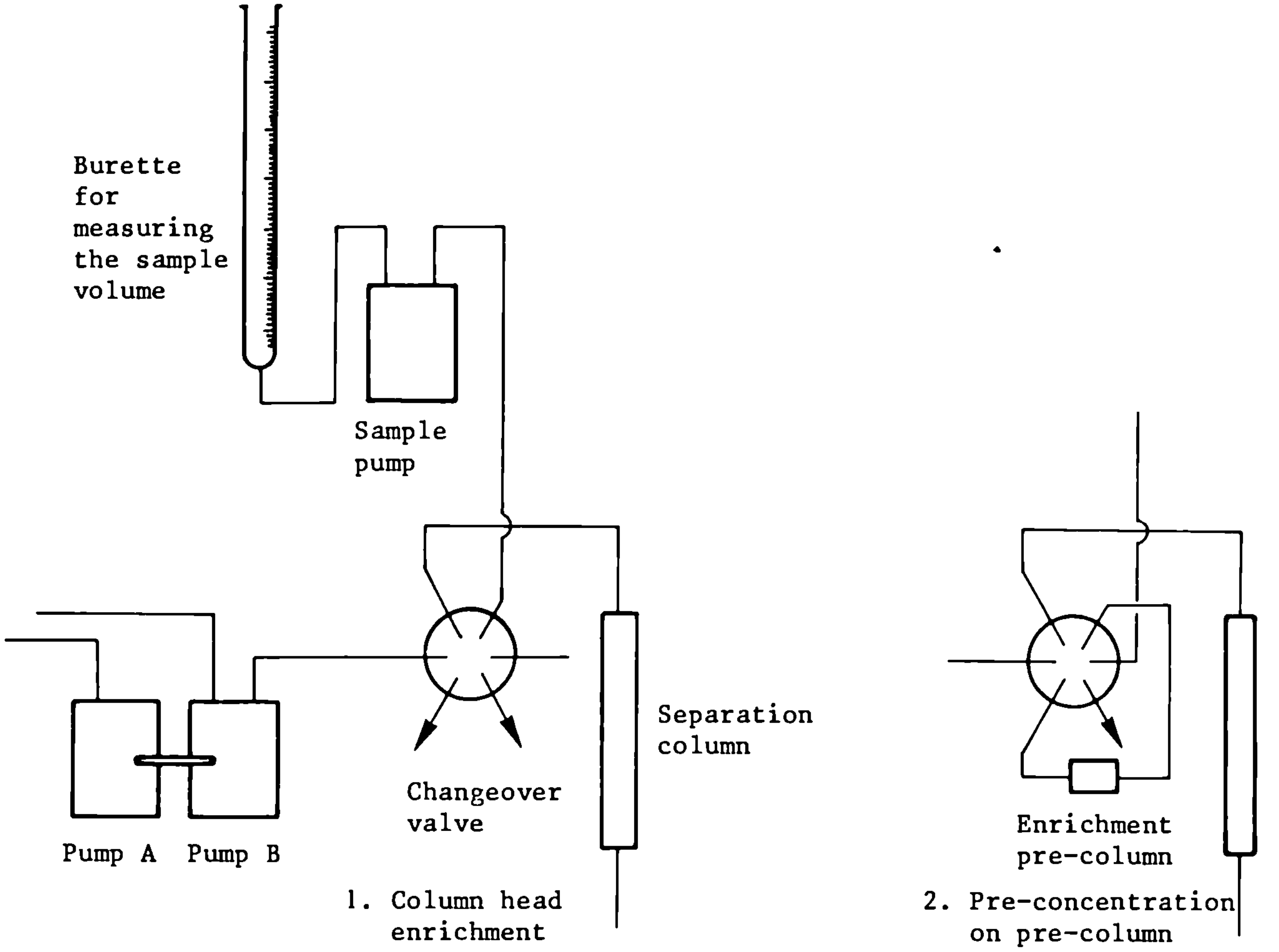
Now the pressure drop in the chromatographic columns calls for a far greater power value than is normally applied according to standards.

The first results, however, are very promising.

2.3. Next steps

Our commitment is now proceeding with the following matters :

1. In-laboratory study of the gradients applied to all trace elements.
2. Improvement of performance regarding the Lanthanides.
3. Final adaptation of the pump.
4. Improvement of the saline load separation.
5. Design of column banks for cation and anion collecting and concentrating purposes.



1. Column head enrichment

2. Pre-concentration on pre-column

Figure 1 - Modification of the injection system for preconcentration

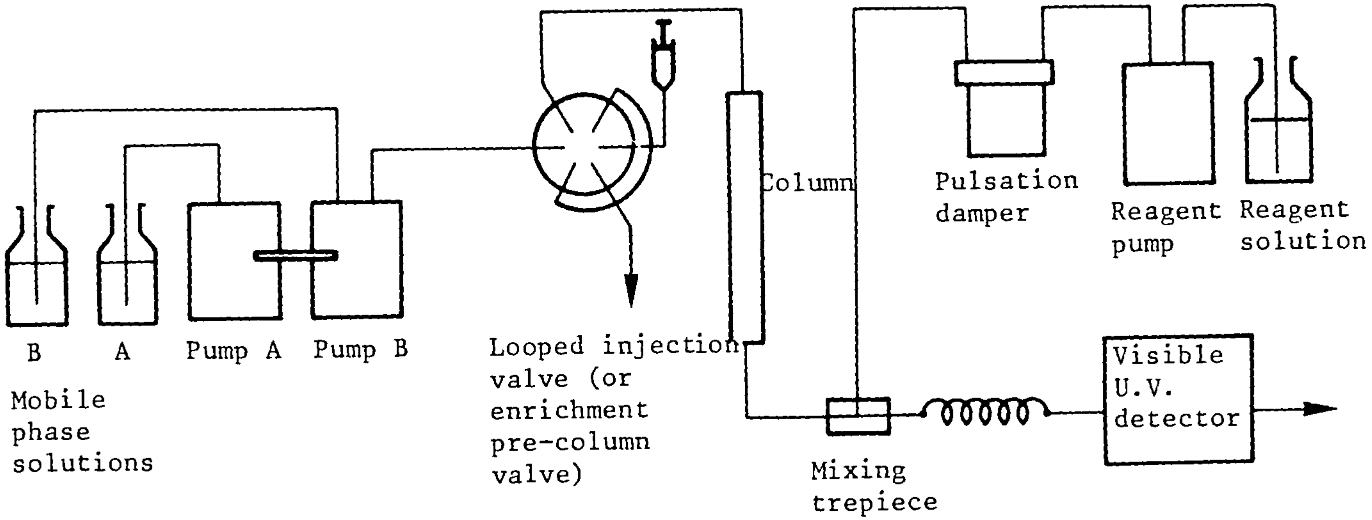


Figure 2 - Test setup schematics

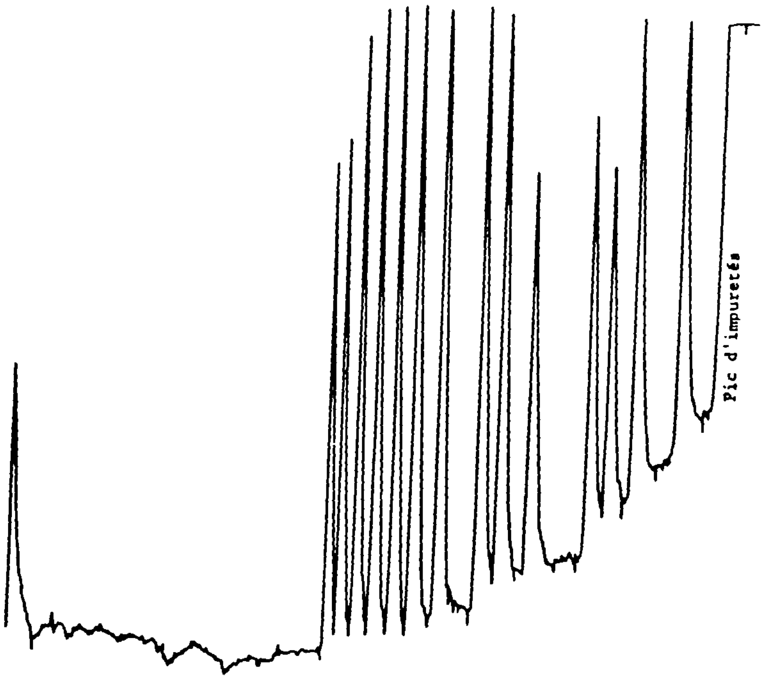


Figure 3 - Lanthanide elution on NUcleosil column
Gradient in two sections

The Detection and Measurement of Faults in Clay

Contractor: University of Exeter, Exeter, UK.
Contract No: FI1W-0088-UK (H1)
Working Period: September 1986 - August 1989
Project Leader: Dr. E.M. Durrance

A. Objectives and Scope

If faults occur in the rock mass surrounding a nuclear waste repository, there is a risk that the return of hazardous radionuclides to the biosphere will take place by migration along these zones of higher permeability. However, the detection and characterisation of faults is difficult, especially in soft rocks such as clay, and little development of techniques has taken place. The objective of this programme is to develop techniques that will be suitable for routine use in both the preliminary and detailed stages of site investigation. The approach used is based on the observation that faults act as zones of preferential migration in the natural degassing of the Earth. Soil gas exploration methods are applied to detect zones of anomalous gas geochemistry. The procedure followed is based upon samples obtained from a depth of about 0.5m along a series of traverse lines. Once a fault has been located, spiking of the high permeability zone from a borehole drilled to intersect the fault plane, will take place with specific gases of different compositions. The ground will then be resurveyed to determine the migration characteristics of the gas within the fault. Test sites in the UK and Italy are to be investigated in co-operation with BGS (Keyworth) and ISMES (Rome). BGS and ISMES are responsible for site selection and the drilling programme, but some trials will be conducted at sites near Exeter.

B. Work Programme

B.1. Equipment development.
B.2. Site selection.
B.3. Soil gas geochemistry.
B.3.1. Reconnaissance soil gas surveys measuring ^{4}He, ^{220}Rn, ^{222}Rn, O_2, CO_2 and some organic gases.
B.3.2. Detailed soil gas surveys of anomalous zones identified in the reconnaissance surveys.
B.3.3. Spiking of vertical boreholes and resurvey of soil gases.
B.3.4. Spiking of inclined boreholes and resurvey of soil gases.
B.4. Modelling and interpretation of results.

C. Progress of work and obtained results

Summary

The main effort has been in the development of a mobile laboratory for soil gas analysis at remote sites. This has involved the modification of a vehicle to house a ^{4}He mass spectrometer and its ancillary equipment. Electronic methods of O_2 and CO_2 analysis have been acquired and modified for soil gas work. An integrated system has been built to allow measurement of these gases with ^{220}Rn and ^{222}Rn. Minor alterations to the CO_2 analyser will permit analysis of some organic gases, but samples for CH_4 analysis must be returned to Exeter. Plastic syringes appear to be adequate for obtaining and transporting these samples. Special soil gas probes have also been built. Possible sites for trial surveys have been identified near Exeter. Literature review, database construction and the development of computer programmes for data presentation and processing are in progress. The programme is approximately on schedule.

Progress and results

The initial period of work has been devoted to items B.1., B.2. and B.4.

1. Equipment development (B.1.)

Analytical systems for gas analysis have been mounted in a vehicle suitable for remote site access. The vehicle now houses a ^{4}He mass spectrometer and associated pumps, transformers, inlet system and coolant storage facility. Provision to utilise mains electrical power from a supply near a remote site is available as an alternative to mobile generators. Electronic CO_2 and O_2 analysers have been modified and tested for use in soil gas work, and suitable housing constructed in the vehicle. An inlet manifold has been designed and built to enable sampling and analysis of ^{220}Rn and ^{222}Rn to be compatible with CO_2 and O_2 sampling. Analysis of some organic gases is possible by modification of the CO_2 analyser, but CH_4 must be analysed at Exeter. Trials have been run of suitable sample acquisition and transfer systems. Simple plastic syringes of the type used for rapid analysis of ^{4}He samples appear adequate for delayed CH_4 analysis. Soil gas probes suitable for integrated analysis of different gases have been designed and built. Minor modification of the vehicle construction has been necessary to accommodate the laboratory.

2. Site selection (B.2.)

A desk study of geological maps and reports has been carried out of possible sites in Dorset and Somerset, where the positions of faults cutting clay formations are known from nearby occurrences of displaced boundaries of other rock types. A number of such sites have been identified as suitable for trial surveys. Some assessment of faulted clay formations in Devon has been made in the field following a similar desk study. The geology of these areas is well known from detailed borehole information. The soil gas signatures in these areas are, as yet, unknown. Preliminary approaches have been made about access to the sites. Reconnaissance surveys should commence in February 1987.

3. Modelling and interpretation (B.4.)

A literature search of soil gas data has been carried out and a review is in preparation. Collation of soil gas results from different geological environments is taking place. Computer programmes for data presentation and processing are in the course of development.

Studies of disposal possibilities in geological formations : investigation in granite media

Contractor: CEA - Fontenay-aux-Roses, F
Contract N°: 127.80.7. WASF (avenant n°1)
Working Period: since december 1982 - february 1986
Project Leader: A. Barbreau

A. Objectives and Scope

Methodological and instrumental studies are still going on, following the geological studies of the Auriat deep exploration boreholes.
Aside from these, a new experiment has been undertaken on the "Thermo-Hydro Mechanical" behaviour of granite. This THM experiment aims at studying the variation of the characteristics in a large volume of granite under a thermal flux, at a depth of 90 to 100 meters below the ground surface. This volume includes a free surface of 10 m x 10 m and a thickness of 3 m.

B. Work Programme

B.1. Methodological and instrumental studies
B.2. Thermo-Hydro-Mechanical Experiment
B.2.1. Geological studies for preselection and selection of site
B.2.2. Excavation of the experimental room
B.2.3. Drilling of instrumentation boreholes
B.2.4. Emplacement of the gauges
B.2.5. Measurements
B.2.6. Interpretration with 2D and 3D codes

C. Progress of work - preliminary results

Methodological and instrumental studies

A borehole water sampler, electrically triggered from the surface, has been devised. It allows the collection at the surface of water samples, under the hydrostatic pressure of the sampling level. The methods previouly used at Auriat required clumsy transfer operations, from a sampler to a transport bottle.

The Auriat granitic body has been retained as an experimental site for the research of deep water outlets and the study of the deep water contribution to springs and rivers. Geochemical and isotopic analyses (^{13}C, ^{3}H, ^{18}O) have been performed, it is not yet possible to be positive as to the presence of waters of deep origin at the surface : the investigation area will be extended around the granitif body itself.

Fracturation studies on borehole walls require improvements on the optic camera. The "borehole televiewer" (Ultra sonic or acoustic televiewer) as tried in other countries (Canada, Switzerland) is being considered.

Chemical equilibriums in the deep underground waters depend on the pressure, on the temperature and on the minerals within contact either from the rock itself or from the fracture filling. When a water sample is brought to the surface, it is modified by the contact with the atmosphere and is no longer representative of the deep conditions. pH and Eh values as measured at the surface differ from those that prevail in the deep. pH and Eh probes have been made, allowing direct in-situ measurements of these parameters.

Thermo-Hydro-Mechanical experiment

The underground chamber site is situated 25 km NNE of Limoges. The experiment started with the structural exploration of the Saint-Sylvestre granitic body. This body has been subjected to extensive mining for uranium ore.

The IPSN experiments do not plan to prepare an underground repository in this area. The studied zones show a high density of fractures, the depth is shallower than 100 m from the surface. Furthermore, they are uranium rich and the reserves may not have been fully discovered.

Among several possible sites, the Tenelles mine has been chosen because of the fracture density, of water saturation and the easy access through a way shaft.

After that selection, a fracture study in the drift allowed the choice of the place which appeared most favorable for the experimental room.

Both sides of the drift were then explored by two cored boreholes (fig.1).

The South-East zone, cut-across by exploration borehole S'1, was finally selected on the basis of fracture orientation and density, with reference to the planned room floor.

Despite the presence of fractures with a permeability of 10^{e-7} m/s, it was not possible to measure water flows, so that water saturation remains dubious. Nevertheless, permeability measurement remain possible, so that changes in the aperture of the fracture will be evaluated.

The excavation work is now finished, and the installation of the heat source is under way. It will be placed below the center of the experimental room, at a depth of 3 meters (fig. 2).

It is made of 5 cyclindrical heaters, 1.5 m in length, placed at 30 cm form each other. They will be placed in 146 mm diameter boreholes drilled from a lateral drift. The total power output will be 1 kW.

The study of the effect of the dissipated heat in the rock volume encompassing the source, in all directions and specially in the ascending vertical way, up to the horizontal free surface (about 100 square meters) in the experimental room, requires the knowledge of the following physical parameters :

- temperature,
- deformation and displacement in the medium and at the free surface, on the floor of the room,
- mechanical stress in the medium,
- permeability (in boreholes),
- water pressure (if any),
- water flow on the room walls (if any).

Different probes will thus be distributed in the volume situated between the room floor and the heaters.

Measurements will be done during both the heating and cooling phases, each of which will last from one and a half to tow months, the duration of the whole experiment being from three to four months.

The position of the probes has been determined according to a theoretical preliminary study, showing the heat distribution in the medium :

66 (temperature gauges) will be placed as follows :

- 33 in the rock body
- 12 on borehole extensometers
- 19 on surface extensometers

Deformations in the rock body will be measured in boreholes equiped with extensometers : 3 such extensometers will be dused, made up of 4 displacement gauges each.

The measurement of surface displacements is important in this experiment, the aim of which is to simulate any possible deformation and displacements of the ground surface above a high-level waste underground repository. 18 automatically recorded surface extensometers will be used, plus 20 reference studs for manual measurements.

The displacement of the room walls will be measured by three dimensional triangulation with the help of an invar-wire distancemeter.

Conclusion

The different instrumental studies aim at completing the tools necessary for the characterization of the geological medium.

The THM experiment required geological studies at different scales (200 m in the drift, 50 meters in the boreholes, 2 to 3 meters on the room floor) allowing the control and quantification of the natural characteristics of the medium. The comparison of the results should allow an improvement of the structural methods of study.

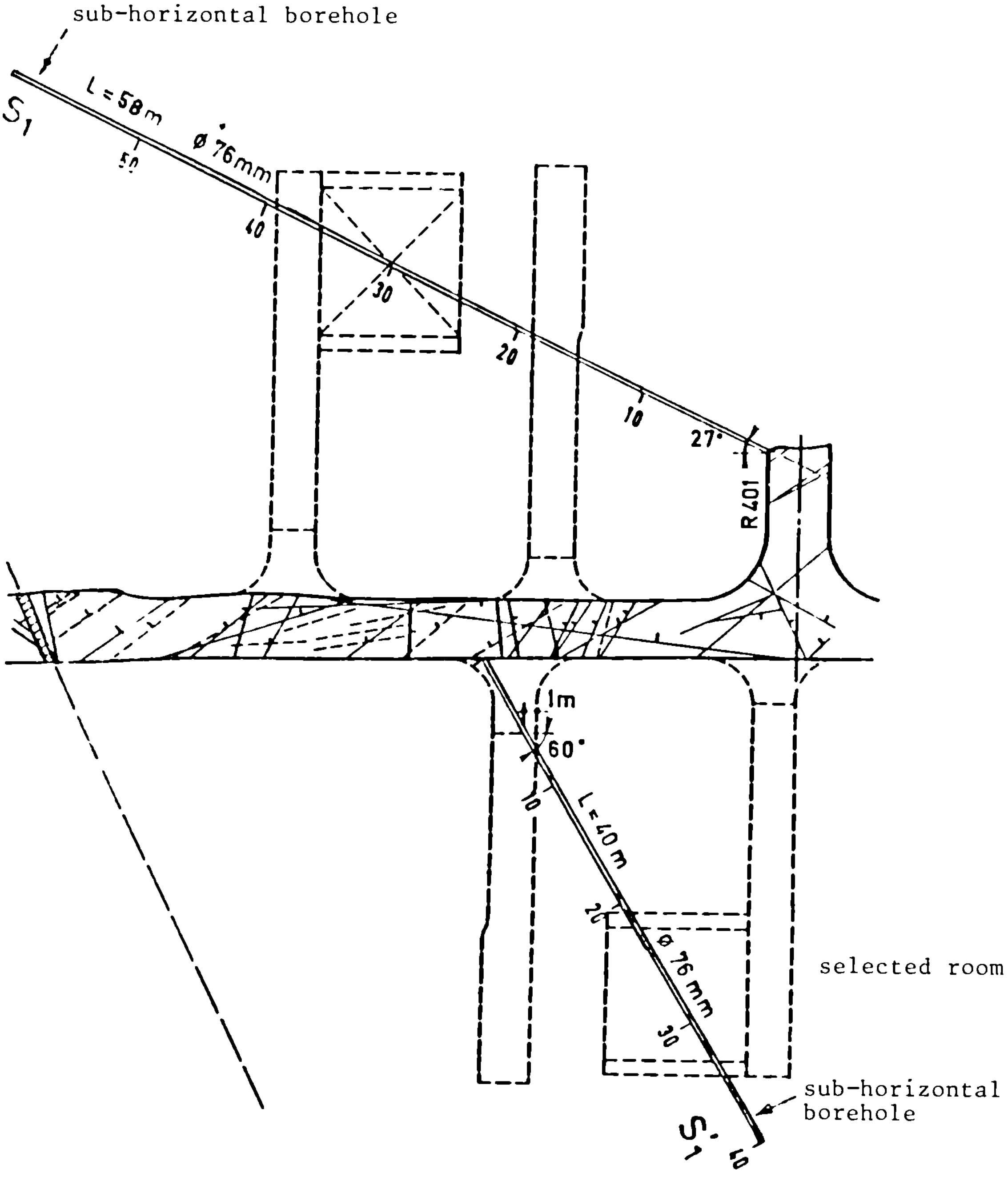


Fig. 1 - Location of the two sub-horizontal boreholes and and final site of the experimental chamber

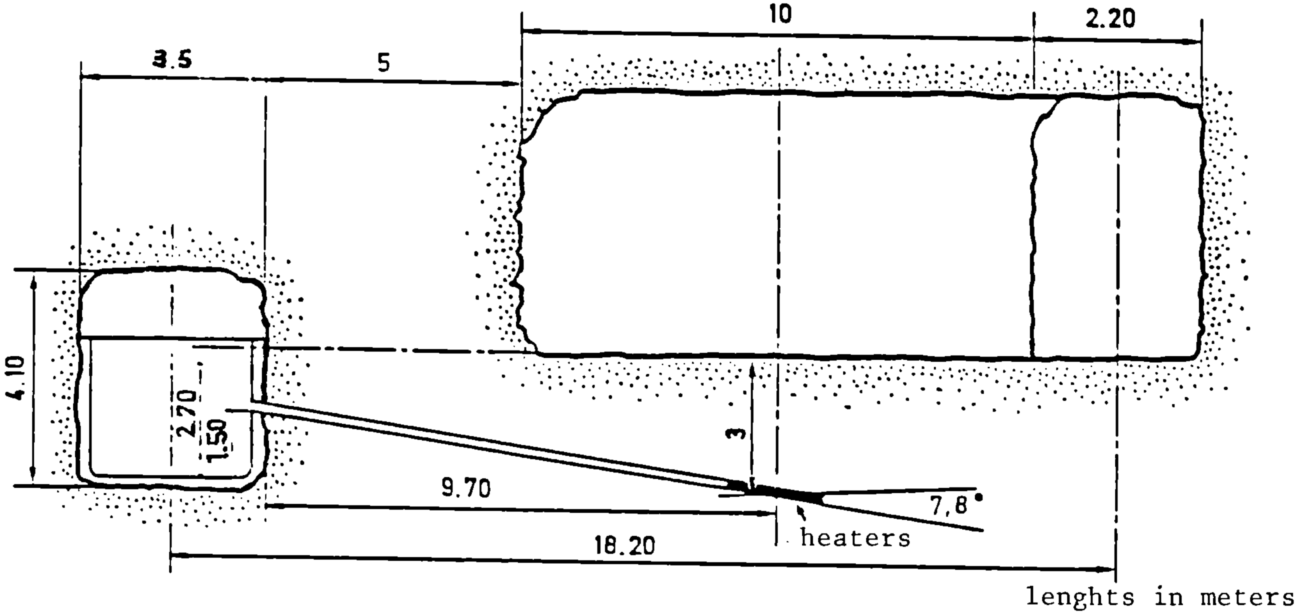


Fig. 2 - Selection across the experimental room and the service drift, showing the position of the heat source

Use of an Underground Cavity as a Test Facility for Radioactive Waste Disposal in Clays

Contractor: ENEA, CRE CASACCIA, ITALIA
Contract N°: 337 - 83 - 7 WASI
Working Period: Jannuary 1984 - December 1986
Project Leader: E. Tassoni

A. Objectives and Scope

Researches have been carried out by ENEA on the Italian territory with the aim of identifying a site suitable for a deep experimental laboratory in a clay formation.

During the tunnel excavation at the choosen site a set of measuring instruments is placed to record the stress changes and the strain behaviour of the clay rock. Moreover the structure of the rock mass and the nature of its discontinuities is described to obtain a more reliable basis for the interpretation of the results which will be obtained from the in situ tests.

Finally an heating experiment is carried out into boreholes drilled in the tunnel floor to record the variations induced in the surrounding clay by a simulated radioactive waste canister.

The final objective of this programme is to carry out a set of experiments under high lithostatic stress, like those in a future waste repository.

B. Work Programme

B.1 Surficial and deep geological investigations to identify local stratigraphy and structural elements.

B.2 Description of the discontinuities in the clay rock during the tunnel excavation.

B.3 Chemical, mineralogical and granulometric analyses on clay samples coming from the tunnel.

B.4 Geotechnical tests carried out on big clay block (30 X 30 X 30 cm) coming from the tunnel.

B.5 Microbiological study to ascertain the bacterial presence and activity in an ancient clay basin.

B.6 Measurements of total pressure and deformation in clay rock and of deformation in the tunnel lining during the excavation.

B.7 Heating experiment using an electric heater simulating the waste and instruments measuring the changes of clay physical parameters.

C. Progress of work and obtained results

State of advancement

During the 1986 the excavation of the tunnel in the Pasquasia mine has been completed. The discontinuities present in the clay rock have been described and several samples have been cut from the clay wall to carry out mineralogical, chemical, granulometric analyses and geotechnical tests which are running. During the excavation different geothecnical instruments, like total pressure cells, strain ganges, extensometers and steel bolts have been installed in the clay and in the tunnel lining to study the displacements and stresses caused by the tunnel excavation in the rock mass. A very preliminary layout of the heating experiment has been made and the suitable instruments are identified. Moreover the surficial investigations have been quite completed and the local stratigraphy has been defined. The general work progress status is as follows:

.B.1.,B.3 and B.4 are progressing normally
.B.2.,B.6 are completed
.B.5.,B.7 are lightly delayed.

Progress and results

B.1. Surficial and deep geological investigations

As a result of site selection studies ENEA decided to install the underground laboratory in a tunnel adjacent to the inclined access adit of the Pasquasia mine (potash salts) in Central Sicily. The Pasquasia mine is placed in the late Miocene Solfifera Series which outcrops in the central Sicilian Basin filled up with a huge quantity of plastic sediments and gravity slides varying in age from the middle Miocene to the Quaternary.The underground laboratory, 50 m long, has been located about 160 m below the surface in a Pliocene clay formation. The geological investigations have shown that, at the laboratory site, the local clay level has a vertical thickness in the range from 90 to 100 m. It is overlain by clayey sands of Middle Pliocene age and is underlain by marly Pliocene limestones (trubi). The contact between clays and "trubi", which is parallel to the clay and "trubi" stratification, dips approximately north with a variable inclination, averaging 18° at the laboratory site.

B.2. Description of the discontinuities in the clay rock

To carefully describe the discontinuities in the clay mass and their nature a description of the structure of the rock has been carried out during the excavation about every 2 m, with particular attention to some important parametres like orientation of joints or faults, as well as their spacing roughness aperture, filling and seepage.The description has been carried out both on the front and on the side-wall of the tunnel; about 300 discontinuities have been identified and described. The results of this work will be very important for the interpretation of future in situ experiments.

B.3. Chemical, mineralogical and granulometric analyses

During the excavation about sixty clay blocks (30 X 30 X 30 cm) have been collected . The following analyses have been carried out on each block:

- mineralogical analyses on the tout-venant and on the $<2\mu$ clayey fraction by means of X-ray diffractometry.
- clay water content (by weight) by drying the samples in oven at 105° C for about 24 hours.
- granulometric analysis by means of sedigraph apparatus.
- carbonate content (by weight) by means of apparatus for $CO2$ gravimetric determination

B.4. Geotechnical tests

Clay big blocks, sampled during the excavation, are tested in edometric and triaxial cells to determine the most important geotechnical parametres. The preliminary values of these parametres are as follows:

- undrained shear strenght	1-2 MPa
- cohesion	0.25 "
- friction angle	35°
- elastic modulus	98 MPa
- permeability coefficent	$2.5\ 10^{-12}$ m/sec

B.5.Microbiological study

The bacterial content of Pasquasia clay sediment will be directly counted by epifluorescent microscopy using a new method of concentration of the sample. At least three samples will be analysed under many replications to know if the bacteria are also present in Pasquasia deep clay sediments; in fact sediment bacteria, if present, are very important because they are involved in chemical trasformations of materials and their activity can determine both different chemical behaviour of radionuclides and anaerobic corrosion of steel structures in sulphate containing sediments.

B.6.Measurements of tunnel deformation

In order to determine the disturbance caused in clay by the tunnel excavation two instrumented sections have been installed at stations 18 and 36 m respectively. In these sections the following measurements have been carried out:

- clay displacement by means of multiple steel rod extensometres placed 6.5 m long boreholes.
- clay convergence by means of steel bolts, cemented at the clay walls.
- rib deformation by means of vibrating wire strain ganges
- radial pressure between clay and lining by means of total pressure cells.

B.7. Heating experiment

An heating experiment is being planned to study the thermal effects in the clay formation under high lithostatic stresses. The experiment will consist in embedding a multiple heater at a depth from 10 to 20 m under the tunnel floor. The dimensions of the cylindrical heater will range from 5 to 10 cm in diameter and from 2 to 4 m in height. The maximum specific power will be 500 KW/m^3 The annulus between the heater and the borehole wall will be filled up with a sealing material, like a mixture of cement and bentonite. Around the heater many different instruments will be placed at different distances ranging from 0.5 to 2.0 m. Temperature measurements will be carried out by means of thermocouples or thermoresistances, strain measurements by means of borehole probes able to measure three-dimensional displacements and pore pressure measurements by means of electric piezometres.

b) Geological repositories and barriers

Title : Study of backfilling and sealing materials for radioactive waste repositories : tests and controls on reduced scale disposal holes and galleries.
Contractor : Solétanche-Entreprise S.A.
6, rue de Watford
F - 92000 NANTERRE
Contract N° : FI 1W/0057/F
Duration of contract : February 1987 - March 1990 (38 months).
Project Leader : D. GOUVENOT

A. Objectives and Scope

- The purpose of this programme is to study rheological, thermal, microstructural and retention characteristics of backfilling and sealing materials. The formulation of these materials will be proposed by Solétanche and CEA;
- After laboratory tests, four of these materials will be selected and used into two vertical and horizontal scale models. Control tests will be performed on these models - during and after the backfilling to test the efficiency of the process;
- The first partner STMI (Société des Techniques en Milieu Ionisant) was replaced by the CEA (Commissariat à l'Energie Atomique).

B. Work Programme

B.1. Laboratory studies

B.1.1. Theoritical studies : proposition of 16 formulations of backfilling materials.

B.1.2. Preselection tests based on rheological characteristics (viscosity, rigidity, shrinkage, workability limit, bleeding).

B.1.3. Selection of 4 materials :

- rheological studies;
- studies on hardened materials : shrinkage, water content, permeability, resistance to aggressive water, behaviour at high temperature, retention of radioactive elements, microstructure.

B.2. Experimental studies

B.2.1. Vertical reduced scale models

Test on 2 identical models will be performed.

- studies of filling technique and instrumentation;
- control tests on fresh and hardened materials in laboratory and in situ;
- improvement of backfilling techniques.

B.2.2. Horizontal models

The same tests will be done on vertical models.

C. Progress of work and obtained results

The work will start on the 1st of February.
The schedule of the first part of the research is :

- February to March 1987 : theoritical studies and selection of 4 formulations.
- April 1987 : preparation of the samples for the further tests.
- May to July 1987 : mechanical characteristics determination;
  permeability test;
  ageing at 120°C.
- August to October 1987 : durability;
  thermal characteristics;
  microstructure.
- May to October 1987 : percolation and diffusion of radioactive elements
  • at CEA's facilities.
- November 1987 to January 1988 : lixiviation tests.
- August 1987 and January 1988 : interim reports.
- February 1988 : start of the second phase : construction of the scale models.

Research on backfilling and sealing of rooms and galleries in a repository in salt

Contractor: GSF/IfT, Braunschweig, FRG
Contract No.: FI1W/0059/D
Working Period: 01.09.1986 - 31.12.1989
Project Leader: Dipl.-Ing. W. Fischle

A. Objectives and Scope

Backfilling and sealing materials are to prevent resp. to delay the inflow of brine or water into a repository or to reduce the transport velocity of nuclides in fluids in case of a hydrogeological incident. The backfill also serves as a filling agent for voids and is to act as a mechanical stabilizer. Technical concepts are to be developed and also tested in situ under increased temperature conditions. The parts of the field into which radioactive wastes have already been emplaced by means of different techniques are to be sealed by bulkheads maintenance-free from those parts of the disposal field still in operation. The sealing systems being developed need to be tested in situ.

B. Work Programme

B.1. Soil mechanical laboratory investigations on gravity stowing to determine backfilling characteristics.

B.2. Geotechnical in situ measurements in the vicinity of chamber 8a, 532 m-level and in the backfilled carnallite stopes at the 750 m-level of the Asse salt mine to determine the interaction backfill/rock.

B.3. Performance of large-scale load consolidation tests on backfilling materials at the Asse salt mine.

C. Progress of work and obtained results

The focal point of the soil mechanical investigations on gravity backfill was to determine the load consolidation behaviour of the bulk material which accumulates in the form of pneumatic- resp. gravity stowing as a consequence of operational activities in the Asse salt mine or which is obtained during gallery mining using a part face heading machine.

As a result it can be said that

- settlement decreases with increasing charge density
- it increases with low load velocity
- settlement increases with increasing moisture content under the same bulk density conditions.

The average settlement rates of the inserted backfill subside relatively fast. During the initial months they range between 1.5 and 4 cm per month, later only between 1 to 3 cm per year.

An evaluation matrix to determine the material parameters of backfilling materials was set up and supplemented by an evaluation matrix for backfill according to technical, safety-relevant criteria.
This scheme is suited for a comparative evaluation of backfilling materials.

The southern lateral road to the east at the 750 m-level of the Asse mine, which had been backfilled over a length of 280 m with crushed salt, was sealed by a bulkhead during the months August/September. The salt concrete was composed of cement: fly ash: water: salt as 1 : 0.5 : 0.65 : 1.15 (wt.%). The flat cells in the roof area indicate that no compression has occurred so far.

The accompanying investigations on the consolidation behaviour of the samples, which were carried out after their 28 days storage in the mine, rendered the following characteristics: Density 1.01 kg/dm^3, E-module (dyn.) 26.02 GPa, compression module (dyn.) 0.2, uniaxial compression strength of cube 30.41 MPa, compressive strain 1.47 %.

A measurement apparatus was developed which enables determination of the permeability of these materials to brine or other liquids supplementary to the laboratory investigations on backfilling materials; the experimental platform has been set up at the 490 m-level. The permeability added values found by means of these tests are compiled in Table 1.

The geotechnical measurement instrumentation has been completed in the course of backfilling of chamber 8a, 532 m-level. The maximum values to date for the pressure build-up in the pillar left for support range at 2 x 10^6 Pa (parallel to strike) in E/W-direction and 4.5 x 10^5 Pa (cross-cut) in N/S-direction. The deformations of the pillar, which are measured using extensometers, are negligible. They range within 0.5 to 1 mm per year.

List of publications

HÄNSEL, W., Laboruntersuchungen nichtsalinarer Versatzmaterialien am Beispiel der Schachtanlage Konrad, GSF-Bericht T-249

KAPPEI, G., Geotechnical Investigations on Backfill Materials in the Asse Salt Mine, GSF-Bericht T-250

KAPPEI, G., Activities Concerning Plugging and Sealing in the Asse Salt Mine, GSF-Bericht T-251

KAPPEI, G., Federal Republic of Germany/Backfilling and Sealing Program Outline, GSF-Bericht T-252

Table 1: Results of permeability tests on the experimental setup to determine the permeability of backfilling and sealing materials

Sample	Pore Volume n (%)	Permeability added value k (m/s)
Solid rock salt	0.5	$7,0 \times 10^{-11}$
rock salt grit (solidified/compacted with 300 bar)	16.0	2.7×10^{-6}
rock salt grit (solidified/compacted with 600 bar)	12.4	5.2×10^{-7}

Study of the thermal behaviour of clay-based buffer materials on reduced scale mok-ups and in underground laboratory

Contractor: CEA - Fontenay aux Roses
Contract N°: FI1W-0061 F(CD)
Working Period: July 1986 - December 1989
Project Leader: M. DARDAINE

A. Objectives and Scope

Clay material could be used as components of engineered barriers put in place between high level waste canisters and host rock.

The purpose of this work is to compare the behaviour of different types of materials, homogeneous or mixed, simultaneously submit to thermal and humidity gradient. Only the early stage of the storage, the so called "dried stage" is simulated in this work.

The instrumental study requires at first the design and construction of an experimental device to reproduce the actual physical conditions of the waste disposal : temperature and water content. In a second step, in collaboration with CEN/SCK, an in situ heat transfer experiment will be carried out in MOL underground experimental facility. An electrical heater will be surrounded with buffer and backfill materials. The whole system will be instrumented with temperature, moisture and pressure sensors. The test will be supported by heat transfer modelling.

B. Work Programme

B.1. Research and Development of water content sensors :
  - thermal sensor
  - capacitive sensor.

B.2. Design and construction of an experimental heat transfer device. Experiments and modelling.

B.3. Properties of backfill materials, determined in the underground experiment facility at MOL (Belgium). In situ experiments of heat transfer and modelling.

C. Progress of work and obtained results

State of advancement

The heat transfer study of highly compacted clay materials used as engineered barriers begins with the research and development of small scale sensors for in situ water content measurements.

Two kinds of sensors are preliminary choosen because the physical phenomena they measure strongly depend on the water content of the studied material. It concerns a thermal sensor for thermal conductivity measurement and a capacitive sensor for the dielectric constant measurement.

After calibration, these sensors may be able to give local values of the water content and so, allow water profile determination in order to estimate the existence of water migration into the clay material due to thermal gradient.

Study concerning the adjustment of the thermal sensors is going forward and leads, in collaboration with Institut de Physique du Globe (University of PARIS VI), to the construction of prototypes for preliminary measurements. The development of capacitive sensors, in collaboration with Laboratoire Central des Ponts et Chaussées (PARIS) is at the beginning.

A testing cell is under operation to test each kind of sensor in clay materials under actual conditions of temperature, pressure and water content.

The second part of the study concerns the heat transfer device project for which all the technical specifications and construction drawings are now defined.

Presently two preliminary heat transfer experiments are undertaken on medium sized cylindrical crowns of highly compacted clays to get practical informations concerning their thermal behaviour.

Progress and results

- The thermal sensor (see fig. 1)

  The thermal sensor consists of a copper wire used as electrical heater and a thermistance which gives temperature value through resistance measurement. Both copper wire and thermistance are introduced in a hollow stainless steel needle and connected inside a plastic head respectively with a stabilized alimentation and a multimeter.

  The sensor is able to measure at transient state, the thermal conductivity of a material in which it is immersed. In practice, it is put in place in an hole previously drilled in the material. When voltage is applied, the needle transmits an heat flow by unit of length Q (W/m.s) through the material, the temperature $\theta(t)$ of which increases as shown in fig. 2.

  A study by monitoring several parameters is undertaken to estimate the influence of the needle calorific capacity, the connection resistance at the needle-material interface and the thermal conductivity of the material, on the time at which the linear relationship $\theta = f(\ln t)$ is valid. In all cases it is shown that this time never exceeds 50 seconds.

  The first measurements implemented with prototype sensors give encourageing results. At present time, their limited number does not allow to definitly conclude on this process reliability.

- The capacity sensor

  Several methods exist for the determination of material dielectric constant. In general, they consist of capacity measurement of a condensator including the material and two electrodes which form the sensor.

  The work program consists at first in choosing among methods for measuring capacities of condensators which are the more suitable for clay materials.

Simultaneously, preliminary measurements of capacities are carried out on highly compacted clay samples at various densities and water contents. A Q-meter is used to estimate experimental relationships between these previous parameters.

A cell is manufactured which allows to submit a highly compacted clay sample to different temperatures, pressures and water contents. At the bottom of the cell are placed an electrical heater and an hydration pipe connected to a water tank. The diameter of the sample is ten centimeters and it is 20 cm high.

At the top of the cell, there is a stress sensor for measuring the swelling pressure which appears during the sample hydration.

On the walls of the cell are placed several tight outlets across which it is possible to introduce thermocouples. One of them is specially designed to introduce a thermal sensor.

Heat transfer study through highly compacted clay materials

Two simple experiments of heating medium sized crowns of highly compacted clays (external diameter = 230 mm, height = 170 mm) were carried out respectively during 4 and 147 days.

In the two cases a pseudo-stationnary state appears for which the temperature near the heater increased respectively up to about 110°C and 80°C. During the tests, bulk density measurements are undertaken along a radius by a gamma densitometry method. Thus it is possible to calculate the corresponding water content variations. It is shown that during the experiments the water content sample variations are only due to water evaporation process.

The main technical specifications of the heat transfer device (see fig.4) are now defined. The material consists of an assembly of three cylindrical crowns (total height : 800 mm, external diameter : 340 mm, internal diameter : 80 mm). The heater includes three independant parts with a total power of 2400 watts.

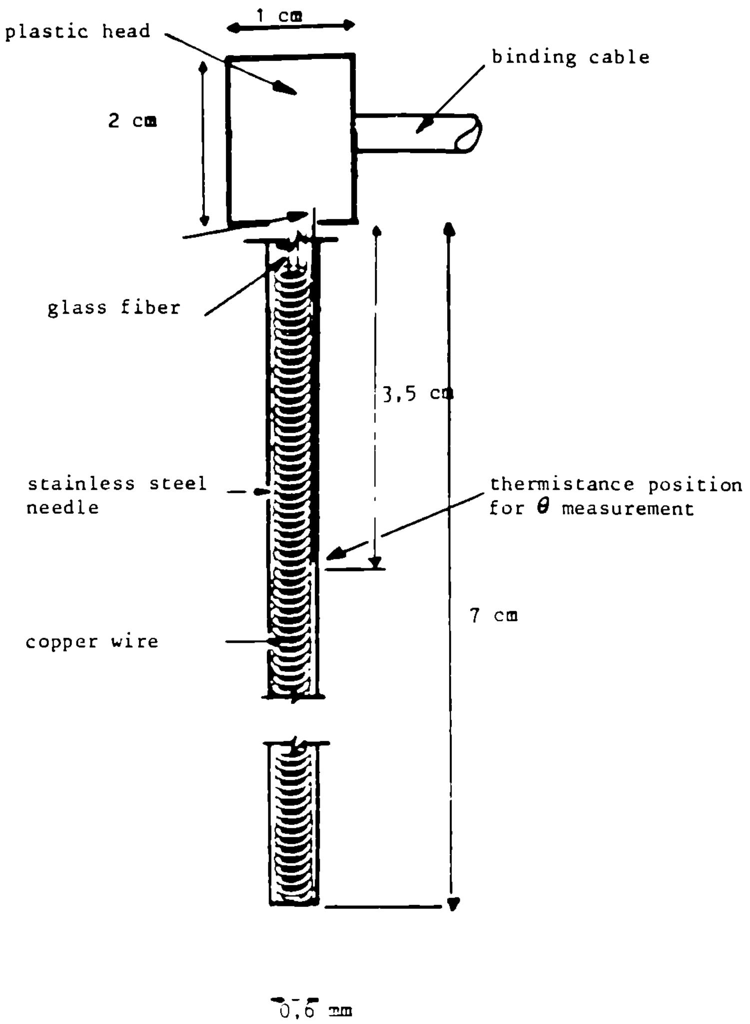
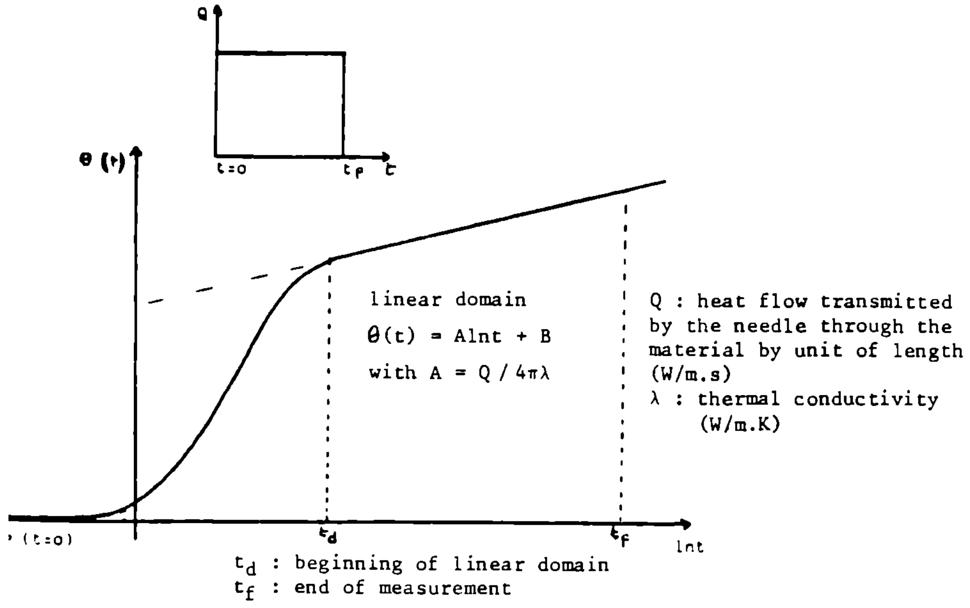


FIGURE 1 : SCHEMA OF THE THERMAL SENSOR PROTOTYPE



$\theta(t) = A\ln t + B$

with $A = Q / 4\pi\lambda$

Q : heat flow transmitted by the needle through the material by unit of length (W/m.s)

λ : thermal conductivity (W/m.K)

t_d : beginning of linear domain

t_f : end of measurement

FIGURE 2 : EXPERIMENTAL RELATIONSHIP BETWEEN TEMPERATURE INCREASE AND TIME.

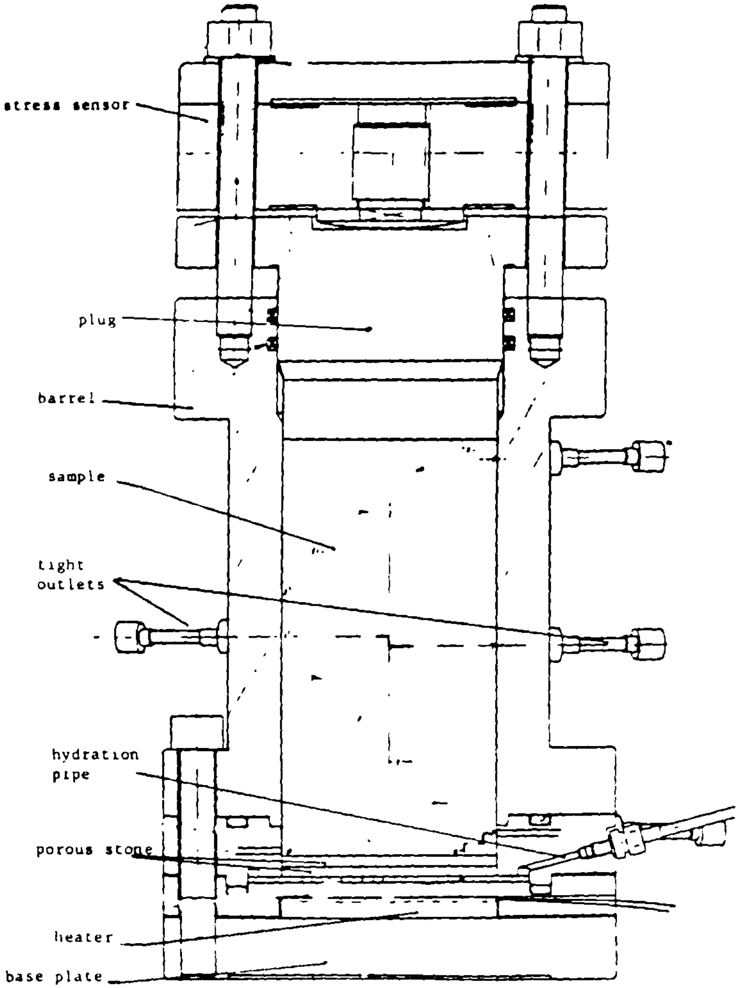


FIGURE 3 : SENSOR TESTING CELL

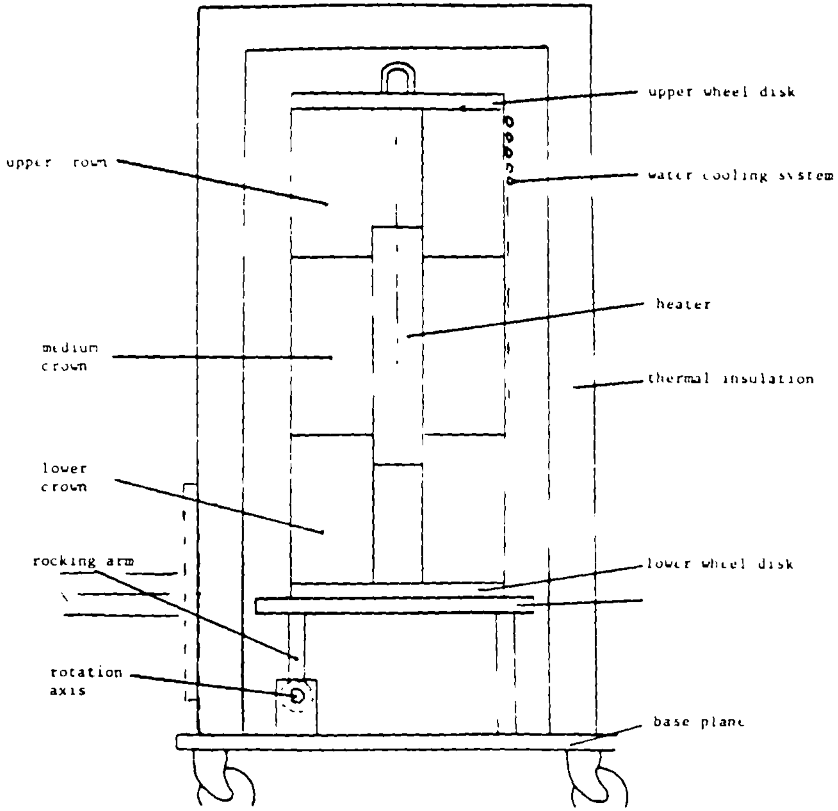


FIGURE 4 : HEAT TRANSFER DEVICE - SCHEMA PROJECT

c) Radionuclide migration in the geosphere

In Situ Determination of the Effects of Organics on the Mobility of Radionuclides in Controlled Conditions of Groundwater Flow

Contractor:	British Geological Survey, Keyworth, Nottingham
Contract No:	FI1W/0064/UK
Duration of Contract:	July 1986 - June 1989
Project Leader:	G.M.Williams

A. Objectives and Scope

The broad objective is to verify by means of *in situ* field tracer tests, predictions of the mobility of radionuclides in a shallow glacial sand aquifer, having taken into account the potential effects of organics (natural and introduced) on radionuclide speciation and mobility.

The tracer tests will be undertaken in a remote part of the low level radioactive waste site at Drigg. Prediction of their outcome is based upon detailed hydraulic characterisation of the field site, coupled with laboratory studies of radionuclide sorption and organic complexation. Liaison has been established with the University of Wales Institute of Science and Technology for radionuclide speciation modelling, Loughborough University for direct speciation measurements, and the Delft Soil Mechanics Laboratory for solute transport modelling.

B.Work Programme

The project is divided into a number of research areas as follows:-

(1) Aquifer characterisation and instrumentation - Involves the determination of aquifer hydraulic properties, its geochemistry, mineralogy and groundwater composition, particularly the nature and amounts of natural organics (humic and fulvic acids) and colloids. Development of instrumentation to monitor groundwater composition and radionuclide migration.

(2) Characterisation of complexes and colloids - interlaboratory comparison within the CEC, to characterise, and determine stability constants with selected radionuclides, for commercially available humic acid and natural organics from Drigg, Mol, Ispra etc. A parallel excercise is underway for colloids.

(3) Laboratory sorption studies - will include batch sorption experiments to determine the effects of natural organics on radionuclide sorption, kinetic measurements, and direct speciation determinations attempted on radionuclides in groundwater after equilibration with the sediment.

(4) Modelling - Speciation models will be used to predict the speciation of radionuclides in the sorption experiments and help to determine the important mobile species in the field test. Deterministic flow modelling will aid in the design of the borehole array for the tracer tests and form a basis for reactive mass transport models.

(5) Field tracer experiments - initial tracer tests will compare various conservative tracers (^{131}I, Cl, and ^{3}H) and provide background data on the hydraulic characteristics of the aquifer. Subsequent tracer tests will involve reactive radionuclide species with the addition of organic solutes.

C. Progress of work and results obtained

State of advance

The project is now underway and a suitable field location has been identified for the tracer array. Groundwater and sediment samples have been obtained for preliminary laboratory analysis and for speciation studies and characterisation of natuaral organics. Progress has been made on the characterisation of the Aldrich Humic acid as part of the COCO study. Laboratory sorption experiments have been started along with preliminary groundwater flow modelling. Capital equipment has been ordered and borehole instrumentation designed and prototypes contructed.

Progress and results

(1) Aquifer characterisation and instrumentation (B1)

The area of the test has been characterised using a specially developed narrow diameter focussed resistivity probe. Over twenty profiles have been recorded to an average depth of 8m on a regularly spaced 3m grid and the detailed morphology and electrical resistivity of the aquifer determined. The sand aquifer is interbedded between two continuous clays, and although the sand varies in thickness and elevation, a suitable area has been identified for construction of the array. A laboratory resistivity cell to correlate resistivity with porosity has been constructed and preliminary results are available.

Specialised drilling techniques using an internally flushed blanked well screen have been developed to eliminate outside disturbance around fully penetrating water injection and tracer release wells. Stainless steel multilevel probes, and a compatible coring device have been manufactured to obtain groundwater and sediment cores at monitoring locations. Of a more practical nature, two portacabins have been set up as a radiochemical field laboratory and office/mess room with electrical power and water supplies.

(2) Complexes and colloids (COCO excercise, B2)

Humic material has been removed from a 250l bulk sample of groundwater using a DEAE resin (Diethylaminoethylcellulose). The absorbed humics are desorbed by elution with 0.5 M NaOH. A field system has also been developed to speciate ionic from organically complexed material in groundwater by passing samples through a series of three columns containing DEAE cellulose, a cationic resin and finally an anionic column.

Work on the COCO exercise using the Aldrich Humic has involved the analysis of major and trace metals (which gave good agreement between ICP-AES and AAS methods) and the determination of E_4/E_6 ratios which indicate the proportion of aliphatic to aromatic components (5.31 and 5.35 on two separate samples). An infra-red spectrum has also been obtained which shows absorbance at 2850 and 2920 cm^{-1} which has been used in one method of humic classification. Other work recently initiated includes the determination of functional groups (hydroxyl, carbonyl, phenolic and carboxylic). Potential organics to be considered in the experiment are acetate (breakdown product of cellulosic materials in the waste) and EDTA (used as a decontaminant) so GC and ultrafiltration methods for their analysis and that of their degradation products are being developed.

As part of the colloid sampling intercomparison excercise groundwater was taken in January 1987 from a public supply borehole at Markham Clinton in Nottinghamshire, using ultrafiltration equipment. Analyses are not yet available.

(3) Laboratory sorption studies (B3)

Detailed plans for the laboratory work have been formulated and work is underway but there are no results to report to date. A contract has been let to Loughborough University for speciation work commencing January 1987.

The behaviour of ^{85}Sr, ^{60}Co, ^{137}Cs and ^{131}I will be studied in batch experiments under a range of experimental conditions, to try to elucidate the effects of both natural and anthropogenic organic compounds on radionuclide sorption. Initially all experiments will be carried out under aerobic, atmospheric conditions, using subsamples of the bulk 'standard' sand, silt and groundwater. The first matrix of experiments will be based on the scheme on table 1.

Each batch sorption test will be performed in triplicate to enable the calculation of distribution coefficients (R_d's), on which some confidence can be placed. In selected cases isotherms and reaction kinetics will also be measured. The rock/water system will be fully equilibrated before the addition of the radionuclide spike. All fluid samples will be ultrafiltered, prior to radiometric analysis, using an Amicon ultrafiltration cell with a filter cut-off of ≤500 Daltons MW, and both the filtrate and unfiltered sample analysed. Once samples are prepared for counting on the Philips PW 4580 batch gamma-counter, acidification will be used where appropriate to stabilise the samples. Information gained from this series of experiments will be used to design the in-situ field tests.

Table 1

WATER	Natural	Minus HA†	Natural & ÷†Org.	Minus HA & Org	Natural & Org	Minus HA&Org
			Equilibrated*		Unequilibrated**	
ROCK						
Natural Sand	X	X	X	X	X	X
Sand Minus HA	X	X	X	X	X	X

†Minus HA - natural organics removed by alkaline extraction (sediment) or adsorption by DEAE cellulose (water)

††Org is either acetate or EDTA added to natural groundwater

*Equilibrated - radionuclide spike and 'organic' pre-equilibrated in water to allow complex formation before exposure to sediment

**Unequilibrated - 'organic' added in sorption experiment after exposure of radionuclide to sediment/water system

(4) Modelling (B4)

Details of the modelling work have been agreed with UWIST and a sub-contract has been let. No detailed work has yet been undertaken.

(5) Field tracer experiments (B5)

A safety case has been submitted to the relevant authorities for permission to undertake tracer tests in spring '87. Formal permission is still awaited.

Development and application of a retention properties measurement system in a geological environment using radioactive tracers in the drill-hole (self-contained probe FORALAB)

Contractor : CEA/IPSN - CEN CADARACHE - F 13108 Saint Paul lez Durance
Contract N° : FI1W 0065
Working period : 36 months
Project Leader : J. Porcheron

A. Objectives and Scope

Radionuclides from a subterraneous waste storage place have to force their way through, and interact with, several barriers prior to reaching the geological medium itself.

They are diluted by the subterraneous water which, by modifying their chemical structure, settles them into a final balance with the medium.

The purpose of this study is to determine the delay term of the radionuclides during their migration through the deep geological environment.

It became evident that it was preposterous to attempt in-laboratory duplication of the prevailing parametric conditions of the natural medium, whether physical, chemical or biological.

To avoid the uncertainties connected to laboratory experiments, the probe "FORALAB", whose performances had already been ascertained during the preceding contract (WAS 3/7-83-7 P), was developed to permit studying the radionuclide sorption-desorption phenomena in a geological environment in a condition of equilibrium with undisturbed subterraneous waters.

The probe need not simulate the environment as it is plunged into it.

The contract scope is the "in-situ" qualification of the probe, using a dual tracing system, i.e. Tritium and Eu on the one hand, Pu and Np on the other hand.

The probe will then be operated in 3 geological sites, of some interest for the Community, i.e. AURIAT (granite), MOL (clay) and GORLEBEN (salt), in order to assess the containment properties of these environments.

The probe is essentially composed of a pump, a syringe, a 20 mm dia., 200 mm long test column and 40 sampling pots. Its double insulation is a safety against drill-hole pollution.

B. Work Program

B.1. Probe Qualification

The probe will be checked for performance in the hole drilled in the granitic site of AURIAT.

The column, filled with Fontainebleau sand, will be traced by means of Europium and Tritium.

The drill-hole water will be circulated in the column for one day before the tracer injection.

B.2. Tests on the Reference Sites

The tests will be performed in the deep holes at AURIAT, MOL and GORLEBEN.

The columns will be filled with a mixture of Fontainebleau sand and 1 to 3 % clay from the site.

The radionuclides used will be Am, Pu and Np.

Each column will be Tritium-calibrated before each individual test.

B.3. Finally the results from each individual test will be mathematically processed to yield the delay terms and the adsorption isotherms of each pollutant used.

C. Work Progress and Results Obtained

C.1. State of Advancement

The probe is presently up-to-80 % achieved.

The various stages have already been tested, first individually, then jointly.

The dependability of the various components was the principal matter of concern of the tests which simulated tracer injections under a pressure of 150 MPa and tracer collection in the fraction collector.

The test results showed that the system and its components had performed in a reliable and reproducible way but the peristaltic pump showed itself unreliable : its stability of operation during the test period could not be kept under control.

Consequently, another device had to be used ; that is, a piston pump as currently used in high pressure chromatography. Such pump was found appropriate after ascertaining its reliability, and is now being incorporated.

The various stage interconnection pipes, fitted for the tests, were flexible with a view to future modification. They are now replaced by metal pipes, as was contemplated.

The Laboratory truck has been delivered.

C.2. Prequalification Test

A test under 100 MPa is now under way.

This test consists of injecting Tritium-traced water into a column filled with Fontainebleau sand (0.25 mm grade). The actual working speed is 3.10^{-3} cm.s^{-1}.

The test, which is manually controlled, will encompass the entire experiment, including the mathematical processing of the column response.

The water is circulated by a high pressure pump similar to that to be installed.

The Role of Organics in the Migration of Radionuclides in the Geosphere

Contractor: Risø National Laboratory, DK
Contract N°: FI1W/0066
Working Period: July 1986 - December 1987
Project Leader: Lars Carlsen

A. Objectives and Scope

A review on the possible role of organic species in the ground water on the migration behaviour of radionuclides in the geosphere is required. Considerable amounts of data are available. They are, however, rather scattered throughout the literature.

An experimental study as well as theoretical considerations in the influence of organic complexing agents on the sorption, and hence migration behaviour of radionuclides are of fundamental interest in attempts to evaluate the possible transport of released radioactive waste with ground water.

Characterization of naturally occurring organics, e.g. humic and fulvic acids is of general interest due to these polymeric species omnipresence in the terrestrial environment and to their known complexing abilities towards metal ions.

B. Work Programme

B.1. Review of available literature on the influence of organic compounds including experimental and theoretical data obtained at Risø
B.2. Batch-type experiments to elucidate the influence of organics on radionuclide sorption
B.3. Column-type experiments to elucidate the influence of organics on radionuclide migration
B.4. Theoretical study to elucidate the effect of complex formation on radionuclide migration
B.5. Participation in the joint programme on characterization of humic acid samples

C. Progress of Work and Obtained Results

Summary

Preparation of the review paper is in progress. The major part of the available literature has been collected. Valuable informations has been obtained through personal contacts to institutes in the United States.
A series of batch-type experiments has been carried out, demonstrating decreased sorption as function of increased ground water ionic strength as well as increased organic ligand concentrations. EDTA and citric acid have been chosen as models for possible ligands found in ground waters. Eu(III) and Co(II) have been used as models for the possible radionuclides.
Column-type experiments have not yet begun.
Theoretical studies visualize enhanced mobility of radionuclides in the presence of complexing agents. Studies on equilibrium reactions have begun. Sofar only one humic acid sample (the sodium salt of a commercially available humic acid) has been received. The analyses are in progress

Progress and Results

1. Review (B.1.)

Based on conventional literature search as well as personal contacts the major part of the relevant literature has been collected. A selection of otherwise only with difficulty accesible reports was obtained through visits at Battelle Columbus and Battelle Northwest laboratories. Valuable personal contacts to research groups activily working in the field of organics in the terrestrial environment and their influence on radionuclide migration were connected. The planning of the report has been carried out. The report will include sections on 'organics present in the geosphere' (naturally occurring as well as artificially introduced), 'the behaviour of organics in the geosphere' (stability, decomposition, migration), 'complex formation with radionuclides', and 'influence of organics on the radionuclide sorption/migration'. Experimental results obtained in this lab will be included in the last section.

2. Experimental and Theoretical Work (B.2., B.3., B.4.)

Batch-type experiments for model systems have been carried out. These systems have used a Dowex50 ion exchange resin as the solid phase to mimic e.g. the well established ion exchange capacity of clays. The 'ground water' systems have been mixtures af NaCl and $CaCl_2$, the total concentration being varied in the range of 0.1 to 0.001 molar. The molar fraction of calcium was studied in the total range, i.e. 0.0 to 1.0 in steps of 0.1. We studied the sorption of cobalt (as model for the transition metals) and europium (as model for the rare earth elements as well as the trivalent actinides). The radionuclides were present in concentrations of approx. 10^{-7} molar. EDTA and citric acid were studied as representatives for naturally occurring low molecular organic acids (citric acid) and artificially introduced complexing agents (EDTA), respectively. The concentrations of the ligands were varied in the range of 10^{-8} - 10^{-3} molar.
The experiments were carried by rippling approx. 1 gr. of the ion exchange resin (equilibrated with the 'ground water') with a portion of the ground water containing the appropriate radionuclide and the ligand in the appropriate concentration. The distribution coefficients were determined by gamma-counting, both the liquid and the solid phase being analyzed.
As mentioned above decrease in the distribution coefficients was observed upon increase in the ground water salt concentration in agreement with our previously obtained results /1/. On increasing the ligand concentration a pronounced decrease in distribution coefficient was noted, the effect of

EDTA being significantly more pronounced than for citric acid, which was expected based on the complexity constants /2/. The more interesting feature to be noted was that even at ligand concentrations as high as 10^{-3}, i.e. 3-4 orders of magnitude above that of the radionuclide, a distribution coefficient different from zero could be calculated. Hence, even in the presence of rather high amounts of ligand, minor sorption could be detected. However, these effects may not necessarily be refound by coulumn-type experiments, which will be carried out in the comming period.
The theoretical work has been carried out by application of the COLUMN2 computer code, developed at Risø /3,4/. Assuming the decreased sorption of the complexed species the enhanced migration could be demonstrated. Preliminary studies on equilibrium systems /4/ strongly suggested that terms as effective retention factors and average elution times have to introduced in order to explain migration behaviour.

/1/ BO, P., and CARLSEN, L., Eur.Appl.Res.Rept.-Nucl.Sci.Technol. 3, 813-873 (1981)
/2/ NILSSON, K., JENSEN, B.S., and CARLSEN, L., ibid. 7, 87-148 (1985)
/3/ NIELSEN, O.J., CARLSEN, L., and BO, P., Risø National Laboratory Report Risø-R-514 (1985)
/4/ CARLSEN, L., NIELSEN, O.J., BO, P., and DITLEVSEN, C., Risø National Laboratory Report Risø-M-2533 (1985)

Actinoide migration phenomena in groundwater: colloid generation and complexation with natural organics

Contractor: Institut für Radiochemie, TU München
Contract No.: FI 1W/0067
Duration of contract: Sept. 1986 - Dec. 1989
Project leader: J.I. Kim

A OBJECTIVE AND SCOPE

Various geochemical processes may govern the migration of actinides in deep geological aquifer systems: hydrolysis reaction, redox reaction, complexation with inorganics as well as organics and colloid generation. Experience suggests that the colloid generation and complexation with natural organics, e.g. humic substances, appear to be the significant geochemical phenomena with regard to actinide migration in many different aquifer systems.

The contract research deals, therefore, with the colloid generation of representative actinides and their complexation with natural organics, particularly humic substances in different groundwaters. The results are expected to give an insight into the migration mechanisms of actinides in the geosphere.

B WORK PROGRAMME

B 1. Actinide colloid generation in groundwater

- Characterization of colloids
- Generation mechanisms of actinide pseudocolloids
- Quantification of colloid generation as a migration medium for actinides

B 2. Actinide complexation with natural organics

- Characterization and complexation study
- Humic substances as organometallic colloids
- Mobility of complex species and colloids in aquifer systems
- Quantification of actinide mobility by humic substances

B 3. Interlaboratory comparison exercise on complexation with natural ligands (COCO-group: TUM, CEN/SCK, KUL, CEA-FAR, Risø Nat. Lab., BGS, IRC-Ispra)

- Intercomparison of characterization methods
- Separation and production of natural humic acids present in the reference sites
- Determination of stability constants and intercomparison of the results

C. PROGRESS OF WORK AND OBTAINED RESULTS

1. State of advancement

Characterization of colloids and humic substances in selected Gorleben groundwaters has been carried out. Since the work is being in progress, only the preliminary analytical results are presented, which show a clear correlation between the DOC concentrations and trace heavy metal concentrations in groundwaters. The dissolved organic carbon (DOC) in groundwaters under investigation appear to consist mainly of humic acid and fulvic acid. These acids are found to be present as an organometallic colloidal species generated through aggregation with trace heavy metal ions of groundwater constituents. The investigation is, therefore, carried out for the characterization of groundwater-colloids and humic substances in parallel.

For the intercomparison exercise, a commercial humic acid (Aldrich: Na salt) is purchased, purified to an acid form and distributed to 6 laboratories of the COCO group. As a site specific reference, humic acid is extracted from one of Gorleben groundwaters (Gohy-573), purified and distributed also to the laboratories.

2. Characterization of humic substances in some Gorleben groundwaters

In groundwaters from Gorleben area, the DOC concentration is varying over a wide range, from less than 0.1 mg C/L to near 100 mg C/L. The DOC is identified as either humic acid or fulvic acid by a commonly used acid-base process [1]. A typical distribution of the two acids in selected Gorleben groundwaters can be seen in Table 1. A decrease of the DOC concentrations is accompanied with an increase of the fulvic acid fraction, while the humic acid fraction decreases. Both acids account for the major part of DOC. The distribution characteristics of the two acids, as shown in Table 1, remains valid for a large part of Gorleben groundwaters.

Table 1: Composition analysis of DOC in selected Gorleben groundwaters

Groundwater	DOC (mg C/L)	Humic acid (%)	Fulvic acid (%)
Gohy-73	97.4	81	14
Gohy-92	40.7	93	7
Gohy-333	10.6	81	17
Gohy-613	5.7	47	37
Gohy-202	3.4	29	59
Gohy-571	0.8	∼0	∼100

A new gel-chromatographic method for the size fractionation of humic acid and fulvic acid is under investigation in order to elucidate their non-aggregated molecular size. For this purpose, their methylation [2] and the use of a particular dipolar-aprotic nonaqueous solvent are under consideration. The definite results are not yet available for the moment but will be given in the next report.

The carboxylic contents of two different humic acids (purified to acid form) from one of the Gorleben groundwaters (Gohy-73) and from Lake Bradford (Florida State Univ.) are determined by a well known pH titration [3]. The results are found to be within the range of 4.0 ∿ 5 meq/g humic acid.

3. Correlation of trace heavy metals with humic substances in groundwaters

Three groundwaters containing different amounts of DOC are selected and analysed for major elements and trace heavy metal contents. The groundwater constituents are given in Table 2 for major constituents and in Table 3 for trace constituents. As shown in Table 2, no direct correlation can be observed between concentrations of DOC and major constituents, neither cations nor anions. However, a direct correlation of DOC concentrations with trace heavy element concentrations is evident in Table 3, except divalent elements like Ba^{2+}, Sr^{2+} etc. All trace elements of oxidation state greater than 2+ are found in a larger quantity in groundwaters with higher DOC concentrations. The relationship between them is proportional, suggesting that the trace heavy metal ions favor the humate complexation. The preponderant trace heavy metal ions in these groundwaters is Fe, which, according to given redox potentials (Eh > 100 mV), may be present as trivalent ions.

Provided the complexation capacity of humic acid or fulvic acid may correspond to the content of carboxylic group of these acids (4.0 ∿ 4.5 meq/g of dry weight), nearly all Fe(III) ions are loaded on humic substances being present through humate complexation. The Fe(III) loading will amount one third of the complexation capacity. The rest capacity may be complexed with other trace heavy metals shown in Table 3. Such metal loaded humates (also fulvates) behave like colloids as well as soluble ion exchangers (see below).

4. Humate colloid generation of trace heavy metal ions

Whether or not the trace heavy metals found in groundwaters under investigation (Table 3) are present as colloids is investigated by ultrafiltration. For this purpose one of the three groundwaters (Gohy-73) with a substantially high DOC concentration is selected, because this groundwater shows higher concentrations of trace heavy metals. The ultrafiltration results are given in Table 4, which shows the filtration effects at 100 nm and 15 nm pore sizes. The elements having oxidation state greater than 2+ under normal conditions can be almost quantitatively filtered at the pore size of 15 nm, whereas the divalent elements like Ba, Sr and the

Table 2: Concentrations of major components in three selected groundwaters from Gorleben aquifer systems

Element		Gohy-73 (pH = 7.8)	Gohy-1012 (pH = 8.2)	Gohy-1061 (pH = 8.2)
Na^+	(10^{-3} mol/L)	25.3	10.9	2.8
Mg^{2+}	(10^{-5} mol/L)	10.5	6.2	9.9
Ca^{2+}	(10^{-4} mol/L)	2.6	2.6	2.6
Cl^-	(10^{-3} mol/L)	8.2	9.4	2.8
Br^-	(10^{-6} mol/L)	2.6	1.9	2.1
NO_3^-	(10^{-5} mol/L)	96.8	<0.5	2.6
SO_4^{2-}	(10^{-5} mol/L)	0.3	18.4	19.6
PO_4^{2-}	(10^{-5} mol/L)	<0.02	1.1	0.6
SiO_3^{2-}	(10^{-4} mol/L)	2.6	6.0	3.9
HCO_3^-	(10^{-3} mol/L)	16.3	3.3	2.0

Table 3: Concentrations of DOC and trace inorganic elements in three selected groundwaters from Gorleben aquifer systems

Element		Gohy-73 (pH = 7.8)	Gohy-1012 (pH = 8.2)	Gohy-1061 (pH = 8.2)
DOC		97.4 mg C/L	7.8 mg C/L	2.0 mg C/L
Ba	(10^{-7} mol/L)	3.7	0.7	0.9
Ce	(10^{-8} mol/L)	70.4	3.2	1.7
Cr	(10^{-8} mol/L)	39.1	4.2	1.7
Eu	(10^{-9} mol/L)	10.9	1.8	0.9
Fe	(10^{-6} mol/L)	48.6	3.7	1.3
Hf	(10^{-9} mol/L)	6.2	0.4	0.2
La	(10^{-8} mol/L)	26.3	1.6	0.8
Nd	(10^{-8} mol/L)	27.0	2.3	1.0
Sb	(10^{-9} mol/L)	2.2	1.6	0.73
Sc	(10^{-9} mol/L)	38.9	6.3	0.4
Sm	(10^{-9} mol/L)	45.0	4.2	2.3
Sr	(10^{-7} mol/L)	20.7	8.4	2.6
Th	(10^{-8} mol/L)	10.5	0.3	0.2
U	(10^{-9} mol/L)	11.0	5.5	0.5
Zr	(10^{-7} mol/L)	12.8	1.7	0.4

amphotere element Sb are much less filtered. As expected the Br^- ion remains in the solution. The filtration results suggest that trace heavy elements with oxidation state greater that 2+ are strongly associated with the soluble humic substance, in other words, they are present as humate colloids.

The trace heavy metals found in this groundwater are chemically natural homologues of actinides and some fission products, which represent elements with oxidation state of II, III, IV and VI. Based on the results shown in Table 4, it is possible to anticipate the extent of humate colloid generation of actinide ions in a given groundwater containing humic substances.

Table 4: Filtration effects on trace heavy metal concentrations in Gohy-73 groundwater (DOC: 97.4 mg C/L)

Element	Filtrate from 400 nm Ø	percent filtered on filters of 100 nm Ø	~15 nm Ø
Ba	3.7×10^{-7} mol/L	50	55
Br	2.6×10^{-6} mol/L	<4	<3
Ce	70.4×10^{-8} mol/L	90	99
Cr	39.1×10^{-8} mol/L	78	83
Eu	10.9×10^{-9} mol/L	72	87
Fe	48.6×10^{-6} mol/L	88	98
Hf	6.2×10^{-9} mol/L	72	90
La	26.3×10^{-9} mol/L	84	~100
Nd	27.0×10^{-8} mol/L	93	~100
Sb	2.2×10^{-9} mol/L	36	46
Sc	38.9×10^{-9} mol/L	78	89
Sm	45.0×10^{-9} mol/L	~100	~100
Sr	2.1×10^{-8} mol/L	48	52
Th	10.5×10^{-8} mol/L	80	~100
U	11.0×10^{-9} mol/L	65	81
Zr	12.8×10^{-7} mol/L	64	91

5. Interlaboratory comparison excercise

As a part of the CEC coordinated project MIRAGE II, the group involved in the research area 2 agreed to launch a joint action in the field of complexation of selected radionuclides with humic acids present in different geological formations. This action starts off by an intercomparison of methods in each of the laboratories concerned. For realizing this action, TUM has prepared the following reference materials and delivered to the laboratories involved in the research area 2.

a) Humic acid (Na salt) from ALDRICH Co.	50 g each
b) Humic acid (H form): purified to an acid form the ALDRICH HA (Na salt)	50 g each
c) Humic acid (H form): separated from Gorleben groundwater (Gohy-573) and purified to an acid form	2 g each

REFERENCES

[1] STEVENSON, F.J., Humus Chemistry, John Wiley + Sons, New York (1982)
[2] WERSHAW, R.L. and PINCKLEY, D.J., Science 189, 906-907 (1978)
[3] BORGGAARD, O.K., Acta Chem. Scand. A26, 121-122 (1974)

Title : Interactions between organic substances and transuranic elements
Contractor : CEA-IRDI/DRDD/SESD/SCPCS - Fontenay-aux-Roses - FRANCE
Contrat n° : FI1W/0068
Duration of contract : 1985-1989 Project leader : M. BILLON-Mme MOULIN

A. Objectives and Scope

The presence of natural organic ligands (humic-fulvic acids) as complexing agents of cations in the deep or shallow aquifers could have a great influence on the mobility of radionuclides in the geosphere /1/.

The study of radionuclides interactions with humic materials constitutes a research area of major importance : up to now the systems cations - humic substances are not well known partly due to a lack of knowledge in the humic substances field (structure, properties, ...). The purpose of the present research is to define in the most complete way : firstly, the properties and characteristics of humic materials, secondly the formation conditions and binding strengthes of humic-radionuclides species.

A chromatographic technique /2/ is retained to study the associations occurring between transuranic elements and humic materials which will be well characterised by different physical and chemical methods. Developments in humic substances analysis (potentiometry, size exclusion chromatography) and on the chromatographic method (chomatographic support, detection,...) will be performed.

The final objective of the programme is to conclude on the contribution of humic substances to the possible transport of radioactivity in the geosphere via groundwaters.

A collaboration with the KBS is undertaken in this research area.

B. Work Programme

B.1. Isolation and characterisation of humic substances

B.1.1. Concentration of humic materials from natural groundwaters : sampling, concentration, fractionation.

B.1.2. Characterisation of humic materials by different physical and chemical methods : elementary, mineral, functionnal, potentiometric and molecular weight (size) analyses.

B.2. Interactions between humic coumpounds and transuranic elements

B.2.1. Development of the chromatographic method chosen for the complexation studies (choice of chromatographic support, system of detection).

B.2.2. Measurement of interaction constants with this chromatographic method as a function of various chemical parameters (pH, ionic strength, metal and ligand concentrations).

B.3. Inter-laboratory comparison exercice on characterisation of humic materials and on complexation of radionuclides with these substances.

C. Progress of work and obtained Results

State of Advancement

A review of the different ways to concentrate humic materials from natural waters has been made : the procedure using an anionic resin /3/ (without any previous water treatment) has been chosen. The prospecting of different sites for sampling granitic deep groundwater (Fanay-Augères) has begun with encouraging results.

The chromatographic technique used for the complexation studies has been improved on the detection system : the method which was first developed with inactive elements (Eu, U, Th, Cu) is applied to radioelements (α and/or γ emitters). Different on-line detectors have been compared and studied : silicium, liquid and solid scintillation detectors. The last of them was chosen.

Experiments with Americium have been made in the different media. Batch studies have determined the appropriate conditions of work in citrate and carbonate buffer systems. Some column experiments with Am and the on-line detector in citrate buffer corroborate the batch studies.

The general work progress status is a follows : B.1., B.2.1., B.3. are progressing normally, B.2.2. is delayed.

Progress and Results

Humic Substances Isolation and Characterisation (B.1.)

The humic substances with which we are working are coming from two origins : a granitic site which could be qualified as a reference site (Fanay- Augères) and a commercially source (ALDRICH Company) which permits to have large quantities of humic materials to develop the experiments.

Prospecting of fissures or boreholes in galeries of different depths (- 260 to - 360 m) has begun. Different water samplings have been made in Fanay-Augères in order to evaluate the dissolved organic carbon (DOC) of the deep groundwaters. (B.1.1.).

To isolate humic and fulvic acids from natural granitic waters we have to concentrate the organic fraction due to the fact that the organic carbon content is very low (≃ 1 mg/l). After a litterature survey of the different procedures on water concentration the resin method was adopted. The described procedure (with the KBS collaboration) is represented on Figure 1.

The characterisation of humic materials (B.1.2.) by different analysis methods is in good progress : elementary, mineral and infrared spectroscopy analysis don't pose any problems and give precious informations on the nature of humic materials (actually the commercial humic acids are studied).

Interaction studies between transuranic elements and humic substances (B.21).

In the chromatographic method development the detection system has been particularly studied in order to have a on-line detector based on the radioactive properties of transuranic elements. The table I summarizes the advantages and drawbacks of three systems : a silicium diode, a solid scintillator detector and a versatile scintillation detector (α, β, γ). The solid scintillator detector /4/ has been retained. This instrument allows the measurement of alpha emitter concentrations in solution continuously by the use of a glass scintillator with very good sensitivities. Elements like Am, Pu, Np, U could be detected. In our case the main emphasis is put on Americium. The figure 2 shows a chromatogram obtained for an injection of Americium with this detector.

In order to apply the gel filtration technique to active elements (the demonstration of this method was made for inactive elements Eu, Th, U, Cu) some batch experiments were undertaken in different buffer systems. Two conditions are required : the predominance of anionic species in the solution and the absence of retention of the species on the chromatographic support. In citrate buffer 10^{-3} M, 10^{-2} M, 10^{-1} M (pH 4.5 - 5 - 6) these conditions are verified, in carbonate buffer it is limited by the americium solubility /5/.

The interlaboratory comparison exercice (COCO) is running in good progress. Another report will be made in a different way (B.3.).

List of publications

- LESOURD-MOULIN V., Rapport CEA-R-5354 (1986).
- MOULIN V., in "Chemie und Migrationsverhalten der Aktinoide und Spaltprodukte in natürlichen aquatischen Systemen", PTB - Bericht (Vorträge des 66.PTB-Seminars), Münich, 24-25 Avril 1986.

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/1/ CHOPPIN R., ALLARD B., Handbook on the Physics and Chemistry of the Actinides, North-Holland Publ. Comp., Amsterdam, 407-429 (1985).

/2/ LESOURD-MOULIN V., Rapport CEA-R-5354 (1986).

/3/ PAXEUSN, ALLARD B., OLOFSSON U., BENGTSSON M., Scientific Basis for Nuclear Waste Management IX, Werme Ed., Vol 50, 525-532 (1986).

/4/ ROBERT A., SELLA C., HEINDL R., Nuclear Instr. and Methods in Physics Research, 225, 179-184 (1984).

/5/ VITORGE P. and al., Rapport Technique DRDD n° 67, Rapport final 1983-1984, Octobre 1985

Table I Different on-line detectors studied

	Silicium Diode	Glass Scintillator	Versatile Scintillator (Liquid or Solid Scintillation)
Nuclearisation (Facility to put in a glove-box) •	Yes	Yes	No
Geometry of the detector	2 π	2 π	4 π
γ Radiation detected	No	No	Yes
β Particles detected	No	Possible	Yes
α Particles detected	Yes	Yes	Possible (never studied)
Limit of Detection for Am . Static . Dynamic	 - 4 μg injected	 10^{-9} M/l 6 ng injected	 - -

Figure 1 Concentration - Fractionation and Purification Steps of Natural Humic Substances from deep Groundwaters

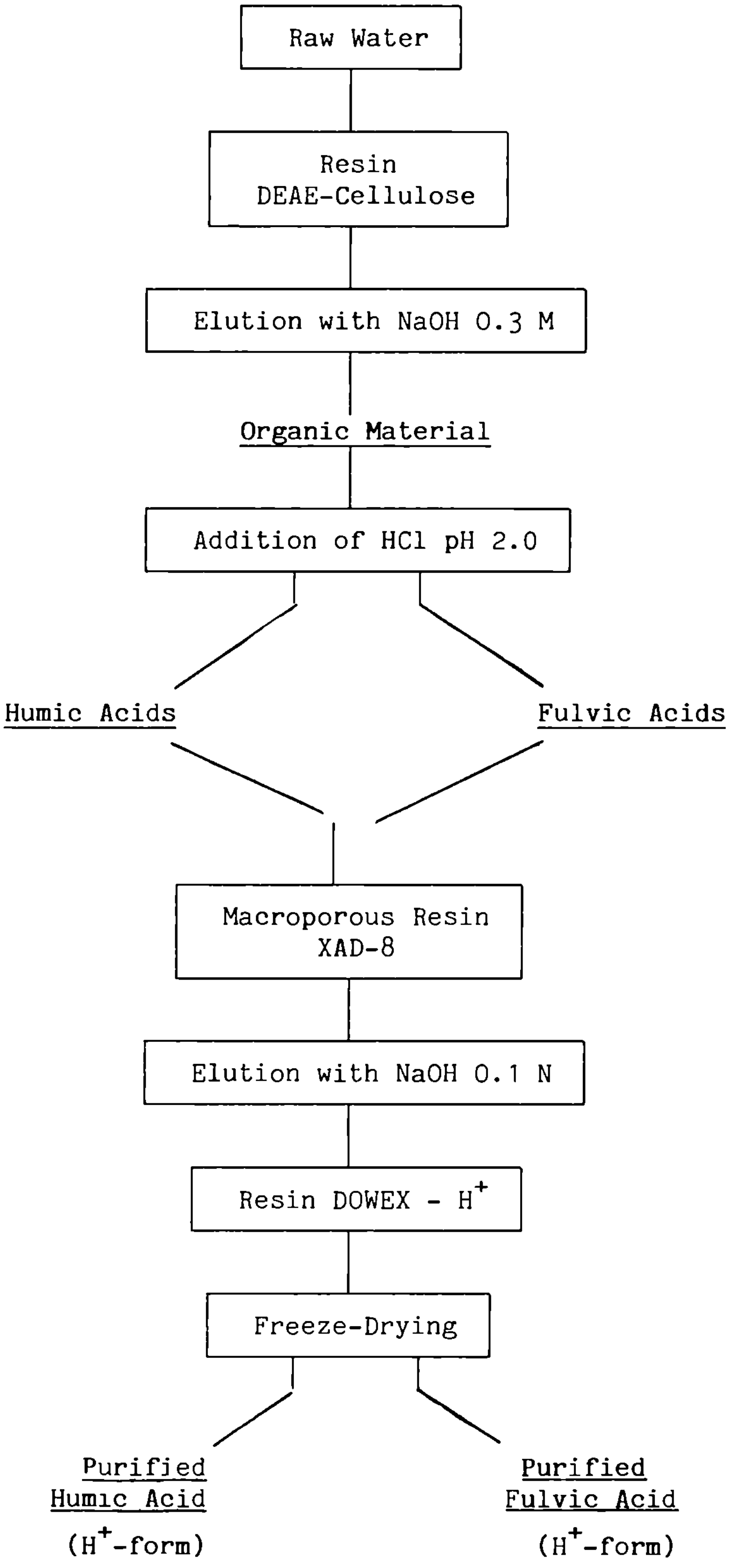
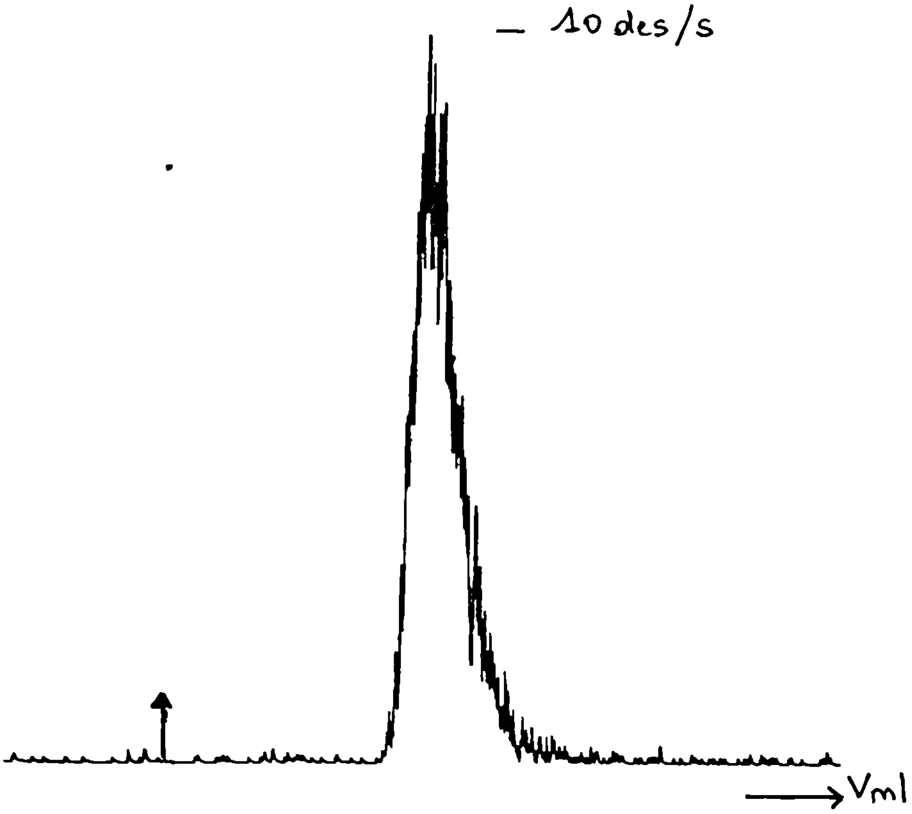


Figure 2 Injection of 72 ng of Am on Sephadex G 15 column in 0.1 N citrate buffer, pH 4.5, I = 0.5 M
Detection : glass scintillator detector



Natural analogues of radionuclide migration in granitic rocks through the study of palaeo-hydrothermal alteration

Contractor : BRGM - Orléans, France
Contract no. : FI 1W/0072/F (CD)
Working period : August 1986 to August 1988
Project leader : P. Peaudecerf

A. Objectives and scope

Mineralized zones in granitic rocks which have been influenced by hot water (hydrothermal activity) over long geologic periods may be considered as useful natural analogues of the conditions occurring around a heat-producing repository in granite. Study of these zones gives valuable information about the migration and retention of elements analogous to the radionuclides present in the repository.

Development of research on one or more sites of former hydrothermal activity in a granite environment will enable an approach to the problems of migration and retention of elements such as the rare earths, uranium and thorium which are themselves analogous to the radionuclides in their geochemical behaviour. The time scale will be that of the geologic environment of 0.1 to 1 million years. The volumes considered will take into account the far field (pervasive alteration) and near field (vein alteration) phenomena. The final aims of this programme are :

1. To define the physicochemical conditions of the alteration examined and the mineralogical carriers of the elements analogous to the radionuclides
2. To test on existing programmes (PATH) or on those being developed, the data supplied by the direct approach (validation of thermodynamic parameters, assessment of the reaction kinetics on natural examples).

B. Work programme

B.1. Petrographic and mineralogical investigation of the various events which have affected the system.

B.2. Analysis of the analogue element carriers in two parts :

B.2.1. Separation of the primary and secondary phases developed by the alteration and quantitative analysis of the analogue elements in the separated phases and in rock samples;

B.2.2. Location of analogue elements by nuclear methods. From these data the mass balance and the distribution and mobility of the analogue elements during the palaeoalteration will be established.

B.3. An indirect approach by using mass transfer codes on major trace and analogue elements to mobilize the geochemical behaviour of the alteration systems.

C. Work progress and results obtained

Summary

Following the signing of contract FI 1W-0072-F in October, it was decided to proceed to selection of an additional site for the study of palaeo-hydrothermal alteration enabling the continuous two- or three-dimensional analysis of a system. This selection was made after a period of exploration during which thirty or so sites were visited in Brittany and the Massif Central.

Once the selection was made, an inter-disciplinary field programme, involving mineralogists and geochemists, took place for a first sampling to enable commencement of the various investigations. Work progress as follows:

B.1. and B.2.1. are under way and the other phases should normally follow on.

B.2.2. A part of this is in progress.

B.3. Development of new software enabling modelling.

Progress and results

Since the contract was signed as recently as October 1986 and considering the time needed to obtain the various data for programme completion and processing, it will be difficult to present a coherent and complete evaluation of the results.

Field-work

This consisted of an inter-disciplinary field programme involving petrographers, geochemists and structural geologists whose objective was to make a preliminary study of the site and an initial sample selection.

During this campaign, a constant-scale survey was made by photomapping to locate the sample points and for computerizing the results.

1. Mineralogy

The mineralogical studies are under way. Their aim is twofold:

1. The investigation and quantitative analysis of the destabilization of the primary igneous phases.
2. The investigation and quantitative analysis of the formation of the new hydrothermal phases.

2. Geochemistry

Analyses of the main and trace elements from the various facies recognized in the field are under way. They will enable a first assessment of the alteration.

3. Location of the trace elements by nuclear methods

The first part of this programme is under way. From a study of apatite and zircon fission tracks, the age of emplacement of the granite and of the hydrothermal system will be determined. From a study of the fission tracks, micromapping of uranium distribution will be made from thin sections. The other operations will depend on the results of the mineralogical study.

4. Modelling

The new programmes required for modelling are being developed and tested on actual examples.

5. Comment

In the context of a thesis, work is progressing on the Langenberg site with aims similar to those of parts B.2.1. and B.2.2. of the present work programme.

The results of these investigations could be included during the modelling of the present project.

Natural Analogue Studies of Radionuclide Migration

Contractor: British Geological Survey/NERC, Keyworth, Nottingham,UK.
Contract No: FI1W/0073/UK
Working Period: July 1986 - June 1989
Project Leader: P J Hooker

A. OBJECTIVES AND SCOPE

It is important to be able to validate and support models of long-term predictions of radionuclide migration in the geosphere. The main aim of this research is to examine natural geochemical discontinuities and gradients as analogues of radionuclide transport in sediments. The mechanisms of processes of mobilisation, advection, diffusion and retardation for natural decay series elements and iodine and bromine will be addressed. This will entail some development of the techniques for measuring small concentrations and the speciations of these elements in both the solid and pore water phases. Analyti cal determinations by alpha spectrometry and neutron activation analysis will be carried out by SURRC (Dr A B MacKenzie) under sub-contract. Support in modelling will come from co-operation with Ecole des Mine de Paris, Fontainbleau.

B. WORK PROGRAMME

B.1. Phase 1986-1987.

B.1.1. Site investigations

B.1.1.1. Collection of fresh Loch Lomond sediments; analysis of I and Br depth profiles; preliminary modelling for effective diffusion coefficients.

B.1.1.2. Pilot investigation of I, Br, U and Th gradients across marl/clay boundaries in a well characterised sediment core from Lundin Castle, Fife, eastern Scotland.

B.1.2. A desk study of surface diffusion as a solute transport process for major cations through clays, with implications for trace radionuclide migration.

B.2. Phase 1988-1989.

B.2.1. Site investigations will be concentrated on measuring and modelling the speciation and mechanisms of distribution of I, Br, U and Th in the Loch Lomond and Lundin Castle sediments.

B.2.2. Application of the desk study conclusions to a field investigation of Ca and Na gradients in a mixed sediment sequence with reference to radionuclide migration.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Previous results obtained on Loch Lomond sediments have demonstrated the need to elucidate the chemical forms of the I and Br distributions in the pore waters and in the marine band deposits. A precipitation cum ion exchange speciation method is being developed (by SURRC) to distinguish between e.g. soluble iodide and iodate, and a gas chromatography technique is being explored (by BGS) for determining pore water organo-iodine compounds. Arrangements have been made to collect fresh cores in the Spring of 1987.

Preliminary results obtained in the pilot Lundin Castle core study indicate significant bromine concentration and uranium activity ratio differences across the marl/clay boundaries; in contrast, there is no evidence of iodine being present. Analytical measurements are continuing.

The general work progress status is as follows: B.1.1. is progressing on time and normally. B.1.2. is progressing slowly.

Progress and results

1. Site investigations (B.1.1.)

B.1.1.1. Loch Lomond

Experiments are being conducted at SURRC with the specific aim of improving techniques for the identification of bromine and iodine speciation in Loch Lomond sediment interstitial water. These developments are necessary because of the small concentrations encountered. Instrumental neutron activation analysis (INAA) is being applied for simultaneous determination of iodine, bromine and chlorine. The suitability of this method is demonstrated by the results shown in Table I.

The counting rates were obtained for solutions containing 1µg each of Cl, Br and I irradiated for 1 minute in a thermal neutron flux of 3 x 10^{12} ncm^{-2} s^{-1} followed by a 30 minute decay period before counting on contact with a 80cc Ge(Li) detector. The sensitivity of the technique could easily be improved if required by longer irradiation, longer counting time or use of a larger detector.

Two approaches are being attempted to differentiate between halide, halate and organo-halogen speciation.

i) Silver precipitation.

The solubility data in Table II suggest that a simple scavenging technique using AgCl carrier could be used to distinguish the three chemical forms being considered The steps proposed are

a) Irradiate the sample
b) Add 10mg Cl^- and precipitate with excess Ag^+
c) Filter and count the activity of the precipitate
d) Reduce the halates remaining in solution to halides and repeat the scavenging
e) Count the organo-halogen species left in solution.

Provided the $BrO3^-$ concentration is less than about 30ppm this technique should give a rapid and simple analysis for Br. The separation between I^- and IO_3 is less effective and is being refined.

ii) Ion exchange separation.

Investigations so far indicate

a) 100% uptake of Cl^-, Br^-, I^-, ClO_3, BrO_3^- and IO_3^- can be achieved from neutral and alkaline solutions using BioRad AG 1x8 anion resin.

b)100% elution of each of these species can be effected using nitric acid or KNO_3 solution.
c) Partial separation of the halides from halates.
Work is continuing on both the silver precipitation and anion exchange techniques; the eventual method may involve a combination of both.

BGS has a gas chromatography method for detecting sub-ppm levels of dissolved alkyl iodides and bromides; the main problem is one of interference from other organic compounds in the pore water.

B.1.1.2. Lundin Castle

The core material was provided by Dr D D Harkness of the NERC Radiocarbon Laboratory who is in collaboration with St Andrews University researching the site. The sediments represent a fossil shallow lake environment. The core is about 6m long and consists of a series of alternating marls and clays. A very pronounced clay horizon corresponding to an age of several thousand years was sampled at its top and bottom boundaries. XRF analysis failed to detect iodine in any of the samples. However, activation analysis show marked differences for Br and other elements between the marls and the clay (Table III). There are also significant uranium activity ratio differences across the boundaries as well (Table IV). Experiments are continuing.

2. Surface diffusion study (B.1.2.)

From the research carried out by the Fluid Processes Research Group at the Harwell Research Site, a need has emerged to support the hydrogeological model for the surrounding area of Mesozoic sedimentary rocks with geochemical data belonging to the major cations, particularly calcium and sodium, in the pore water phases. It is proposed to initiate a desk study of the theoretical implications of the solute-surface diffusion process which may be important for the migration of radionuclides through what are generally considered impermeable microporous media viz. buried clay horizons. It is important to assess the contribution of this particular surface mechansism in the overall migration scheme for a radionuclide solute in a clay formation, and to analyse the sensitivity of the changes in the net transport rate to a variation in each one of the controlling parameters. So far the desk study has been limited to a literature search of key papers.

List of publications

Hooker, P.J. and Chapman, N.A. 1986. Euratom activities in natural analogues. Presented at the 6th Technical Meeting of the Co-operative Agreement between EURATOM and AECL, 9th & 10th October 1986, Brussels.

TABLE I: INAA for the halogens

Element	γ-Photopeak Counting Rate cps	1σ uncertainty for 5 minute count.
Cl	4.4	3.0
Br	0.44	16.0
I	2.6	4.3

TABLE II. Water solubilities of halides and halates

SPECIES	SOLUBILITY g/100 ml at 25°C
$Ag\ Cl$	8.9×10^{-5}
$Ag\ ClO_3$	10
$Ag\ Br$	8.4×10^{-6}
$Ag\ BrO_3$	0.196
$Ag\ I$	2.8×10^{-7}
$Ag\ IO_3$	0.003

TABLE III: INAA results for Lundin Castle sediment samples

SAMPLE	Na %	K %	Sc	Cr	Fe %	Co	Relative Br
1. UPPER MARL	0.08	0.15	2.3	22	2.3	4.0	4.2
2. CLAY (TOP)	0.60	1.9	17.9	139	4.9	20.2	2.6
3. CLAY (BOTTOM)	0.47	1.7	20.0	153	4.8	27.6	1.0
4. LOWER MARL	0.10	0.24	3.3	21	1.7	5.9	6.2

SAMPLE	Cs	La	Sm	Eu	Hf	Ta	Th
1. UPPER MARL	0.7	5.1	1.0	0.23	9.2	ND	1.7
2. CLAY (TOP)	3.3	42.2	7.4	1.8	65.4	1.8	11.7
3. CLAY (BOTTOM)	3.0	47.9	8.7	2.2	68.3	2.3	13.9
4. LOWER MARL	0.8	6.4	1.4	0.28	12.8	ND	1.9

Concentrations in ppm unless otherwise stated. ND - not detected.

TABLE IV: Uranium in Lundin Castle sediments

SAMPLE	^{238}U dpm g^{-1}	^{234}U dpm g^{-1}	$^{234}U/^{238}U$
1. UPPER MARL	1.15 ± 0.03	1.72 ± 0.05	1.49 ± 0.04
2. CLAY (TOP)	2.04 ± 0.04	2.17 ± 0.04	1.06 ± 0.02
3. CLAY (BOTTOM)	1.97 ± 0.04	2.05 ± 0.04	1.04 ± 0.03
4. LOWER MARL	1.30 ± 0.04	1.85 ± 0.05	1.42 ± 0.05

Long-term diffusion in rock : natural analogue

Contractor: UKAEA, Harwell Laboratory, UK
Contract No: FI1W/0074/UK
Working Period: 1.7.86 - 1.7.87
Project Leader: Mr. P.J. Bourke

A. Objectives and Scope

Diffusion through rock is important as a mechanism both for radionuclide transport in rock without water flow and for retardation of transport in flow through fractured rock. Laboratory measurements of diffusivity and porosity of various rocks of interest are being made but, because of the low values being obtained, measurements cannot be obtained over more than centimetre distances in conveniently short times.

It is unknown whether or not the pores through which diffusion occurs in centimetre test specimens are continuous through greater thicknesses of rock. The observed porosity may be either all of open, inter-connected pores or partly of pores closed at one end. If some of the pores which are continuous through the centimetre specimens terminate over greater distances, a model assuming all the measured porosity to be open is invalid.

The principle of the method to be used is to measure the diffusion of chloride from the sea into rocks which have been below water level in harbours and sea walls for known, long times. Cores of these rocks will be obtained and sectioned. Analyses of these sections for chlorine will provide the reqired data. The objectives of this contract are therefore to study diffusion which has occured naturally over long distances and times and to test the validity of the different models compatible with the short-distance laboratory data.

B. Work Programme

B.1. Identify a site where a granite block, from a known locality, has been immersed in sea water for a known length of time.
B.2. Obtain permission from the relevant authorities to retrieve the granite block.
B.3. Lift block from the sea and drill through it to obtain cores.
B.4. Cut the core into sections and measure the amount of chloride within the pore water of each section.
B.5. Calculate the effective diffusion coefficient of the granite from an analysis of the chloride concentration profile within the block.

C. Progress of work and obtained results

A suitable site has been identified and permission to retrieve the block has been obtained. The block will be lifted on 2.2.87.

In summary, items B.1. and B.2. are complete. It is anticipated that B.3. will be completed on 2.2.87. Items B.4. and B.5. will be completed by 1.7.87.

Geochemical Modelling

Contractor: Chemistry Department, Risø National Laboratory, DK
Contract N^{o}: FI1W/0079/DK
Working Period: July 1986 - July 1988
Project Leader: B. Skytte Jensen

A. Objectives and Scope

The final objective of the project is to provide a versatile and easily used geochemical programme package, the WHATIF series. The programmes will handle multielement adsorption processes, ion-exchange as well as co-precipitations and allow for an easy introduction of new data and reaction schemes.

B. Work Programme

B.1. Arrange the programmes for easy introduction of new reactions and data.
B.2. To enlarge the database such that the programmes can handle most elements of environmental concern.
B.3. The formation of polymeric species and homocolloids will be introduced and discussed.
B.4. Oxygen pressure/concentrations will be introduced as input parameter. Redox potential will be discussed.
B.5. The existing WHATIF series will be used as the frame, when the new programmes are written in PASCAL.
B.6. The need and possibility for establishing an expert-system for environmental geochemistry will be considered.

C. Progress of work and obtained results

Summary

The work progress status is that B.1.-B.6. are progressing normally, closely following the rewriting and reshaping of the WHATIF programmes in the PASCAL language. New procedures for handling co-precipitation and multielement ion-exchange have been constructed and tested.

Other procedures for a selfadjusting calculation of the simultaneous speciation and precipitation-dissolution reactions are also developed and tested on systems comprised of a limited number of elements. In this relatively simple system a complete reaction-path calculation can be done within a few minutes. It is intended to explore the possibility of making a general procedure handling any combination of elements found in ground waters.

The final structure and content of the database(s) will await the results of the project "Geochemical databases", No FI1W-0080-DK.

Geochemical Databases

Contractor: Chemistry Department, Risø National Laboratory, DK
Subcontractor: INTERA Technologies, Texas, USA
Contract N°: FI1W/0080/DK
Working Period: July 1986 - July 1988
Project Leader: B. Skytte Jensen

A. Objectives and Scope

The final objective of the project is to develop a database management system and to collect an internally consistent dataset for geochemical modelling of phenomena arising in connection with geological disposal of radioactive waste. This does not only comprise the data for actual waste components, but also for the major components in the media which the waste may encounter.

B. Work Programme

B.1. Development of a database management system. INTERA.
B.2. Fix range of conditions taken into account. INTERA and Risø.
B.3. Write discussions of arguments for choosing or omitting reactions with data. INTERA and Risø.
B.4. Collect relevant data, both old and new. INTERA and Risø.
B.5. Final presentation of database and database management system.

C. Progress of Work and Obtained Results

Summary

Till now, the major effort has been concerning B.2., i.e. choosing ranges of conditions within which the data collected should be reliable. For the majority of applications, consistent data in the temperature range 0-100°C are considered satisfactory. The effect of pressure on chemical equilibria will have to be considered in the case of deep disposal sites, especially so because increase in pressure generally will increase the solubility of ionic solids. The pressure effect will be discussed and the thermodynamic data necessary for its calculation included in the database.

The effect of ionic strength on the geochemical equilibria will be discussed as well as methods for extrapolating experimental data to conditions of zero ionic strength.

The data will apply to geochemical models using the ion-pair concept, which is useful for describing solutions of moderate ionic strength.

The formation of polymeric species and homocolloids in ground water systems will be discussed to clarify, which role they may play in such systems. If their formation is considered significant, the relevant data will be included in the database.

The data in the database will be presented as the logarithm of equilibrium constants as a function of temperature and pressure, i.e.

$$\log(K) = F(T,P)$$

as an interpolation formula.

The data will in addition contain information on literature source, a rating of data quality and for solid phases in addition and indication of its probability of formation under given conditions. This last rating will to a certain extent take care of kinetic factors not considered in geochemical calculations. Similar ratings may be given to redox-reactions whose rates of attaining equilibrium are known to vary from fast to extremely slow.

The development of the database management system, B.1., is in good progress, as is the search for data, B. 4. Discussions, B.3., will be presented as an introduction to the final report.

Migration of radionuclides by high concentration brine: finalisation of the METROPOL code.

Contractor : RIVM, Bilthoven, NL
Contract No. : FI1W/0081
Working Period : November 1986 - December 1986
Project Leaders : Ir.P.Glasbergen, Ir.A.Leijnse

A. Objective and Scope

One of the key problems for the safety of disposal of radionuclides in salt, is the transport of radionuclides by high concentration brine after a possible release of radionuclides from a salt dome repository. An initial contract (383-83-7 WASNL) was carried out in the period 1983-1984. This original project consisted of the development of (a family of) computer codes (METROPOL) that can deal with transport of radionuclides by groundwater in case of high density gradients.

The objective of the present contract is to complete the development of the METROPOL code, including pre-and post-processing facilities and testing of the code for situations with extreme density differences.

B. Work programme

B.1. Inclusion of an adaptive time integration scheme to make the long simulation times feasible.
B.2. Documentation of the codes developed so far.
B.3. Development of several postprocessing facilities, like e.g. particle tracking, contouring, etc.
B.4. Inclusion of physical realistic boundary conditions, especially concerning the dissolution/precipation of salt at the salt dome/ groundwater interface.
B.5. Testing and validating the code.
B.6. Inclusion of physico/chemical processes and thermal effects.

Note, that points B1 through B5 are not carried out sequentially.

C. Progress of work and obtained results.

So far, three computer programs in the METROPOL family are operational:
METROPOL-0 : a 3-D mesh generator
METROPOL-1 : a steady state groundwater flow model with constant density.
METROPOL-2 : a transient groundwater flow model with constant density.

The documentation for these programs is in draft version finished. The programs have been extensively tested.

METROPOL-3 : a transient model for the transport of high concentration brine, is at the moment being tested. Some numerical problems remain to be solved, mainly with respect to the time integration procedure.

Post processing programs have been developed that can generate 3-D path lines or pressure and/or concentration contours in 2-D cross sections.

Theoretical work has been carried out with respect to 1) the formulation of boundary conditions in case of high solute concentrations and 2) the formulation of the basic equations.

Publications

/1/ F.Sauter and N.Praagman:
A simulation model for the transport of radionuclides by groundwater in the vicinity of a salt-dome. Proc. 6th Intern Conference on Finite Elements in Water Resources, Lisboa, 1986.
/2/ S.M.Hassanizadeh:
Derivation of basic equations of mass transport in porous media, Part 1. Macroscopic balance laws. Advances in Water Resources ; 9:196-206 (1986).
/3/ S.M. Hassanizadeh:
Derivation of basic equations of mass transport in porous media, Part 2. Generalized Darcy´s and Fick´s laws. Advances in Water Resources ; 9:207-222 (1986).

CHAPTER 5

TASK No. 5 : SAFETY OF GEOLOGICAL DISPOSAL

CHAPTER 5

TASK No. 5 : SAFETY OF GEOLOGICAL DISPOSAL

A. Objective

Assessment of the perfermance of isolation systems for radioactive waste and of the corresponding radiological risks.

B. Research performed under the 1980-1984 programme

Initiation and implementation of the first phase of the PAGIS (Performance Assessment of Geological Isolation Systems) project, the purpose of which is to assess the capacities offered by the various geological disposal options (salt, clay, crystalline and marine sediments) for the containment of high-activity waste.

Characterization and determination of the properties of alpha-contaminated waste and of medium- and low-activity waste.

C. 1985-1989 programme

The studies to be conducted will concern :

a) Continuation and completion of the PAGIS project, in accordance with the plans and procedure adopted during the previous programme

b) Assessment of the performance of disposal repositories for radioactive waste contaminated with alpha emitters and for medium- and low-activity waste buried and geological formations; assessment of the corresponding radiological risks

c) Support activities.

D. Implementation of the programme

3 additional contracts have been signed for PAGIS; the new project on the assessment of the performance of confinement of repositories for alpha and medium level activity waste, called PACOMA, has been started and the first 3 contracts signed.

The available information is listed thereafter.

5 a) PAGIS project

Performance evaluation of HLW-waste disposal in geological formations - PAGIS 2 project : clay options

Contractor : SCK/CEN, Mol, Belgium
Contract N° : FI1W/0001-B
Duration of Contract : January 1985 - March 1987
Project leader : A. Bonne

A. Objectives and Scope

The essential objective of the PAGIS project is an evaluation of the capability of selected geological formations and of the associated engineering barriers to confine vitrified high level waste. During phase 1 of PAGIS a methodology has been set up and scenarios, data and models have been selected. In phase 2 various models are combined to enable realistic assessments of the repository system performance. As well deterministic "best estimate" calculations as probabilistic calculations, allowing for sensitivity and uncertainty analyses, are performed. For the clay option, calculations are made for the reference site at Mol (Belgium) and for the variant sites at Harwell (U.K.) and at Val d'Era (Italy).

B. Work Programme

B.1. Preliminary best estimate evaluation of doses and risks to individuals and populations.
B.2. Estimation of the probability of occurence for all relevant scenarios.
B.3. Definition and selection of parameters for sensitivity and uncertainty analyses.
B.4. Sensitivity analysis.
B.5. Uncertainty analysis.
B.6. Final assessment

C. Progress of Work and Obtained Results

State of advancement

Most of the work carried out until now has been focused on the reference site at Mol (Belgium). The preliminary best estimate evaluation and the scenario analysis have been elaborated during the preceding years.

During 1986 probabilistic calculations have been performed for the case of the normal evolution scenario and some variant scenarios. The results of these calculations have been used to carry out sensitivity and uncertainty analyses. Some deterministic and more detailed probabilistic calculations have been performed for the case of a faulting scenario.

For the variant site at Harwell (U.K.) relevant data have been collected.

For the variant site at Val d'Era (Italy) however some data are available but essential information on the hydrology of the region is missing.

Progress and results

1. Probabilistic calculations in the case of the normal evolution scenario for the reference site at Mol

Probabilistic calculations have been introduced in performance assessment studies in order to take into account the considerable uncertainties which arise when the behaviour of the complex repository system is predicted over long periods of time.

Probabilistic calculations of the radiological consequences of a repository in a clay layer are performed by making use of a modified version of the LISA code. The original LISA code, which has been developed at J.R.C. Ispra, is adapted to improve the simulation of the migration of radionuclides from a repository in a clay layer into the biosphere.

The normal evolution scenario is considered together with some altered evolution scenarios, such as climatic changes and secondary glaciation effects, which do not affect the integrity of the clay layer but which may modify drastically the hydrological conditions in the repository area. The results of 500 run simulations, wherein the parameter values are sampled by Latin Hypercube Sampling, are used to elaborate as well sensitivity as uncertainty analyses.

The performances of several sensitivity estimators based on correlation and regression techniques and on non-parametric statistics have been compared. Spearman rank correlation coefficients and Smirnov tests are among the most stable and robust estimators. The ranking of the model parameters obtained by applying these methods at 5 million years is given in Table 1. The most influential parameters are the retardation coefficient of Np in clay, the effective thickness of the clay layer, the Darcy velocity in the aquifer and the hydraulic gradient over the clay layer.

The uncertainties on the results obtained are illustrated by the histograms of the calculated annual doses at reference time points. Figure 1 shows the histogram of the calculated doses at 5 million years. The arithmetic mean together with its 95 % upper confidence limit and the median of the calculated annual doses are shown as a function of time in Figure 2. The considerable difference between the expectation value and the median is due to the uncertainties on the model parameters.

Parameter	Spearman value ranking	Smirnov value ranking
Thickness clay layer	-0.49 (2)	0.47 (2)
Hydraulic gradient	0.22 (4)	0.22 (4)
Darcy velocity aquifer	-0.44 (3)	0.45 (3)
Dispersivity aquifer	0.02	0.09
Retardation coefficient of Cs in clay	-0.07	0.11
Retardation coefficient of Np in clay	-0.63 (1)	0.62 (1)
Retardation coefficient of Cs in aquifer	-0.03	0.09
Retardation coefficient of Np in aquifer	-0.02	0.09

Table 1 Sensitivity analysis ; values of the Spearman rank correlation coefficients and of the Smirnov T statistics.

2. Faulting scenario for the reference site at Mol

In this scenario the occurence of a fault in the clay layer through the repository area is considered. The fault plain is assumed to remain filled with clay. In the vicinity of the fault the structure of the clay will be considerably altered. Evidences of tectonic activities indicate that the faults in the area are the result of many small displacements of a few centimeters. However, in order to avoid the need for complicated models considering the varying geometry of the fault zone, it is conservatively assumed that a fault with a throw of a few meters is generated instantaneously.

A probabilistic analysis only allows to account for the probabilistic nature of the considered phenomena. To ensure that for each considered reference time point t a sufficient number of relevant runs is available to obtain a realistic estimate of the distribution function of the annual doses, seperate Monte Carlo simulations are performed for each reference time point. Again 500 run simulations are performed and the time of occurence of the fault is sampled from the interval (0,t). The histogram of the calculated annual doses 300,000 years after closure of the repository is shown in Figure 3. The total risk resulting from the considered scenario is the expectation value of the product of the consequences and of the occurrence probability of this scenario which is much lower than one for all considered time points. The estimated risks are shown as a function of time in Figure 4.

The faulting scenario yields annual doses of the same order of magnitude as those estimated for the normal evolution scenario. These rather small doses can be explained by the small fraction of the total activity disposed of in the repository which is affected by the fault. The estimated risks are some orders of magnitude lower than in the case of the normal evolution scenario because of the low probability of occurence of the faulting scenario.

List of publications

A. Saltelli and J. Marivoet
Performances of non-parametric statistics in sensitivity analysis and parameter ranking
CEC, Luxemburg, EUR 10851 EN

J. Marivoet, A. Saltelli and N. Cadelli
Uncertainty analysis techniques
CEC, Luxemburg, EUR 10934 EN

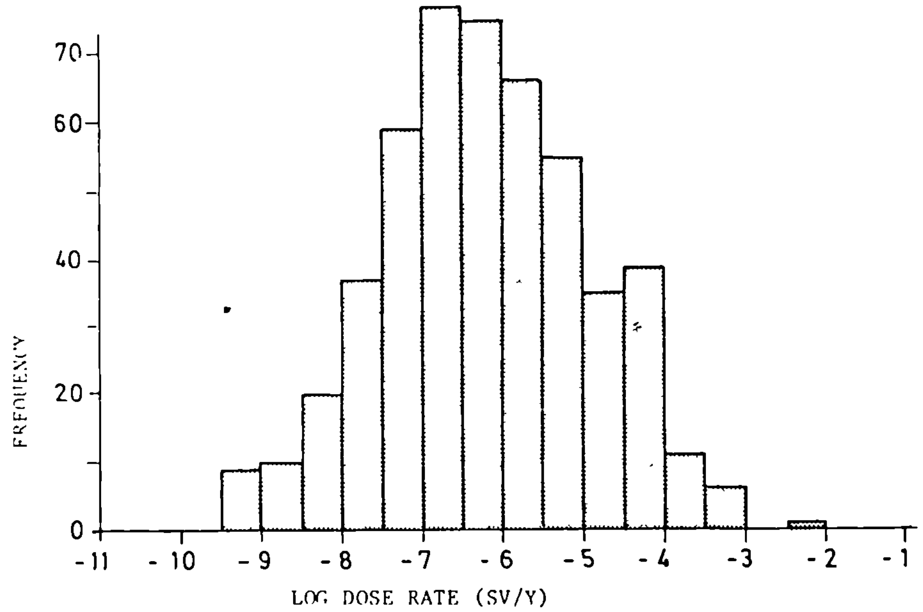
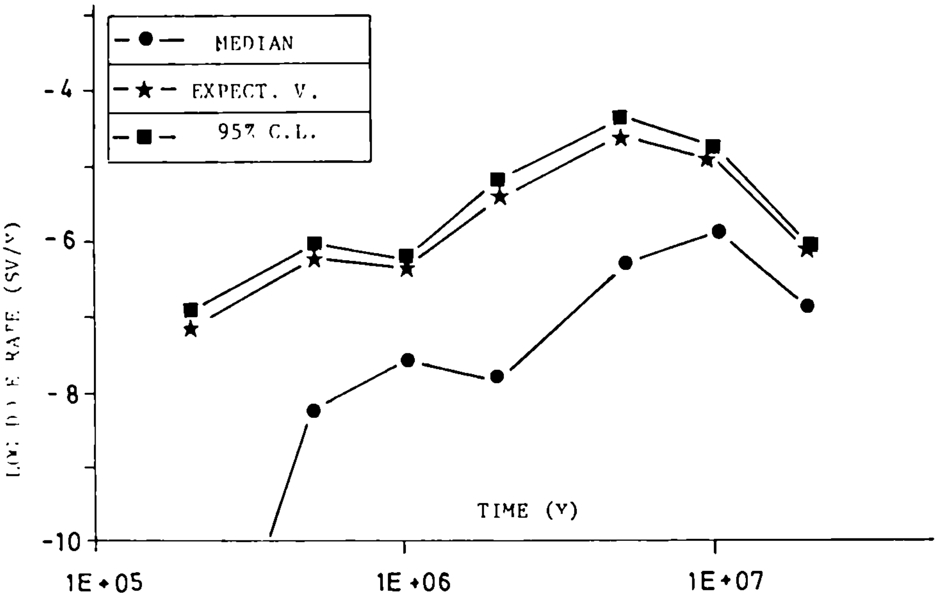


Figure 1. Histogram of the calculated annual doses at 5 million years in the case of the normal evolution scenario

Figure 2. Expectation value with its 95% upper confidence limit and the median of the calculated annual doses as a function of time (normal evolution scenario)


EXPECTATION DOSE RATE

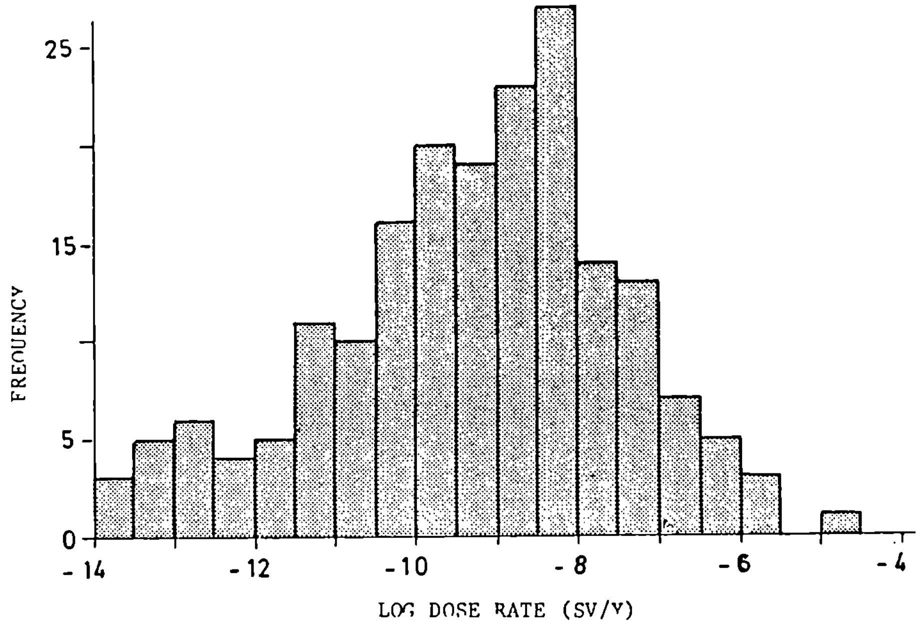
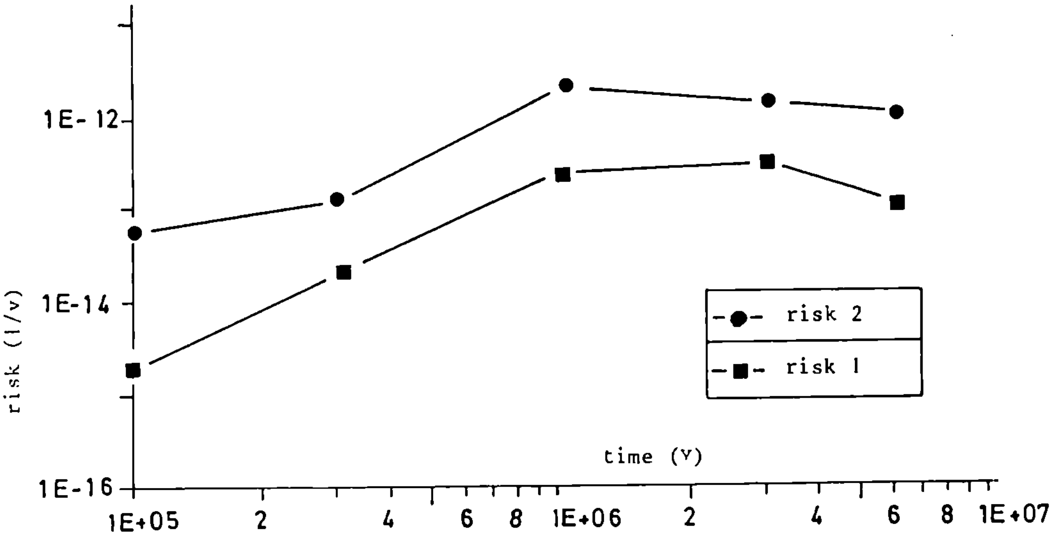


Figure 3. Histogram of the calculated annual doses at 300,000 years in the case of the faulting scenario.

Figure 4. Estimated risks as a function of time due to the faulting scenario (risk 1 : constant fault frequency ; risk 2 : sampled fault frequency).



Performance Evaluation of HLW Waste Disposal in Geological Formations - PAGIS 2 Project: Salt Rock Option

Contractor	:	GSF - IfT Braunschweig, FRG
Contract No.	:	FI1W-0002-D
Duration of Contract	:	July 1984 - March 1987
Project Leader	:	R. Storck

A. OBJECTIVES AND SCOPE

The concerted action PAGIS has been started by the CEC to collect and assess the experience gained in the various countries of the EC in the field of HLW disposal. Based on the data, parameters, and models selected and the methodology developed in phase 1, the repository performance is under investigation in the current phase 2. In the assessment best estimate and uncertainty calculations are performed for the combined system of repository, overburden, and biosphere. Doses to man resulting from the release of radioactivity from the repository are obtained. The sensitivity to the system parameters is studied. Among others it shows how far appropriate choices of the repository design parameters can improve the performance of the whole system. This is done for a selected reference site and the main release scenarios. Also variant sites are considered. Simultaneously the geological formation clay is considered in Belgium, granite in France, and the sub-seabed option in the UK.

B. WORK PROGRAMME

B.1. Best estimate calculations
B.2. Probability estimates
B.3. Definition and selection of parameters for sensitivity and uncertainty analyses
B.4. Sensitivity study
B.5. Uncertainty analysis
B.6. Final assessment

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Preliminary best estimate calculations for the anhydrite and human intrusion scenario as well as sensitivity studies have been performed. In several iteration steps between best estimate calculations and sensitivity studies as well as Monte Carlo calculations appropriate parameters and frequency distributions for parameters have been selected. For the anhydrite scenario there is no release of radioactivity in the best estimate case.

For the uncertainty analysis the main problem encountered is the large variability of the system parameters. It affects the numerical stability and an optimal linking of the different parts of the system. Among others the tackling of these problems and also long computation times per run caused a delay of the final uncertainty analysis.

For the variant site of bedded salt in France 2-d hydrological calculations for the overburden have been performed. A best estimate calculation for the transport of radioactivity is planned.

B.1. to B.4. have been completed for the reference site. B.5. has been started and will be completed together with B.6. during the rest of the working period.

Progress and results

B.1. and B.2.: Best estimate calculations and probability estimates

Connected with the refinement of the repository compartment modelling in 1985 was a revision of the modelling foundations of convective exchange processes between the compartments. This work was completed in the reference year. The altered scenario of water intrusion through the main anhydrite has been extended by a limited intrusion from an undetected brine pocket in the vicinity of the repository. Probability density distribution have been generated for the parameters with relevant variability ranges. Best estimate values have been fixed according to these distributions.

On this basis preliminary best estimate calculations for the anhydrite scenario have been performed with the code EMOS. There is no release of radioactivity from the repository in the best estimate case. This is due to the high creep rate of salt rock at the elevated temperature of the HLW field leading to rapid closure of the void spaces.

For the anhydrite scenario the selection of distribution functions and best estimate values was done in an iterative procedure. The system response has been studied by varying system parameters between minimal and maximal values. Besides a test of the numerical stability of the code and subsequent improvements it turned out that more conservative assumptions had to be included in the scenario definition. This was necessary in order to produce during the Monte Carlo calculations a significant number of runs with a release from the repository different from zero. The refinement of the scenario parameters at the same time lowers the probability of the occurence of the scenario.

A 3-d calculation with the code SWIFT of the hydrological situation of the reference site has been performed with a sweet water model. Pathways to the biosphere could be determined by particle tracking. Transport equations for these pathways have then been solved with the 1-d code TROUGH which is implemented in EMOS. For the SWIFT model area the influence of salinity on the pathways to the biosphere is under investigation with the code METROPOL.

For the variant site of bedded salt in France 2-d hydrogeological calculations have been performed with the code CFEST. Pathways between repository and biosphere have been found by particle tracking. For a common source term for the reference and variant site the migration of radionuclides through the overburden will then be calculated with the 1-d code TROUGH.

A preliminary best estimate calculation for a human intrusion scenario of solution mining of a cavern has been performed and probabilities of occurence have been discussed. Unintentional intrusion scenarios in the form of solution mining are found to be more important than conventional mining or borehole drilling. The transport of radionuclides released into the overburden has been treated the same way as for the anhydrite scenario.

Dose conversion factors have been generated with the biosphere code ECOSYS. Individual doses to man are obtained from these factors and radionuclide concentrations in ground-water near the surface.

In all scenarios it was found that convection processes induced by temperature gradients and flow of gas do not contribute significantly to the transport of radionuclides out of the repository.

B.3. and B.4.: Definition and selection of parameters for sensitivity and uncertainty analyses and sensitivity studies

The definition and selection of parameters was an iterative process in succession with best estimate and sensitivity analyses. Ranges of variability were estimated and if found to be important, frequency distributions have been selected. There was no need of using simplified models in the uncertainty calculations since no significant reduction of computation time could be expected.

Parameters determining the flow of brine in the repository turned out to be most important. These are convergence rates as driving forces and permeabilities of various resistances in the repository. Depending on the attained values, a few parameters have the potential of switching on and off the release of radioactivity from the repository.

B.5.: Uncertainty analyses

Statistical routines have been prepared in close cooperation with the other contractors. The Latin hypercube sampling technique is being used for the generation of data sets for each run from the frequency distributions supplied.

The main problem encountered is the large variability of the system parameters during the Monte Carlo simulation. It was difficult to check and guarantee the numerical stability of the codes and also to perform an optimal linking of the different parts of the system under these conditions. Long computation times per run which partly result from lacking optimization do not allow to run the desired large size statistical ensembles. The need for refinements of parameters and distribution functions caused some delay. The final uncertainty analysis could not be completed during the reference year.

Performance evaluation of HLW waste disposal in geological formations - PAGIS 2 project: granite option

Contractor:	Commissariat à l'Energie Atomique, 31-33 rue de la Fédération F - 75752 PARIS
Contract N°:	427-84-9-WAS-F
Working Period:	January 1984, December 1986
Project Leaders:	J. LEWI, F. VAN KOTE

A. Objective and Scope

The second phase of the PAGIS action is devoted to the evaluation of performances of repositories in granite for high level vitrified waste.

The disposal system is divided prior to calculation in three spatial zones or subsystems: the near-field, the far-field and the biosphere.

For the granite option the approach has consisted first in studying each sub-system in detail, and then in performing global studies: therefore Nearfield, Farfield and Biosphere are presented through separated studies involving the codes AQUASAT-AQUAMIGR, TRASH and BIOS respectively. Global calculations (best-estimate and global sensitivity analysis) are involving the code MELODIE, which covers the whole system including the Biosphere.

B. Work Programme

B.1. Preliminary investigations on subsystems.
B.2. "Best-estimate" calculations.
    B.2.1. reference site (normal and altered scenarios).
    B.2.2. first variant (normal scenario).
    B.2.3. second variant (normal scenario).
B.3. Sensitivity analysis.
    B.3.1. Parametric studies for subsystems.
    B.3.2. Global sensitivity studies on reference case.
B.4. Uncertainty analysis on reference case.

C. Work progress and obtained results

. "best-estimate" calculations: normal evolution scenario for the three cases

"Best-estimate" calculations are currently performed in three steps. The first step consists in a detailed study of regional groundwater flow conditions following a two dimensionnal approach. A map of hydraulic head, pore water velocities and particle trajectories in the chosen 2D cut of the studied geosphere is established.

This step allows to optimize the repository location in accordance with normal evolution scenario assumptions (at reasonnable depth and as far as possible from main discharge zones) and to identify the predictible mainly contamined discharge zones. During the second step the biosphere is modelled, the representation of which being focused on these discharge zones. At last, the third step concerns the simulation of radionucleides transfer from the repository to the Biosphere and the evaluation of the radiological impact to individuals.

All these calculations are performed with the code MELODIE developed by CEA/IPSN(*).

- Reference site (point B.2.1.)

  The three steps have been completed during the year 1986. Many developments have been necessary to treat actinides decay chains (especially the family of Neptunium 237) concerning both the Nearfield and the Geosphere submodels.

  Around the repository the calculated pore water velocities are about 2.10^{-3}m/year.

  The main discharge zone is a small group of rivers named "Les pallands".

  Calculated maximum dose rates to individuals are presented through table 1 for the two concepts of repository (cases A and B : assumed cooling time of 30 and 100 y,resp.). These results are concerning fissions products (^{135}Cs, ^{99}Tc, ^{93}Zr) and the Neptunium decay chain (^{237}Np, ^{233}U, ^{229}Th).
- First variant (point B.2.2.)

  For the site of BARFLEUR which represents an example of a coastal site the possibility of a release of activity in the sea has lead to the implementation of a sea-compartment in the Biosphere model: Its description is, at first, based upon the evaluation of dilution effects due to the currents (calculations performed during the second half of 1986) and then upon the seafood consumption.

  The last step of best-estimate calculations covering the first variant will be achieved by the end of January 1987.
- Second variant (point B.2.3.)

  The UK notional site's description has been established in accordance with BGC experts recommandations.

  Hydrogeology of the site has been first studied at a very large scale in order to get a reduced 2D cut, which dimensions are more manageable for the transfer simulations. The chosen repository location is at 980 meters of relative depth (300 meters under the top of the granite formation). In these conditions, without retardation effects particle travel duration through geosphere is about one half million year (figure 1).

  Preliminary transfer calculations have shown the very strong dependency of the résults on the retention properties of the cover.

. "Best-estimate" calculations: altered evolution scenarios

A study of the radiological impact of human intrusion for the reference site has been performed (point B.2.1.).

The intrusion is defined as the exploitation of concentrated mine resources assumed to be of economical interest for man from 1000 to 100.000 years after the closure of the repository. The exploitation leads to the creation of a cubic cavity of 100 m x 100 m x 100 m in the granite, very near from the repository. Contaminated water collected by the cavity is assumed to be rejected to the surface during the mining activities (50 years).

* Commissariat à l'Energie Atomique/Institut de Protection et de Sûreté Nucléaire.

Some additionnal pessimistic assumptions have been made:

- The host-rock hydraulic conductivity is assumed to be locally altered due to implementation of the repository: its value is a hundred times higher than the initial one (see table 2).
- A second profile of permabilities has been studied in addition to the reference one: for this second profile all the permabilities are emphasized by one to two orders of magnitude (see table 3).

Three contamination scenario have been considered. The first one concerne the workers exposed to external irradition and inhalation due to contamined rocks and dusts. The two others are considering the existence of a small animal husbandry and a small garden supposed to be contaminated by the activity rejected from the cavity.

Results are presented through tables 2 and 3.

. Sensitivity analysis: parametric studies for subsystems (points B.1. and B.3.1)

1. Near field (figures 2 and 3)

Two simplified analytical models were developed by CEA/ANDRA(*) in order to describe the near field and to evaluate the isolation capacity of this subsystem. In these models the reference configuration is limited to a single borehole.

Calculations are carried out for each parameter within a range of values scanning from the most severe to the mean conditions. This range of variation reflects the uncertainty affecting the parameters which takes into account both the variability of the medium characteristics and the experimental errors involved in the determination of the characteristics themselves.

The hydratation process of backfilling has been analysed with the AQUASAT model. For the reference configuration, the time required for the saturation of backfilling is about 8 months. Following are the most important parameters that affect the variability of the time for saturation (which ranges between the values in parenthesis):

- the hydraulic conductivity (10.6 years - 2 months)
- the borehole radius (3.2 months - 2 years)
- the hydrostatic pressure (1.1 year - 6.1 months).

The results show that the backfilling resaturation is a short term phenomenon which is insignificant in first approximation in the best estimate calculations.

The migration of the radionuclides through the near field has been analysed through the AQUAMIGR model. We have appreciated the influence of some parameters on the release of radionuclides on the one hand from the backfilling to the granite and on the other hand to the geosphere after 10 meters of rock granite:

- radionuclide dependent parameters (diffusion coefficients, distribution coefficients),
- thickness of bentonite,
- host rock characteristics (distance between fissures, hydraulic conductivity in the fissures and in the matrix).

The results obtained can be summarised as follows:

- the isolation capacity of backfilling can range from one year to a few thousand years depending on radionuclide and conditions,
- the isolation capacity of the granite rock (10 meters) can range from a few years to a few million years.

For medium lived radionuclides the backfilling can be very important for the isolation capacity of near field in the short term, if in presence of fractured rocks of high permeability. If the host rock is not altered around the borehole, the isolation is slightly modified by the thickness of backfilling.

(*) ANDRA: Agence Nationale pour la Gestion des Déchets Radioactifs.

2. Far field

Using the assumptium of an equivalent porous medium for the granite, two aspects of the hydrological modelling of a site have been studied:

- the differences between two and three demensional representation,
- the influence of discret fracture zone location in two dimensional calculation.

These studies are performed on the AURIAT reference site. The informations used are topography of the site, the estimation of boundaries of the massif and source hydrological properties.

The mains assumptions for both cases are:

- équivalent porous media with permeability and porosity function of depth,
- hydraulic head equal to elevation at the top boundary, no flow conditions on bottom and lateral boundaries.

The calculations are performed using the TRASH computer code developped at CEA-DEMT, which is a numerical model.

The main results of the first study is that there are no possibilities in this configuration to find a 2D cut in the 3D mesh which gives the same results as the 3D calculation (in terms of flow rate in an hypothetical storage area or in terms of particles paths). In the second study we can summarize the results as follow:

- if the fractures are not connected, their influences on hydrological field is only local and there are no important modifications in the homogeneous media (in terms of flow rate for example),
- if they are connected, the results can be very different depending on media and fractures.

3. Biosphere

We have studied two kinds of sites:

- Auriat site, which is a terrestrial site with a release to a small river, where we have considered a local compartment and a regional compartment.
- Barfleur site, which is a costal site, and where the discharge zone of radionuclides is the local marine environment in the sea.

We have used the BIOS code which has been developped by the NRPB, assuming a unit source term for each of the following radionuclides: ^{99}Tc,^{135}Cs, ^{233}U,^{237}Np, ^{241}Am. For a release to a stream the BIOS model assumes instantaneous mixing in the discharge zone. For the radionuclide dependent parameters and for specific parameters of the environment of two sites, best estimates are suggested and, range are chosen for human individual consumption rates. In the different sites the figure 4 shows the major exposure pathways in short term and in long term.

For each radionuclide, attenuation factor of biospheres has been computed:

$$\text{AF (attenuation factor)} = \frac{\text{release to a discharge zone Bq.y}^{-1}}{\text{ingested or inhaled rate Bq.y}^{-1}}$$

For the ingestion for example, AF is higher than:

10^5 for ^{135}Cs, 5.10^6 for ^{99}Tc and 10^7 for actinides.

For a specific site, the uncertainties of this factor arise from our ignorance of the biosphere in long term especially of the dilution capacity of the discharge zone (river, lake...).

. Global sensitivity analysis on reference site (point B.3.2.)

A sensitivity analysis algorithm has been implemented in MELODIE. It is based upon the latin hypercube sampling technique and a statistical analysis of the response surface. The transfer simulations involve a reduced representation of geosphere (1D) whose physical caracteristics are extracted from best-estimate calculations: this 1D pathway represents a flow tube of constant section, starting at the highest topographical point crossing the repository and ending at the main discharge zone of the system.

Preliminary calculations have shown the very high sensitivity of the results with respect to the variability of permeability, porosity, retardation factor of the mediums. The less influent parameters seem to be all related to the source term.

In order to ensure a certain consistency with other participants approach, the algorithm has been entirely revised in collaboration with the JRC of ISPRA, during the end of 1986. Final results are planned for the beginning of 1987.

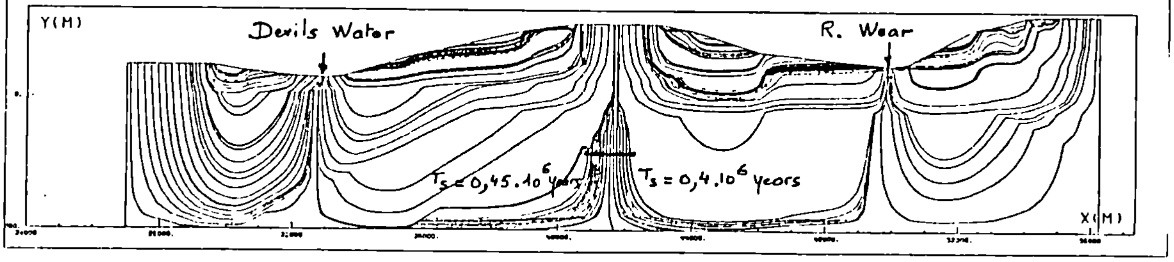
. Uncertainty analysis (point B.4.)

The analysis of the few available permeability measurements related the reference site, and a bibliographical study of available distribution coefficients for granite have shown that data where insufficient to allow an objective evaluation of uncertainties. Anyhow, uncertainty will be evaluated for the reference case, using subjective ranges for the most parameters. This evaluation will be performed with the code provided by the JRC of ISPRA at the end of 1986.

Case	Radionu-clides	Time of occurrence of the peak value (years)	Peak value for individual dose rate (Sv/year)
A	^{135}Cs	2 300 000	10^{-7}
	^{99}Tc	250 000	2.10^{-8}
	^{93}Zr	6 000 000	$1,5.10^{-9}$
	^{237}Np	3 000 000	3.10^{-5}
	^{233}U	3 000 000	6.10^{-7}
	^{229}Th	3 000 000	$1,5.10^{-6}$
B	^{135}Cs	3 000 000	5.10^{-9}
	^{99}Tc	300 000	10^{-9}
	^{93}Zr	6 000 000	10^{-10}
	^{277}Np	5 000 000	10^{-5}
	^{233}U	5 000 000	$1,5.10^{-7}$
	^{229}Th	5 000 000	4.10^{-7}

Table 1

Figure 1 : UK notional site.
Particle trajectories through geosphere



SCENARIO		1000 ans	5000 ans	20 000 ans	30 000 ans	50 000 ans	100 000 ans
A	α (Np^{237} et Th^{229})	5,5.10^{-5}	3.10^{-6}	2,5.10^{-5}	3,4.10^{-5}	3,5.10^{-5}	2,1.10^{-5}
	PF (Tc^{99} et Zr^{93})	2,4.10^{-9}	5,8.10^{-8}	2,3.10^{-7}	5.10^{-7}	6,5.10^{-7}	1,26.10^{-6}
	Total	5,5.10^{-5}	3.10^{-6}	2,5.10^{-5}	3,4.10^{-5}	3,5.10^{-5}	2,1.10^{-5}
B	α (Np^{237})	4,3.10^{-9}	2,17.10^{-8}	1,8.10^{-7}	2,4.10^{-7}	2,17.10^{-7}	10^{-7}
	PF (Tc^{99})	2,7.10^{-8}	6.10^{-7}	1,9.10^{-6}	2.10^{-6}	1,6.10^{-6}	6,3.10^{-7}
	Total	3.10^{-8}	6,2.10^{-7}	2,1.10^{-6}	2,24.10^{-6}	1,8.10^{-6}	7,3.10^{-7}
C	α (Np^{237})	2.10^{-5}	10^{-6}	8,9.10^{-6}	1,1.10^{-5}	10^{-5}	4,5.10^{-6}
	PF	4,5.10^{-8}	10^{-8}	3.10^{-8}	3,4.10^{-8}	2,6.10^{-8}	10^{-8}
	Total	2.10^{-5}	10^{-6}	8,9.10^{-6}	1,1.10^{-5}	10^{-5}	4,5.10^{-6}

Table 2 : Profile 1 (hydraulic conductivity 100 times higher than the initial one)

Radiological impact of human intrusion for the reference site. Maximum annual dose rates to individuals in Sv/y for the two profiles (profiles 1 and 2)

A : Worker
B : Animal husbandry
C : Garden

Table 3 : Profile 2 (all permeabilities higher by one to two orders of magnitude than the initial ones)

SCENARIO		1000 ans	5000 ans	20 000 ans	50 000 ans	100 000 ans
A	α (Np^{237} et Th^{229})	7,6.10^{-3}	3,8.10^{-3}	1,5.10^{-3}	5,7.10^{-3}	1,6.10^{-2}
	PF (Tc^{99} et Zr^{93})	8,9.10^{-9}	4.10^{-8}	6.10^{-7}	2,15.10^{-6}	1,7.10^{-6}
	Total	7,6.10^{-3}	3,8.10^{-3}	1,5.10^{-3}	5,7.10^{-3}	1,6.10^{-2}
B	α (Np^{237})	2,8.10^{-11}	1,4.10^{-10}	5,7.10^{-9}	1,7.10^{-9}	5.10^{-9}
	PF (Tc^{99})	10^{-9}	5.10^{-9}	7.10^{-8}	2,3 10^{-7}	1,25.10^{-7}
	Total	1,3.10^{-9}	5,16.10^{-9}	7,6.10^{-8}	2,3.10^{-7}	1,3.10^{-7}
C	α (Np^{237})	10^{-7}	5.10^{-7}	2,3.10^{-6}	5.10^{-6}	1,4.10^{-5}
	PF (Tc^{99})	1,7.10^{-9}	8.10^{-9}	1,2.10^{-7}	4.10^{-7}	2.10^{-7}
	Total	10^{-7}	5.10^{-7}	2,4.10^{-6}	5,4.10^{-6}	1,44.10^{-5}

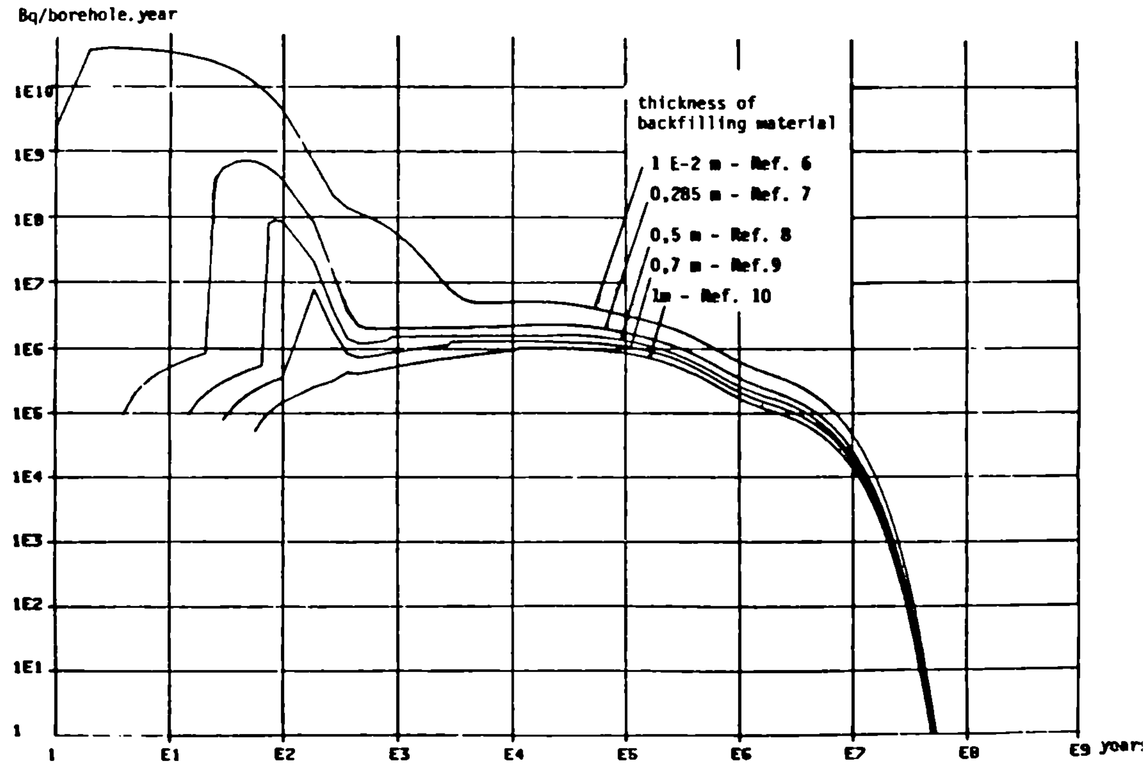
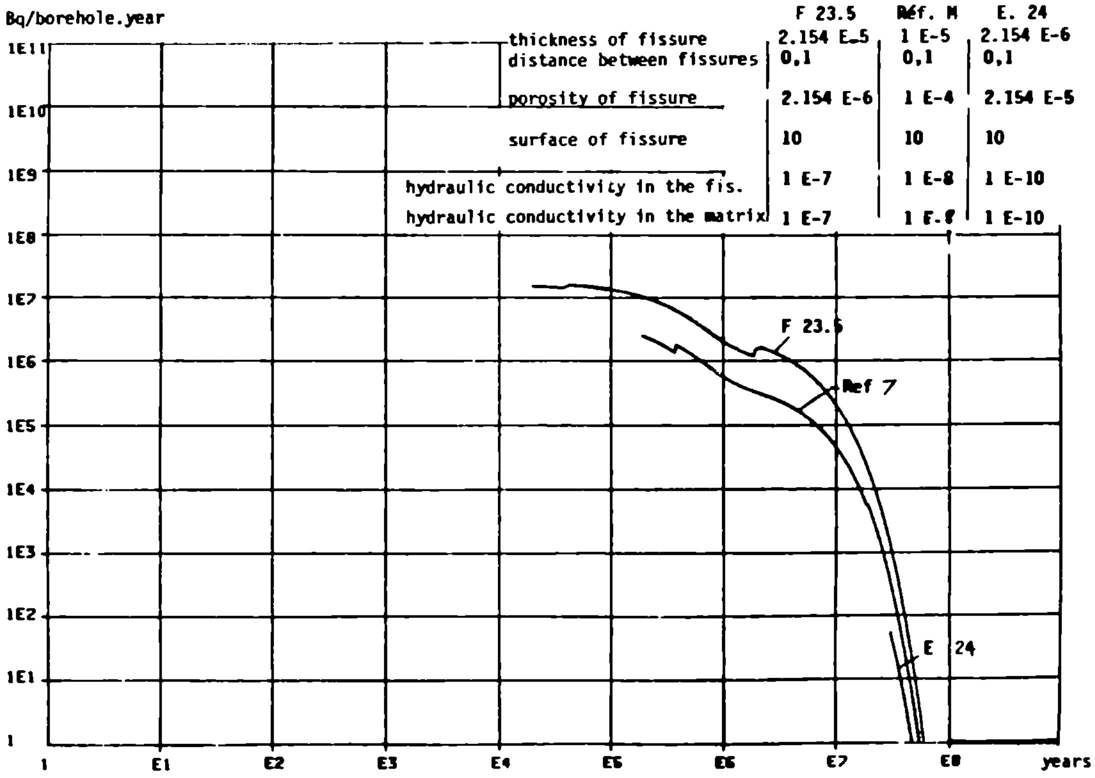


FIGURE 2 : Cumulative release to the interface backfilling/granite as function of time. The source term is a borehole (26,6 T. initial uranium métal).



	F 23.5	Réf. M	E. 24
thickness of fissure	2.154 E-5	1 E-5	2.154 E-6
distance between fissures	0,1	0,1	0,1
porosity of fissure	2.154 E-6	1 E-4	2.154 E-5
surface of fissure	10	10	10
hydraulic conductivity in the fis.	1 E-7	1 E-8	1 E-10
hydraulic conductivity in the matrix	1 E-7	1 E-8	1 E-10

FIGURE 3 : Cumulative release to the geosphere, after 10 met ers of rock granite, as a function of time. The source term is a borehole (26,6 T. initial uranium métal).

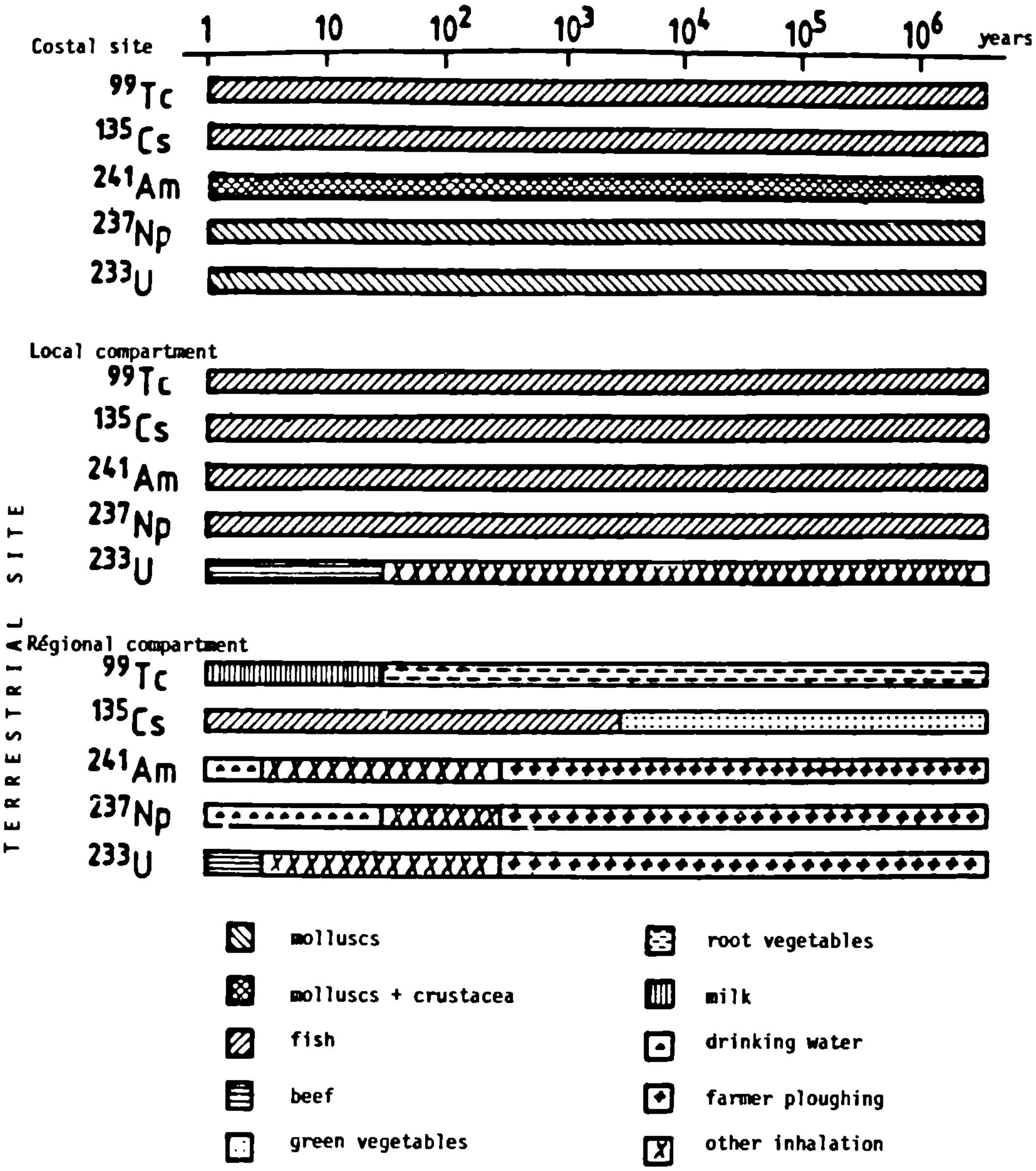


FIGURE 4: major exposure pathways as a function of time.

Performance Evaluation of HLW Waste Disposal in Geological Formations - PAGIS 2 Project: Sub-Seabed Option

Contractor: NRPB, Chilton, UK
Contract No: WAS-430-84-9-UK (H)
Working Period: Part 1 of Phase 2 : 1 July 1984 - 31 December 1984;
Part 2 of Phase 2 : 1 July 1985 - 31 December 1986
Project Leader: Ms M D Hill

A. Objectives and Scope

The main objective of PAGIS is to evaluate the capacity of various geological formations to act as repositories for vitrified high-level radioactive waste, using common assessment methodologies where possible. This contract is concerned with the sub-seabed disposal option; others are assessing disposal in clay, granite and salt formations on land.

In Phase 1 of PAGIS, which was completed in June 1984, the sites and waste emplacement techniques to be considered were selected. The reference site is at Great Meteor East (GME) and two variant sites were selected - one in the Cape Verde Plateau (CV) and the other in the Southern Nares Abyssal plain (SNAP). All these sites are in the Atlantic Ocean, and have been investigated in international studies of the feasibility of sub-seabed disposal.

The scope of Phase 2 is i) to perform a preliminary radiological assessment using the models and data chosen in Phase 1 ii) to undertake sensitivity and uncertainty analyses iii) to reappraise the data and models and to perform an improved assessment of potential doses and risks to individuals and populations.

B. Work Programme

B.1. Preliminary 'best estimates' of doses and risks to individuals and populations.
B.2. Estimates of the probabilities of occurrence as a function of time of various scenarios.
B.3. Definition and selection of parameters for sensitivity and uncertainty analyses.
B.4. Investigation of the sensitivity of the model results to variations in the values of parameters.
B.5. Quantification of the uncertainty in the model output.
B.6. Improved assessment using the best available models and data which have been selected considering results from B.2.-B.5.

C. Progress of work and obtained results

Summary

The calculations of maximum individual doses, collective doses and collective dose rates using 'best estimate' models and data have been completed. They cover the following cases for penetrator emplacement i) normal evolution scenarios at GME, SNAP and CV ii) altered evolution scenarios at GME and iii) local sensitivity studies for emplacement at GME. In addition, the calculations have been finished for the normal evolution scenario for drilled emplacement at GME. Probabilities are now being assigned to the various altered evolution scenarios so that risks can be estimated.

Models and data have been assembled for the uncertainty and global sensitivity analyses; the calculations are complete and the results are being evaluated. The general work progress is as follows:

. B.1. is completed
. B.2., B.3., B.4. and B.6. are progressing normally
. B.5. is delayed.

Progress and results

1. Best estimate calculations (B.1., B.2., B.6.)

In the normal and altered evolution scenario calculations the migration of radionuclides through seabed sediments was modelled using the code TROUGH-2D /1/ and the dispersion and advection in the world's oceans using the NRPB/MAFF ocean model COMMA /2/. The concentrations of radionuclides in water and sediments were used to calculate doses to critical groups arising from all the relevant pathways /3/.

- Normal evolution scenario

  The preliminary best estimate calculations for penetrator emplacement at the reference site of Great Meteor East were done in 1985. The peak individual dose and the collective dose truncated at various times were calculated. In both cases ^{237}Np was the major contributor. Since then the database has been revised paying particular attention to the important parameters, such as K_ds, identified in the sensitivity studies. The seabed working group of the NEA was consulted during this process. The most significant change was an increase in the K_d for neptunium from 100 to 2000. Following comments received on the preliminary calculations the quantity of waste was increased three fold to take into account arisings from the total existing European nuclear power programme. The doses from the final best estimate calculations are lower, largely because of a reduced contribution from neptunium. Similar doses have been calculated for penetrator emplacement at the variant site of Southern Nares Abyssal Plain. Doses have not been calculated for the variant site at Cape Verde rise. There is only a limited amount of data available for this site and, in any case, its proximity to GME suggests that doses would be similar.

- Normal evolution scenario: drilled variant

  Calculations have been done for the variant of drilled emplacement at GME. In this the wastes are assumed to be placed much deeper in the sediments and the doses are much lower than those arising from penetrator emplacement. However, we have assumed that reducing conditions exist at these depths and that the K_ds for the redox sensitive elements Tc and Np are correspondingly increased; this may not be the case and further sensitivity studies are being done.

- Altered evolution scenarios

  Several altered evolution scenarios have been identified for the penetrator option. These include incomplete hole closure, penetrators lying on the seabed, differential compaction of sediments leading to enhanced pore water flow and human intrusio by exploratory drilling or mining of ferromanganese nodules. Some of these can arise from more than one cause; for example, penetrators may fail to emplace and lie on the seabed because of hitting a glacial erratic or following the shipwreck of the conveying vessel. This will be taken into account when assigning probabilities to the various scenarios. The calculations of the consequences of the altered evolution scenarios in terms of maximum individual doses, collective doses and collective dose rates have been completed.

Probabilities are being assigned to the altered evolution scenarios and these will be combined with the radiological consequences to produce risks.

- Local sensitivity studies

  Local sensitivity studies are done by varying parameters, one at a time, in the best estimate models and comparing the output with the reference case. These studies show that predicted doses are sensitive to i) K_d values appropriate for both bed sediments and sediments in the water column and ii) the pore water velocity within the bed sediment.

2. Uncertainty analyses and global sensitivity analyses (B.3., B.4., B.5.)

These analyses involve sampling parameters from their distributions and require a large number of computer runs; for reasons of economy of time and money it is often impracticable to use the best estimate models. For this reason, a simplified version of the MAFF/NRPB ocean model has been finalised and tested. This has been interfaced with TROUGH-1D /5/ which is a simpler geosphere model. The input parameters are sampled using a Latin hypercube sampling program /5/ and the output is analysed using a Partial Correlation Coefficient and Standardised Regression Coefficient program /6/.

- Uncertainty analyses

  This is a study of the propogation of input data uncertainty through the models to the output. Input parameter distribution functions, such as ranges for K_ds, have been obtained by consultation with the Seabed Working Group of the NEA. The analyses have been done for the normal evolution scenario for penetrator emplacement and also for a selection of altered evolution scenarios such as poor emplacement. The results are now being evaluated.

- Global sensitivity analyses

  This is a study of the sensitivity of the model output to parameter changes while other parameters are varying across their normal ranges. These studies have covered the normal scenario; wider parameter ranges have also been used to represent altered evolution scenarios. The calculations have been completed and the results are being evaluated.

References

/1/ GILBEY, D.J., AND HOPKIRK, R.J., TROUGH-2D User's Handbook and Theoretical Description, Polydynamics Ltd., Zurich (1983).

/2/ NEA, Review of the Continued Suitability of the Dumping Site for Radioactive Waste in the North-East Atlantic, Nuclear Energy Agency (OECD), Paris (1985).

/3/ IAEA, The Oceanographic and Radiological Basis for the Definition of High Level Wastes Unsuitable for Dumping at Sea, Safety Series No. 66, International Atomic Energy Agency, Vienna (1984).

/4/ GILBEY, D.J., HOPKIRK, R.J. AND SCHWANNER, I., TROUGH-1D User's Handbook and Theoretical Description, Polydynamics Ltd., Zurich (1984).

/5/ IMAN, R.L. AND SHORTENCARIER, M.J., A Fortran 77 Program and User's Guide for the Generation of Latin Hypercube and Random Samples for Use with Computer Models, Sandia Laboratory Report SAND83-2365 (1984).

/6/ IMAN, R.L., SHORTENCARIER, M.J. AND JOHNSON, J.D., A Fortran 77 Program and User's Guide for the Calculation of Partial Correlation and Standardized Regression Coefficients, Sandia Laboratory Report SAND85-0044 (1985).

Table I

Summary of Results from Phase 2 'Best Estimate: Normal Evolution' Dose Calculations$^+$

Calculation	Site	Max. Ind. dose ($Sv\ a^{-1}$)	Dominant Nuclide	Collective dose (man Sv) truncated at		
				10^3 a	10^6 a	∞
A. Penetrator Emplacement						
Preliminary*	GME	$3.7\ 10^{-10}$	^{237}Np	$3.5\ 10^{-4}$	$1.4\ 10^4$	$2.6\ 10^4$
Final	GME	$1.3\ 10^{-10}$	^{99}Tc	$7.5\ 10^{-14}$	$4.2\ 10^3$	$6.3\ 10^3$
Final	SNAP	$1.3\ 10^{-10}$	^{99}Tc	$5.5\ 10^{-12}$	$4.2\ 10^3$	$9.5\ 10^3$
B. Drilled Emplacement						
Final	GME	$2.2\ 10^{-16}$	^{79}Se	0	$1.2\ 10^{-2}$	$1.8\ 10^{-2}$

$^+$These calculations assume that the total inventory of HLW is successfully emplaced (this is equivalent to 14,700 penetrators). The inventory does not include ^{129}I or ^{14}C.

*The preliminary calculations assume a smaller nuclear power programme and the total amount of HLW is one third of that adopted in the final calculations.

Table II

Summary of Results from Phase 2 'Best Estimate: Altered Evolution' Dose Calculations^{+}

Scenario	Max. Ind. Dose ($Sv\ a^{-1}$)	Dominant Nuclide	Collective dose (man Sv) truncated at		
			10^{3} a	10^{6} a	∞
Normal (ie undamaged, 50 m burial, zero pore water velocity)	$8.2\ 10^{-15}$	^{99}Tc	$5.1\ 10^{-18}$	$2.9\ 10^{-1}$	$4.3\ 10^{-1}$
Damaged penetrator lying on seabed	$6.9\ 10^{-11}$	^{240}Pu	$1.8\ 10^{-2}$	$6.0\ 10^{1}$	$7.2\ 10^{1}$
Damaged penetrator lying 10 m deep in sediment	$2.4\ 10^{-13}$	^{229}Th	$5.5\ 10^{-8}$	1.3	7.1
Enhanced pore-water velocity ($0.1\ m\ a^{-1}$) Undamaged penetrator, 50 m burial	$1.3\ 10^{-12}$	^{229}Th	$2.6\ 10^{-10}$	$1.4\ 10^{1}$	$3.6\ 10^{1}$
Failure of penetrator and canister casing, 50 m burial	$8.4\ 10^{-15}$	^{99}Tc	$1.4\ 10^{-16}$	$3.0\ 10^{-1}$	$4.4\ 10^{-1}$

$^{+}$The doses are presented for one penetrator and all of the scenarios are for penetrator emplacement at GME. The doses arising from the 'normal' emplacement of one penetrator are presented for comparative purposes.

Summary and Review of PAGIS - Phase 2

Contractor: Associated Nuclear Services, UK
Contract No.: FI1W/0104-UK(H1)
Duration of contract: September 1986 - August 1987
Project Leader: T.J. Sumerling

A. Objectives and Scope

The objectives of the work are;

- to prepare a summary of the results and conclusions of the performance assessments of the repositories for HLW in deep geological formations covering four options (clay, granite, salt and the seabed); and
- to review criticality the basis, methods, models and data used for the performance assessments and to prepare a report setting out comments and suggestions relevant to Phase III of the PAGIS project.

The 'Summary' report is intended for wide distribution and is to be written in relatively simple terms. The 'Comments and suggestions' report is for use by the Commission and the PAGIS secretaries.

B. Work programme

B.1. Discussions with the nominated representatives of the CEC and agreement of the study basis, including identification of the reference project reports.

B.2. Collation and initial review of the PAGIS phase I, and as they became available, phase II documents and supporting material.

B.3. Discussions with PAGIS secretaries and other relevant organisations, with the aims of assessing background and clarifying published material.

B.4. Preparation of a draft 'Summary' report of 200 to 250 pages, giving comprehensive coverage of the results and conclusions of the performance assessments for the four geological options.

B.5. Detailed critical review of the approach, the methodologies, models and data, and preparation of a draft 'Comments and suggestions' report.

B.6. Collaboration with the PAGIS secretaries and the CEC representatives to produce final versions of the two reports.

B.7. Production of master copies of the final reports.

C. Progress of work and obtained results

Summary

Phase 1 comprehensive reports and some preliminary Phase 2 topical reports have been received. Initial review work has been carried out to ascertain the approaches adopted, nature of work being carried out and state of documentation for each option. Draft plans for the 'Summary' and 'Comments and Suggestions' reports have been prepared for presentation at the 5th PAGIS Steering Committee Meeting.

Progress and results

1. Initial review (B.2.)

Initial inspection reveals that, while providing useful background and introductory material, the presently available material does not constitute a sufficient basis for detailed summary and review work to begin. The basic methodology adopted in PAGIS Phase 1 is being followed, although, the emphasis given to 'best estimate' calculations, sensitivity analysis and uncertainty analysis differs between options. It is noted that the modelling approaches, adopted for each option, have evolved from those presented in Phase 1 documents; models have been subject to improvements and a number of new models and techniques have been introduced.

2. Draft report outlines (B.1., B.2)

Draft outlines for the 'Summary' and the 'Comments and Suggestions' reports have been prepared and submitted to the Commission. These will be presented at the 5th PAGIS Steering Committee Meeting. Although these form the intended basis for the reports, it is anticipated that they may be revised to take account of the views of the Commission representatives and Steering Committee. The structure of each report is modelled on the PAGIS Phase 1 Summary Report but greater emphasis is given to continuity within the discussion of each option.

5 b) PACOMA project

Performance Assessment of Confinements for MLW and Alpha Waste (PACOMA Project)

Contractor: NRPB, Chilton, UK
Contract No: FI1W/0041-UK(H)
Working Period: October 1986 - December 1988
Project Leader: Ms M D Hill

A. Objectives and Scope

The overall objectives of the UK contribution to the PACOMA Project are to develop and demonstrate procedures for assessing the radiological impact of disposal of intermediate level waste in a deep repository located in a clay formation. The hypothetical repository considered is assumed to be at Harwell in Oxfordshire. The research is co-ordinated by the UK Department of Environment and is being carried out by four organisations:

National Radiological Protection Board (NRPB)
Theoretical Physics Division, AERE
Electrowatt Engineering Ltd
CAP Scientific Ltd

The NRPB work is in two phases. The objectives in Phase I are to establish a detailed methodology for the assessment, to collect data for biosphere modelling and to carry out preliminary calculations. In Phase II the aim is to carry out the assessment, using information provided by other UK contractors and in consultation with other participants in PACOMA, particularly CEN/SCK.

B. Work Programme

B.1. Adaptation of PAGIS methodology for use in the assessment of intermediate level waste disposal, identification of radionuclide release scenarios.
B.2. Review of available biosphere data, and preliminary calculations for typical releases.
B.3. Detailed planning of calculations to be carried out in the full assessment, finalising biosphere data and assumptions for each scenario.
B.4. Best estimates of doses and risks to individuals and populations for each scenario.
B.5. Sensitivity and uncertainty calculations.
B.6. Co-ordination of joint report by the four UK contractors.

C. Progress of work and obtained results

State of advancement

Work has been started on items B.1. and B.2. Previous assessments of disposal of wastes in a hypothetical deep repository have been reviewed for the purpose of scenario identification and collation of biosphere data. Difficulties which could be encountered in applying the PAGIS methodology have been considered and ways in which they might be resolved are being investigated. Work on items B.3.-B.6. is not due to begin until April 1987.

Progress and results

1. Assessment methodology and release scenarios (B.1.)

Although it is clear that the basic methodology used in PAGIS can be applied to assessing the disposal of intermediate level waste at Harwell, there are some, as yet unresolved, problems which were discovered during PAGIS. One of these is that it is not entirely clear how to sum the risks to individuals from the various release scenarios, nor how to combine the probabilities of the scenarios and the radiological consequences for populations. Another problem is that there are two alternative ways of calculating risks: one which takes into account the probability that a scenario will occur but not the probabilities that parameters used to calculate the consequences of the scenario will have particular values, and one which includes all these probabilities. A paper describing these problems in more detail is being prepared for discussion with CEC and other PACOMA participants.

The review of previous assessments of disposal of wastes in hypothetical repositories at Harwell has shown that none of these have included a sufficient number of "altered evolution" scenarios. Appropriate scenarios are therefore being identified, mainly from studies of other clay sites eg Mol.

2. Biosphere data and calculations (B.2.)

The available data have been reviewed and additional data are being collected from the literature. Plans are being made for preliminary sensitivity and uncertainty analyses using the BIOS model.

Validation of the Vault Computer Model 'VERMIN' for Post-closure Behaviour of Repositories in Geological Formations

Contractor:	Electrowatt Engineering Services (UK) Ltd.
Contract No.:	FI1W-0047-UK (H1)
Duration of Contract:	October 1986 - June 1987
Project Leader:	Z. A. Gralewski

A. Objectives and Scope

The computer model VERMIN has been developed to simulate the post-closure time dependent behaviour of the vault section of shallow and deep land burial types of repository. Development was carried out within the constraints of the probabilistic assessment computer code SYVAC/1/.

The present research conducted for the UK Department of Environment involves both the gathering of experimental data and its use in validating the VERMIN sub-model within SYVAC. The experimental data will be used to validate the processes currently modelled of nuclide migration and groundwater movement in a repository. To update VERMIN where the results of the validation exercise suggest that it is necessary. To identify needs for further experimental work in order to validate aspects of VERMIN and possible new aspects of the vault model for which no applicable data exist. Finally, to ensure that VERMIN provides a suitable source term for the AERE geosphere model. Concerning this last objective, final agreement on the UK inventory must also be reached.

B. Work Programme

B.1. Identification of fundamental physical and chemical processes for each element of the repository model.

B.2. Gathering and sorting experimental data for the processes identified.

B.3. Areas requiring further experimental work must be identified and experiments suggested.

B.4. Validation of VERMIN model.

B.5. Refinements to the VERMIN model where the results of the validation exercise suggest it is necessary, including the possible addition of new physical and chemical processes.

B.6. Achievement of a final agreement on the UK inventory.

B.7. VERMIN will be adapted as necessary to provide a compatible source term for the AERE geosphere model.

C. Progress of work and obtained results

Summary

The physical and chemical processes used within VERMIN have been identified and sorted in order to from the basis for categorisation of experimental and theoretical research (Figure 1). A first survey of the literature on the subject has been conducted and contacts have been established with various groups in order to obtain more detailed data from experimental research.
The leaching process of nuclides from the waste matrix is used as an example in this paper to present the methodology used for the validation of VERMIN. This will demonstrate how the validation exercise may suggest refinements to the actual model, and how further experimental work can be identified.

Progress and results

1. Definition of Concepts (B1, B3)

The chart presented in Figure 1 summarises the identification of the physical and chemical processes modelled by VERMIN according to their nature and to the medium considered. Parameters involved in these processes are listed on the chart. These parameters are part of the input data to VERMIN and therefore values are to be obtained from experimental work. The processes are categorised as follows:

- Degradation of barriers to enable resaturation of the vault
- Groundwater flow
- Nuclide migration

These processes are in general governed by time dependent parameters. In its present state VERMIN considers all the parameters listed to be time independent and they are therefore constant within a deterministic run. The validation exercise should indicate whether this assumption is reasonable without losing accuracy in the results. Important parameters most likely to be time dependent are also listed on the chart of Figure 1.

2. Validation methodology (B2, B3, B4, B5)

Once a mechanism has been identified and relevant experimental studies of the mechanism has been found, validation may proceed.

Firstly the comparison that will be performed must be well defined. Indeed, in most cases the characteristics of experimental studies and theoretical model do not correspond. These characteristics include: presentation of the results, units, geometry etc. The example presented later in this paper is fairly representative of the likely problems associated in comparing theoretical models to experimental studies. Furthermore, it will be seen that very often the purpose of an experimental study is to find values of a parameter which cannot be measured directly, and therefore the experimentalist uses a model to calculate it. We must therefore be careful that we are not comparing a model versus a model, and if we do so that the experimental study validated the model used by the experimentalist.

Once the comparison has been performed, and the differences (if any) explained, the model of the process can be considered as validated. This was when the process examined was isolated from the rest of the system. Therefore the combined effect of several processes must also be validated. If no experimental studies exist, the needs for further experimental work must be clearly defined and described. Furthermore the experimental study used for comparison may contain additional factors that can be used for refinement of the model if this factor is proved to have important consequences.

2.2 Illustration of the validation methodology through an example of the leaching process

The leaching model used in VERMIN is based on the diffusion in a cylinder (see /1/ and /2/).

Because VERMIN can simulate several processes simultaneously including flow, it was convenient to define a leach rate factor L_R (m/a). Therefore the quantity of diffusing substance Q_t through unit length of the cylinder in time t is given by:

$$Q_t = L_R \, S_a \, \Delta C$$

where S_a is the surface area of diffusion (m²), and ΔC is the concentraction difference between the waste matrix and the surrounding material (moles/m³). The output of the process in VERMIN is Q_t versus time in moles per year.

An experimental study of the leaching process was conducted by L. Buckley/3/. The sample used consists of a bituminized waste cylinder leached in water, exposing the entire surface area. The observed variable is the radioactivity leached (Bq) from which the cumulative fraction leached (m) was deduced to present the results. A model (Fick's law) was then used to calculate the effective diffusion coefficient (m²/a).

One of the advantages of using the leach rate concept in VERMIN is that we could directly derive it from the experiment results by differentiation of the cumulative fraction leached. In other words, the leach rate is an observable parameter while the diffusion coefficient must be calculated using a model.

The geometrical data were then adjusted to fit as closely as possible to the experimental conditions. The concentration gradient had also to be ensured to consider the permanent "wash out" effect given in the experiment where the sample is leached in water.

Once the output of the VERMIN leaching model has been converted in the proper units and transformed to the cumulative fraction leached, the comparison was performed.

As shown in Figure 2, despite the many dfferent characteristics of the two studies we reached a good agreement between VERMIN and this experimental study.

In this exercise the leaching process was isolated from any other processes. Since the driving force of this process is the concentration gradient the single effect of the wash-out given by the experimental study is very important. Let us consider Figure 3 where the fraction leached obtained by the same experimental study is compared with the leaching process used in VERMIN in the same conditions but this time the water is confined in a restricted volume. Since the concentration in the water increases the concentration gradient decreases and therefore the fraction leached obtained is much lower than in the previous case. The consideration of a diffusion in the backfill would have shown the same type of differences.

References

1. Electrowatt Engineering Services (UK) Ltd., Report No. DoE/RW/83. EWE/FWOC-2518 (1983). "Development of Vault Model 'VERMIN' for Post Closure Bahaviour of Repositories for Non-heat Generating Radioactive Wastes.

2. J. Crank, 'The Mathematics of Diffusion', Oxford Science Publication, Second Edition (1983), Chapter 5.

3. L.P. Buckley, "Waste Packages and Engineered Barriers for the Chalk River Nuclear Laboratories' Disposal Programme", AECL Report, AECL-8853 (1985).

Figure 1. Definition of concepts

——→ water front
– – –→ nuclide front
(arrows represent time advance)

t_i : time at which barrier i is reached (a)

Δt_i : time taken to pass through barrier i ($\Delta t_i = t_i - t_{i-1}$) (a)

θ_i : thickness of barrier i (a)

A_i : surface area of barrier i (inner) (m^2)

A_i' : surface area of barrier i (outer) (m^2)

$V_p(i)$: pore velocity barrier i (m/a)

1) Degradation of barriers to enable flow in the first stage

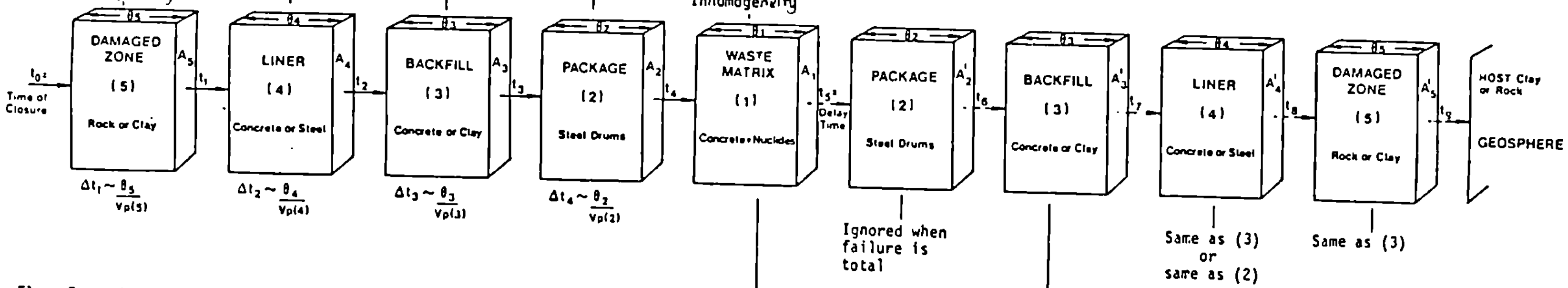
- Cracks
  K : hydraulic conductivity (m/a)
- Inhomogeneity

- Cracks & Inh. or corrosion

- Cracks Inhomogeneity

Corrosion
X_r: Corrosion rate (m/a)
H_θ: Average thickness (m)
σ : Standard deviation

Inhomogeneity



2) Flow Darcy Law

$$Q_i = A_i K_i \frac{\Delta P_i}{\theta_i} \quad (m^3/a)$$

ΔP_i : Pressure difference (m)

3) Transport of Nuclides

Leaching Process ($Q = L_r . S_a . \Delta C$)

l_r: leaching rate (m/a)
D : Effective diffusion (m^2/a)
S_a: Surface of diffusion (m^2)

Solubility Limit

Advection ($F_a = \epsilon U C_i dS$)

ϵ : Porosity
U : Average pore velocity (m/n)
C_i: concentration (Bq/m^3)
dS: element of surface (m^2)

Dispersion-Diffusion ($F = -\epsilon (D_m + a_x U) \frac{\partial C_i}{\partial x} dS$)

a_x: dispersivity (x direction)

Retardation ($1 + \frac{Kd \rho}{\epsilon}$)

Solubility limit C_s (mole/h) for each element is respected

Colloidal : to be investigated

4) Time dependant parameters

4.1) Degradation mechanism
- X_r : Corrosion rate
- K : hydraulic conductivity by crack extension
- H : homogeneity

4.2) Transport
- L_r : Leach rate
- ϵ : porosity
- R : Retardation

Figure 2: Illustration of the validation methodology through an example of the leaching process

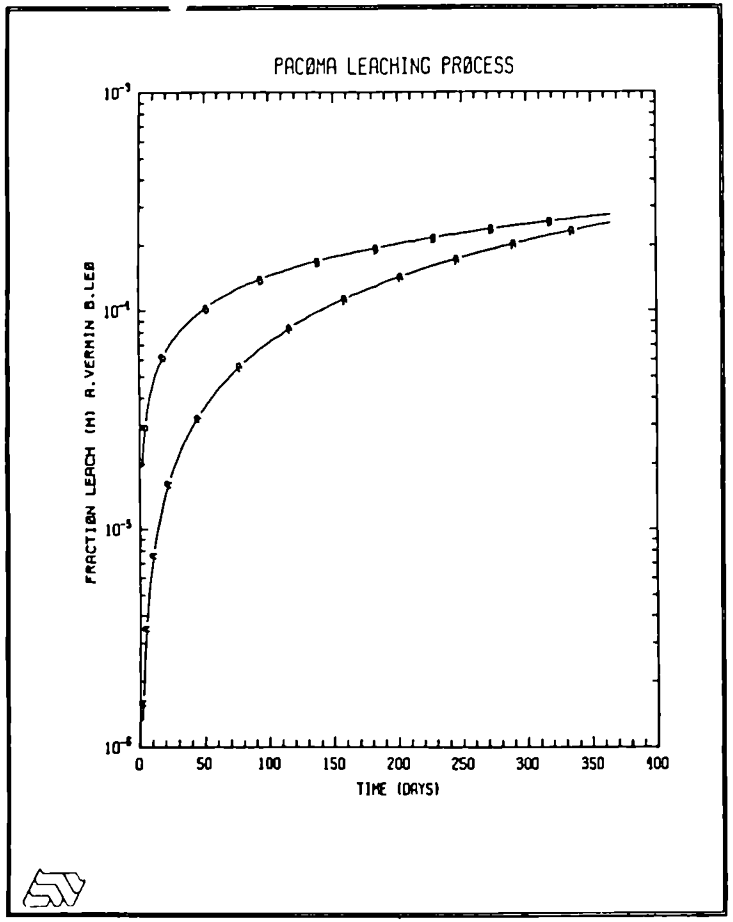
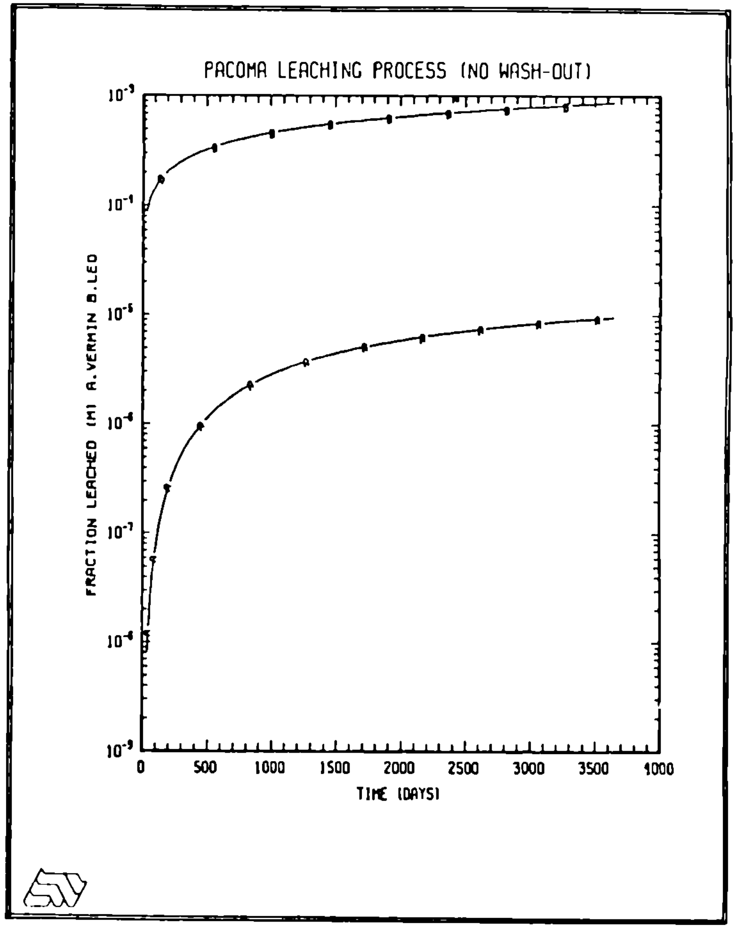


Figure 3: Effect of not considering the washout within the model



ACQUISITION OF SUBJECTIVE DATA FOR USE IN MODELS FOR WASTE SITE ASSESSMENTS (PACOMA PROJECT)

Contractor : CAP Scientific, London UK
Contract No : FI1W/0042-UK (H1)
Working Period : October 1986 - December 1987
Project Leader : R S Laundy

A. Objectives and Scope

In the modelling of radionuclide movement from a repository, a compromise must be achieved between accuracy and cost. For probabilistic site assessment using Monte Carlo simulation, one dimensional models are used due to their small computational cost whereas for deterministic modelling more detailed two- and three-dimensional models are used. The objectives of this programme of work is to develop and demonstrate consistent data acquisition and preparation techniques for probabilistic site assessment and for detailed deterministic modelling of radionuclide movement from a repository for intermediate level waste under the Harwell site. A comparison of radionuclide risks derived from both assessment procedures will be made and any inconsistencies in the input data and resulting inconsistencies in the risk estimates will be investigated.

B. Work Programme

B.1 Research Programme: development of methodology for comparing probabilistic site assessment codes and detailed deterministic models; planning for the data acquisition exercise.

B.2 Data Acquisition: the use of expert opinion to acquire data for 5 to 10 parameters.

B.3 Model Comparison: comparison of input data and expected risks.

C. Progress of Work and Obtained results summary

Summary

The data requirements for a comparison between deterministic modelling and probabilistic risk assessment of the radionuclide release from a repository situated beneath the Harwell site have been determined. The appropriate parameters have been defined for the first stage of the data acquisition exercise.

B.1 is progressing normally.

Progress and Results

1. Research Programme

As part of the work for the PACOMA project a comparison will be made between the results of deterministic modelling of the Harwell site using the NAM series of codes developed at AERE, Harwell and the results of a probabilistic risk assessment using the SYVAC D code. In order to reduce the resources required to collect data and perform the modelling only data for the geosphere models will be collected.

The data requirements for this model comparison have been identified and the appropriate parameters have been defined. These definitions will be given to experts as the starting point for encoding probability distributions using the procedures developed at SRI International/1/. Table 1 below gives a provisional list of the parameters for which data will be collected. The final list of parameters for the NAM series of models will be agreed with AERE.

Parameter (units)	Layer	Type	1D Model	2D model
Hydraulic Conductivity (m/yr)	Top aquifer	PDF	-	Y
	Clay layer	PDF	-	Y
	Bottom aquifer	PDF	-	Y
Atmospheric Pressures (Pa)	surface	PDF	-	Y
Infiltration rates (m/yr)	surface	PDF	-	Y
Path length (m)	Clay layer	PDF	Y	-
	Bottom aquifer	PDF	Y	-
Average velocity (m/yr)	Clay layer	PDF	Y	-
	Bottom aquifer	PDF	Y	-
Variation of hydraulic Conductivity with depth	Clay layer	Function	-	Y
	Bottom aquifer	Function	-	Y
Porosity (-)	3 layers	PDF	-	Y
Sorption (-)	3 layers	PDF	Y	Y
Density (kg/m^3)	3 layers	Constant	Y	Y
Dispersivity (m)	3 layers	PDF	Y	Y

Y = data required for model

Top aquifer = Lower chalk and Upper greensand
Clay = Gault clay and Kimmeridge clay
Bottom aquifer = Corallian aquifer

Table 1 - Data requirements for 1D and 2D models

The parameters have been defined in the following way:

Hydraulic Conductivity

The required probability distributions are of:

1. The hydraulic conductivity for horizontal flow in the lower chalk and upper greensand at a depth of 40m below the Harwell site.
2. The hydraulic conductivity for vertical flow in the Gault and Kimmeridge clays at a depth of 135m below the Harwell site.
3. The hydraulic conductivity for horizontal flow in the Corallian aquifer at a depth of 205m below the Harwell site.

In addition to these probability distributions it is necessary to know:

1. The relationship between hydraulic conductivity in the Gault and Kimmeridge clays in the South Oxfordshire region and the depth of overburden.
2. The relationship between hydraulic conductivity in the Corallian aquifer in the South Oxfordshire region and the depth of overburden.

Pressure

It is required to determine the probability distribution of atmospheric pressure, from meteorological data.

Path Length

To be able to collect data for the one-dimensional model it is necessary to know the dominant pathway. For comparison purposes, the same dominant transport pathway should be modelled in detail by AERE. For this study we use the following definitions of the dominant pathway which has been determined by a previous study /2/.

The dominant pathway is from a repository situated in the Gault Clay beneath the Harwell site, downwards through the clay layer to the Corallian aquifer, along the aquifer to streams in the Vale of the White Horse.

The definitions of the path lengths for which probability distribution functions are required are given below.

1. The length of the dominant pathway down through the Gault and Kimmeridge clays.
2. The length of the dominant pathway along the Corallian aquifer.

Average Velocities

The input data for the SYVAC D model requires the probability distribution functions of the following groundwater velocities.

1. The average horizontal groundwater velocity along the Corallian aquifer in the South Oxfordshire region.
2. The average vertical groundwater velocity down through the Gault and Kimmeridge clays in the region of the Harwell site.

Porosity

The definition of porosity that will be used will be:

- the volume of a material not occupied by solids

The average porosity is required for the three layers.

Sorption

The definition of sorption variation coefficient that will be used will be:

- the concentration of nuclides on the rock surface divided by the concentration of nuclides in the groundwater.

The sorption variation coefficient is required for all three layers and for all nuclides that are being considered. For the present study a limited number of nuclides will be considered to simplify the data acquisition exercise.

Dispersivity

The definition of dispersivity that will be used will be:

- a length-scale factor, derived from results of tracer studies, which when multiplied by the pore water velocity gives the longitudinal dispersion coefficient, a measure of the convective dispersion along the flow path.

The dispersivity is required for the three layers.

References

/1/ Stael von Holstein, C.S. and Matheson, J.E., A manual for encoding probability distributions. SRI International report 7078 (1979).
/2/Thompson, B.G.J. et al, 'DRY RUN 2': Development of a methodology for Post-Closure Radiological Risk Analysis of Underground Waste Repositories. Illustrative Assessment of the Harwell site. Report No EWE-2529.

5 c) Support studies

Safety studies of HLW disposal in the Mors salt dome - support to the salt option of the PAGIS project.

Contractor: ELSAM, DK-7000 Fredericia, Denmark.
Contract no.: WAS-2-455-DK (AD).
Duration of contract: Apr. 1985 - Dec. 1986
Project leader: Arne Pedersen.

A. Objectives and Scope

This contract is part of the PAGIS 2 evaluation of the safety of high level waste disposal in salt domes. The Danish salt dome Mors is a variant site in this evaluation.

The scope of the contract is to support PAGIS 2 with data from the Mors site and with descriptions of special methods of calculation used at an earlier Danish study.

B. Work programme

The programme consists of three tasks covering:

1. Description of a model for evaluation of a cavern scenario in salt domes.
2. Description of a model for brine intrusion scenario in salt domes.
3. Supply of hydrogeological data for the Mors dome to be used for 3-dimensional hydrological calculations on the Mors dome.

C. Progress of work and results obtained

State of advancements

The contract was finished in 1986 and all the three tasks of the work programme has been completed.

Progress and results

1. The cavern scenario model

A model was developed for evaluation of a scenario where a cavern hits a high level waste repository without discovering the waste. During the solution mining operation the leaching of salt uncovers the waste, which falls down into the sump of mainly anhydrite.

After the operation period of the cavern, the leaching of waste begins and continues, until the cavern closes by convergence. By the convergence the contaminated brine is assumed to be pressed up into the exploitable surface groundwater.

For a cavern of 1.0e6 m3 the amount of anhydrite is of the order of 1.0e5 tons. Existing experiments from Research Center Risø in Denmark has shown that anhydrite has an appreciable retention capability for most radioactive isotopes. The anhydrite in the sump therefore acts as a filter for radioactive materials being transported through the sump.

With very conservative assumptions concerning the time for leaching the waste and closure of the cavern the concentrations of radioactive materials in the surface discharge stream (Lyngbro brook) are about 10-1,500 times smaller than the associated derived permissible concentrations for the previous Danish design study.

2. The brine intrusion model

This model was developed for evaluation of a scenario, where a high level waste repository in salt inadvertently is located close to a major brine pocket which subsequently releases its brine content through defects in the repository to the surface discharge stream for the catchment area.

In the Danish waste disposal study the waste cylinders are located in deep disposal holes each containing 645 cylinders and extending from 1200 m to 2500 m below the surface.

In the scenario it is assumed that the sealing around and above the waste is cracked in such a way that there is a hydraulic connection through the waste to the surface groundwater above the waste.

Further the brine pocket is assumed to get contact with the fissured sealing around the waste, and brine will be pressed out of the pocket and through the fissured sealing. The flow of brine might leach the waste, and radioactive materials be released into the exploitable groundwater.

With very conservative assumptions concerning the volume of the brine pocket and the permeability of the fissured concrete, the concentrations of radioactive materials in the surface discharge stream (Lyngbro brook) are all well below the derived permissible concentrations except for Am 241, which has a little higher concentration.

3. Hydrogeological data for the Mors site

Hydrogeological data from the previous site investigation programme is described and collected.

The data are given both for the surface layer and the deep layers down to app. 700 m . They include

- ground water potentials

- precipitation and recharge
- porosity and permeability
- temperature profiles
- salinity profiles.

The deep layers consist mostly of different kinds of chalk/ limestone and appear to have very low permeabilities.

List of publications

/1/ K. E. Lindstrøm Jensen, "Evaluation of cavern intrusion into a high level waste repository", Nov. 6, 1985, Elsam notat P85/148.

/2/ K. E. Lindstrøm Jensen, "Model for brine intrusion into a high level waste repository", Sep. 12, 1986, Elsam notat P86/105.

/3/ K. E. Lindstrøm Jensen, "Hydrological data for the Mors salt dome site", Sep. 25, 1986, Elsam notat P86/143.

References

/1/ Elsam and Elkraft, "Disposal of high-level waste from nuclear power plants in Denmark, salt dome investigations vol. I-V". June 1981.

Definition of standards of quality assurance performance assessment codes for waste disposal

Contractor: Cedar Design Systems Ltd. London, U.K.
Contract No: FI1W/0039 - UK (H1)
Duration of contract: January 1987 - March 1989
Project Leader: I. E. Hill

A. Objectives and Scope

The research project will produce a definition of an acceptable and appropriate set of procedures for quality assurance, verification, and validation. These procedures would form the basis for establishing uniform standards for risk assessment software, which could be implemented throughout the European nuclear industry.

The value and effectiveness of the procedures will be demonstrated by their practical implementation as part of the work of the UK contractors on the CEC PACOMA projects. Included in this practical implementation will be the introduction of software tools for automating quality assurance procedures, where such tools are available or can be developed.

The work will be subdivided into 4 stages covering respectively, analysis of existing procedures and definition of requirements; a case study of the use of existing procedures in the UK Department of the Environment; definition of procedures; and implementation of procedures.

In order to ensure that the work done is appropriate to the development of risk assessment codes, reference will be made to the other UK contractors for the CEC PACOMA project. In particular, the stages have been chosen to be compatible with the assessment schedule proposed by the National Radiological Protection Board (NRPB) for their PACOMA contract.

B. Work Programme

B.1 Review of existing software quality assurance standards and definition of requirements.

B.2 Case study of existing UK DoE procedures.

B.3 Definition of procedures.

B.4 Implementation of procedures.

C. Programme of work and obtained results

Summary

The start of the project has been delayed until January 1987. There is no progress to report.

CHAPTER 6

TASK No. 6 : JOINT ELABORATION OF RADIOACTIVE WASTE MANAGEMENT POLICIES

CHAPTER 6

TASK No. 6 : JOINT ELABORATION OF RADIOACTIVE WASTE MANAGEMENT POLICIES

A. Objective

Joint elaboration of waste management and disposal criteria

Evaluation of possible approaches, at Community scale, for waste disposal.

B. Research topics dealt with under the 1980-1984 programme

These research topics were not included in the 1980-1984 programme.

C. 1985-1989 programme

The following activities are foreseen :

- Development and harmonization of acceptance criteria for radioactive waste conditioning with respect to their handling and final disposal

- Development of radiological criteria for disposal, especially for the periods of time involved in geological disposal

- Elaboration of recommendations concerning the satisfactory execution, taking into account the safety and environmental protection standards, of the various operations involved in the management and disposal of radioactive waste

- Study of "de minimis" criteria with regard to alpha/non-alpha and radioactive/non-radioactive waste

- Multi-national dimensions of waste management; influences on its optimization; regional disposal.

D. Implementation of the programme

A working group of national experts has been set up to deal with task 6 activities. Topics of first priority have been identified as items (b) and (d) of paragraph C above; a working plan is being prepared and will be presented to the competent Management and Co-ordination Advisory Committee in 1987.

PART B

CONSTRUCTION AND/OR OPERATION OF UNDERGROUND - EXPERIMENTAL FACILITIES OPEN TO COMMUNITY JOINT ACTIVITIES

CHAPTER 7

CONSTRUCTION AND/OR OPERATION OF UNDERGROUND EXPERIMENTAL FACILITIES

A. Objective

To confirm the technical options and the numerical values of the parameters to be taken into consideration for building industrial disposal facilities and to develop radioactive waste emplacement techniques.

B. Research performed under the 1980-1984 programme

The large-scale verification of the properties and behaviour of geological formations started thanks to the construction and the putting into service of experimental cavities or underground laboratories.
In this way, an experimental chamber was constructed at a depth of 225m in the plastic Boom clay formation beneath the Mol site in Belgium.

Some existing galleries in the Asse salt mine were adapted to receive full-scale tests, i.e. in-situ heating tests, stress and strain measurements and surveys of the quantities of fluids and gases released by the salt. In addition, a 300 m deep borehole between the -750m and -1050m levels was dry-drilled from one chamber of the mine and its stability was monitored over almost two years.

C. 1985-1989 programme

The specific projects involved in this part of the programme are open to Community co-operation by the responsible bodies in the Member States on whose territory the facilities will be built. They deal with experimental and pilot facilities without industrial utilization.

These facilities will reproduce at full scale and in real geological conditions the essential parts of a large and industrial underground disposal plan of the future.

These facilities will also make it possible to confirm on site the numerical values of the parameters to be taken into consideration for building industrial facilities and to develop radioactive waste emplacement techniques.

Radioactive waste or materials, which will be used in some projects for studying the operating conditions of an industrial facility, will be retrievable.

The co-operation includes, inter alia, participation of scientists of other Member States to the above-mentioned projects, especially by means of temporary secondment of personnel, and the possibility of completing the programmes with own specific activities, according to modalities to be specified on a case-by-case basis.

The control and the responsibility of the projects will be ensured by the hosting bodies.

In addition to the following three projects, other projects could be added in the course of the programme.

PROJECT No. 1 : PILOT UNDERGROUND FACILITY IN THE ASSE SALT MINE (FEDERAL REPUBLIC OF GERMANY)

PROJECT No. 2 : PILOT UNDERGROUND FACILITY IN THE ARGILLACEOUS LAYER UNDER THE MOL NUCLEAR SITE (BELGIUM)

PROJECT No. 3 : EXPERIMENTAL UNDERGROUND FACILITY IN FRANCE IN A GEOLOGICAL MEDIUM OF COMPLEMENTARY NATURE

D. Programme implementation

Contracts have been signed for projects no. 1 and 2.
The launch of project no. 3 has been delayed by the French authorities to a later date. The Spanish authorities presented to the Commission a proposal for a fourth project, to be developed in a granitic geological formation.

Available information dealing with projects no. 1 (so called HAW project) and no. 2 (so called HADES project) is given thereafter.

The HADES project : a pilot underground facility in the argillaceous layers located under the Mol nuclear site with a view to demonstrating the feasibility of radioactive waste disposal

Contractor : SCK/CEN, Mol, Belgium
Contract N° : FI1W/0004/B
Duration of contract : January 1985 - December 1989
Project Leader : A.A. Bonne

A. Objectives and Scope

In 1974 SCK/CEN launched a R&D-programme concerning the possibilities for disposal of high level solidified and alpha-bearing radioactive wastes in a continental stratiform clay formation (Boom clay) situated below its own site. Site investigations, safety studies, repository design, conceptualisations and in situ research confirm progressively the favourable characteristics of the host rock and the site for disposal of radioactive wastes.

Many particular areas require further studies and tests on a larger scale and in situ demonstrations under realistic conditions. The areas identified are related to the construction on an industrial scale of an underground repository in plastic clay, the operation of an underground facility, the interaction between the repository and the immediate surrounding geological medium and the safety. These technological tests, studies and demonstrations will contribute to increase the confidence in the technical practicability, the economical feasibility and the safety of the disposal option in deep clay.

The direct demonstrations deal with the constructability of real scale galleries without particular conditioning of the rock, the choice and dimensioning of a realistic lining and support system, the interaction between the underground structures and the immediate geological environment, the influence of heat and radiation upon the underground structures and the immediate geologic environment, the handling of hot and radioactive canisters, the backfilling and its behaviour in time, the performance of various system components during the operational phase and monitoring systems.

B. Work Programme

The demonstration/pilot phase of the HADES project is developed in two phases, which are complementary to each other and in part parallel.

B.1. Phase I : the construction and operation of a test drift with tests related to :

- B.1.1. mining technology (digging, lining, extrados backfilling, rheology) ;
- B.1.2. radioactive waste disposal (experimental emplacement, backfilling, degradation of waste matrices and migration of radionuclides, in situ irradiation of clay, thermo-mechanical behaviour of clay and gallery structures, monitoring and auscultation systems).

B.2. Phase II concerning :

- B.2.1. construction of a pilot facility with a new shaft and extended gallery, experimental disposal pipes, connecting chamber and utility structures ;
- B.2.2. tests and observations on handling, emplacement, backfilling and retrieval of dummies and finally actual radioactive wastes.

The performance of B.2 is scheduled beyond the actual contract period.

C. Progress of work and obtained results

State of advancement

The construction design of the test drift of phase 1 of the HADES demonstration/pilot phase is completed. Two tunnelling concepts were selected for the test drift : a stiff tunnel lining concept with concrete liners is foreseen for the first section of the test drift ; ANDRA (F) proposes a second section of the drift to be supported by sliding steel ribs ; the plans, construction procedures and measurement programme satisfying the requirements for investigating the capabilities and conditions for tunnelling with stiff lining were established. All construction related issues for this test drift portion are on schedule.
The geotechnical auscultation of the clay mass (mine-by-test) around the section of the test drift with stiff lining has been defined and constructed. Some measuring devices, part of the mine-by-test programme (piezometer profile), were already installed at the end of 1986
Efforts were devoted to a preliminary design study for testing the in situ behaviour of clay, of structural materials, of backfilling and of the concrete gallery lining in a combined radiation-heater test.

Progress and results

1. Test drift construction works

According to the design developed at present, the works on the HADES site will include :

- an opening in the crossing chamber at the bottom of the actual shaft, the size of the opening will be limited because of the size of the presence of metallic reinforcement rings in the crossing chamber ;
- the first part of about 4 m length the gallery passes through the disturbed clay which has been frozen during the construction of the access shaft. It is foreseen to use a concrete lining in this section for ease of emplacement and cost reduction ;
- a connection plug of reinforced concrete, enlarging the test drift to a circular section of 3.5 m inner diameter,
- the main portion of the test drift, of 3.5 m inner diameter, 20 m long, circularly lined with concrete blocks.
  The "final" design for this gallery foresees 3 rings of concrete blocks per meter (64 blocks per ring), each ring having a thickness of 60 cm.
  The concrete segments will be prefabricated at 2 mm tolerances with regard to the theoretical dimensions and will have a characteristic resistance of 55 MPa when tested at 28 days, with a maximum standard deviation of 4 MPa.
  The water-cement ratio will be as low as possible and in any case lower than 0.45. The final porosity will be minimal and in any case lower than 4 percent. The cement should be resistant to sulphate attack.
  The intercalary plates, 8 mm thick, will be of the "Linex" type and previously treated in order to be imputrescible.
  The void space between the concrete segments and the excavated wall will be backfilled directly after positioning of each ring, with a non-clayey material of continuous granulometry, appropriate for later injection. This injection will take place every 3 m and at least once a week ;
- the placing of several special frames, designed to provide access to the clay body is foreseen during construction works ;
  The number of openings was reduced in order to fit better to the planned experimental programme and includes the following :
  - 760 mm diameter opening : 1,
  - 400 mm diameter opening : 10,
  - 200 mm diameter opening : 25.

Andra proposes to build as a test a section of a drift with sliding ribs as support. Braces and plates between the ribs act as liners of the drift wall and allow to make extrados injections in order to ensure the continuity. Special joint elements will allow a limited sliding when a predefined stress threshold is reached. The dimensioning and engineering of this section of the test drift is in progress. A safety device is foreseen in order to stop any irregular or important convergence of the sliding drift lining.

2. Mine-by-test around the stiff section of the test drift

The planned geotechnical programme is briefly described hereafter. It is to be noted that several types of measurements are foreseen to allow cross-checking and improvement of the interpretation.

- Convergence measurements on the lining
  Five sections of the drift will be equipped with convergence studs before emplacement. At each section, four diameters will be measured using the "distomatic" device of Telemac. By this device the distance variations between two opposite points anchored in the lining are measured.
- Underground topographic surveying
  The position of the gallery in X, Y, Z will be regularly controlled. Equipment, space between the measurement sections and timing are to be settled.
- Pressure build-up on the lining
  Three of the five measuring sections will be equipped with pressure cells behind the lining and load cells between the concrete segments. In the most representative section, centered in the test drift, 12 total pressure cells are foreseen to be positioned in order to measure radial stress. Also 8 load cells are foreseen in this section. Emplacement methods, dimensions and types as well as possible inclusion in concrete segments are now further studied.
- Deflectometers
  Two horizontal inclinometers of 12 and 23 m length and a tassometer series (35 m) are foreseen in the roof of the drift in order to record the deformations in the clay due to the excavation works.
- Pore water pressure measurements
  Piezometers (screens) and hydraulic pore water pressure cells (Gloetzl) were installed starting from the crossing chamber and extending to different distances from the new drift in order to quantify the pore water dissipation expected during excavation.
- Clay front auscultation
  Convergence measurements in the last ring of the gallery will be complemented by deformation measurements at the clay front. Steel rods or multi-point extensometers will be anchored at different distances in the clay front.

3. Geotechnical auscultation of the clay

In addition to the geotechnical auscultation just described in the framework of the mine-by-test, a test is planned to determine the coefficient of the earth pressure at rest. This test is to be performed by a self boring pressuremeter immediately after the construction phase at a greater distance from the test drift. This test will not only give information about the observed pattern of in situ lateral stresses but also about in situ properties of clay such as undrained shear strength and in situ moduli.

4. Combined radiation/heater test

A concept has been developed for performing a combined radiation and heating test in the clay mass in the floor of the test drift. Preliminary calculations indicate that a combined radiation/heater test may well simulate the near-field of a stack of 50 years aged HLSW. The most appropriate configuration is obtained by a linear Co-60 radiation source of 13 kCi, taken between two linear heaters (one above and one below the linear radiation source). For this test possibly loaded at 2 m below the floor of the test gallery the aim is to study the effects of such a source on the clay environment, the structural materials (hole casings, gallery lining) and backfill materials. Further development of the concept of the radiation/heater test is needed.

List of publications

L.H. Baetslé, A. Bonne, P. Dejonghe
The HADES demonstration project for radwaste disposal in deep clay
Proceed. Int. Conf. on Rad. Waste Management, Winipeg, 7-11th Sept. 1986.

The HAW project: demonstration facility for high-level waste disposal in the Asse salt mine

Contractor: GSF-IfT, Braunschweig, FRG
Contract-No.: FI1W/0003/D
Working Period: January 1985 - December 1986
Project Leader: T. Rothfuchs

A. Objectives and Scope

Since 1968 the GSF has been carrying out research and development programs for the final disposal of high-level radioactive waste (HLW) in salt formations. The heat producing waste has been simulated so far by means of electrical heaters and also cobalt-60-sources. In order to improve the final concept for HLW disposal in salt formations the complete technical system of an underground repository is to be tested in a one-to-one scale test facility.

To satisfy the test objectives thirty high radioactive canisters containing the radionuclides Cs-137 and Sr-90 will be emplaced in six boreholes located in two test galleries at the 800 m-level in the Asse Salt Mine. The duration of testing will be approximately five years.

For the handling of the radioactive canisters and their emplacement into the boreholes a complete disposal system consisting of transportation casks, transportation vehicle, disposal machine, and borehole slider will be developed and tested. The actual scientific investigation program is based on the estimation and observation of the interaction between the radioactive canisters and the rock salt. This program includes measurement of thermally and radiolytically induced water and gas release from the rock salt and the radiolytical decomposition of salt minerals. Also the thermally induced stress and deformation fields in the surrounding rock mass will be investigated carefully.

The project is funded by the BMFT and the CEC and carried out in close cooperation with the Netherlands Research Foundation (ECN).

B. Work Program

B.1. Elaboration of the test plan and the supporting documents for the licensing procedure.

B.2. Development and procurement of the technical componenents for handling and emplacement of the radioactive canisters.

B.3. Procurement and installation of the data collection system.

B.4. Mining of the test field, drilling of the boreholes, installation of the measuring equipment and preparation for the emplacement of the HLW canisters.

B.5. Test disposal including operation of electrical tests for comparison and assessment of the technical components.

B.6. In situ measurements of released water and gas from the salt, of thermally induced stress and deformation in the rock mass, and performance of seismic and ultrasonic measurements.

B.7. Accompanying and complementary laboratory investigations to ensure the transferability of the results to other sites.

C. Progress of work and obtained results

State of advancement

The test disposal of high-level radioactive waste canisters in the Asse salt mine will be performed with a view to the planning, design and licensing procedure for a national repository in the FRG. In the working period 1985 to 1986 most emphasis has been given to the final development of the technical components and the preparation of the underground test field. Therefore, in situ results from the interaction between the HLW canisters and the rock salt are not available at this time. The present schedule of the project foresees the emplacement of the radioactive canisters in May 1988.

1. Elaboration of the test plan

The test plan was prepared in 1984/1985 and the final version was issued in December 1985/1/. It contains a detailed description of the scope, issues, and objectives and also of the test program.

Nearly all the technical papers including the design calculations could be submitted to the responsible licensing authority (Bergamt Goslar).

2. Development and procurement of the technical components

The design of most components for handling and emplacement of the radioactive canisters was completed in 1985. The final development and construction proceeded very well in 1986. Most of the purchase orders could be placed to start fabrication of the components partly in late 1986.

The Asse internal transportation cask Asse TB1 which needs a type B(U) certification by the Physikalisch-Technische Bundesanstalt (PTB) has undergone its fall test (Figure 1) very successfully. The required fire tests will be performed in early 1987.

The development of the canister guiding system (CGS) as well as the gap monitoring system (GMS) to derive the tube deformation has been completed by ECN. The layout of both systems (see Figure 2), which will guarantee the retrievability of canisters, has been accepted by the licensing authorities. The test programs have been developed and adapted according to suggestions of TÜV. The prototype for CGS and GMS as well as the test rigs themselves are in the final stage of construction.

The development of the heaters which simulate the canisters during the prewarning heatup and the operational phase of the HLW test field are in the final stage of design.

3. Procurement and installation of the data collection system

The design for the Data Collection System (DCS) hardware has been finished in 1985, and the components have been delivered to ECN. The full-scale installment of the DCS takes place in Petten as well as the thorough testing of the different components.

The development of the DCS software has partly been finished. The application software of data transport and handling controlling the heaters and generating the tube deformation data and alarms is being specified and partly under development.

4. Mining and preparation of the test field

The underground test field, consisting of two parallel galleries, each 60 m long, 10 m wide, and 8 m high, was completely mined in 1985. By the end of 1986 about 70 % of the measuring boreholes were drilled and about 60 % of the extensometers and 40 % of the stressmeters could be installed.

5. Test Disposal

Due to delayed fabrication of the radioactive canisters and the time consuming final definition and specification of retrievability requirements and technical components the time schedule of the project is delayed. The emplacement of the radioactive canisters is now foreseen for May 1988.

6. In situ measurements

First in situ measurements were already started prior to the mining of the test field. A so-called stress monitoring station was installed in the pillar between the two galleries approximately 3 m above the floor of the test room. The measurements indicated a vertical stress component of about 14 MPa prior to the mining activities which increased to about 19 MPa after mining of the galleries. The resulting deformation of the pillar could be observed by measuring the room closure between the pillar wall and the opposite gallery wall which amounts to approx. 70 mm after 510 days (see Fig. 3). However, to evaluate the absolute displacement of the pillar wall it is necessary to wait for the results of the pillar extensometers which will be installed later. Additional geochemical measurements show that CH_4, CO_2 and H_2S are present in rock salt and are released to drilled boreholes at natural mine temperature.

The special instrumentation developed for obtaining the salt pressure from borehole tube deformation is in the final stage of design. The acoustic measuring techniques to be used for crack detection are further tested, the necessary equipment is in the final stage of fabrication so that it can be installed at the beginning of 1987.

7. Accompanying laboratory investigations

The laboratory program accompanying the test disposal is concentrated on the influence of parameters concerning the geochemical and mechanical aspects of HLW disposal that cannot be studied in situ. These are mainly variation of temperature, dose, dose rate, stress, strain and mineralogical composition of the salt.

Theoretical calculations on the neutron irradiation of the rock salt indicated that after a five year emplacement of HLW the following maximal activities may be found: Na-24: 52 Bq/cm^3, P-32: 17 Bq/cm^3, S-35: 1700 Bq/cm^3, Cl-36: 420 Bq/cm^3, Br-82: 178 Bq/cm^3.

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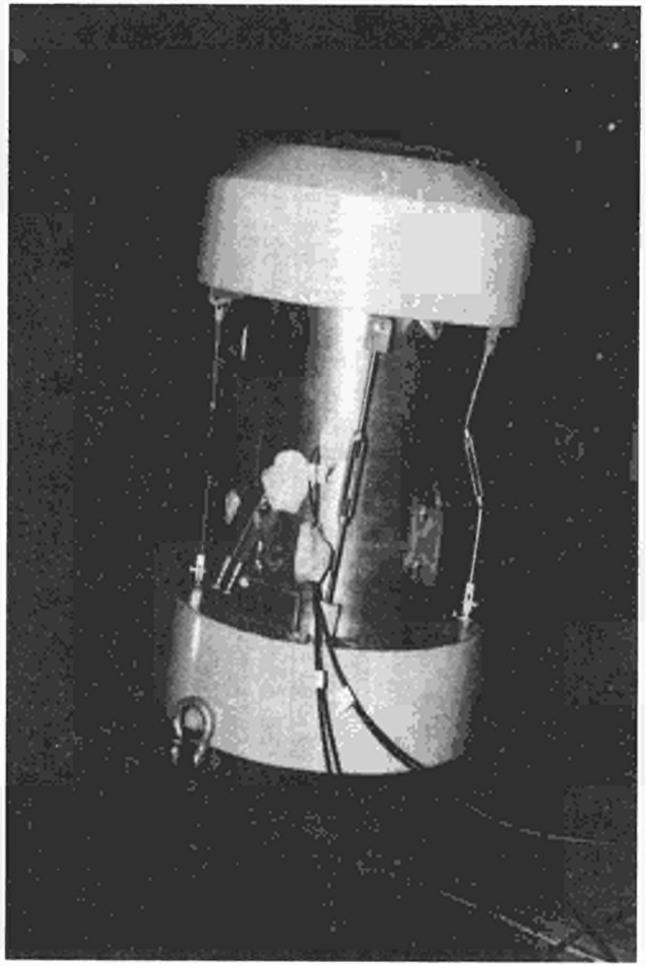

Figure 1: 1:4-model of the transportation cask Asse TB1 after the fall test

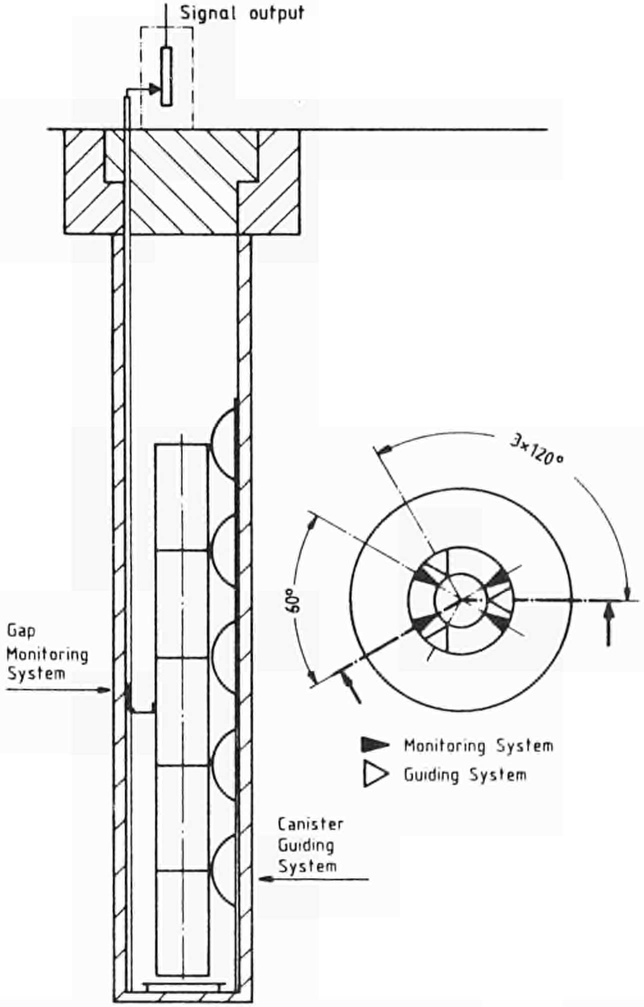

Figure 2: Schematic layout of the canister guiding system and gap monitoring system

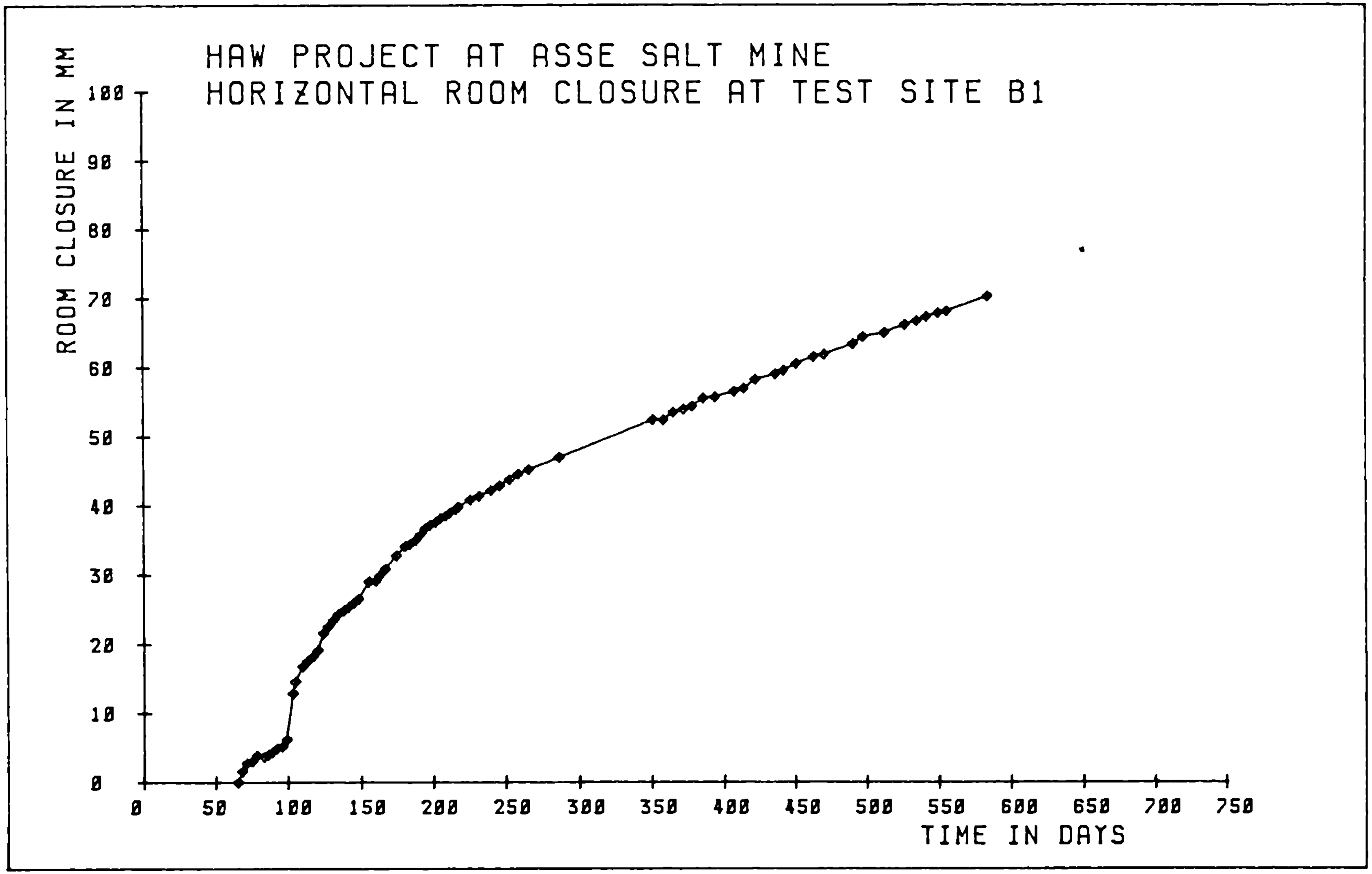

Figure 3: HAW-Project - Horizontal Room Closure at Test Site B1

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STAUPENDAHL, G: Geomechanical Aspects of in situ Experiments and of Laboratory Investigations on Rock Salt Samples from the Asse Salt Mine. Ecole d'Eté de Thermocécanique des Roches, Alès 9-12 Sept. 1986, Proceedings (to be printed)

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(2) Entered in 1986.

(3) Retired in 1986.

European Communities — Commission

EUR 11089 — The Community's research and development programme on radioactive waste management and storage — Shared cost action — Annual progress report 1986

Edited by: *S. Orlowski, J.M. Gandolfo*

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This first report describes the work to be carried out under the research contracts already concluded before end of 1986 as well as the initial work performed and the first results obtained.

For each contract, paragraph C 'Progress of work and obtained results' was prepared by the contractor under the responsibility of the project leader.

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