Commission of the European Communities

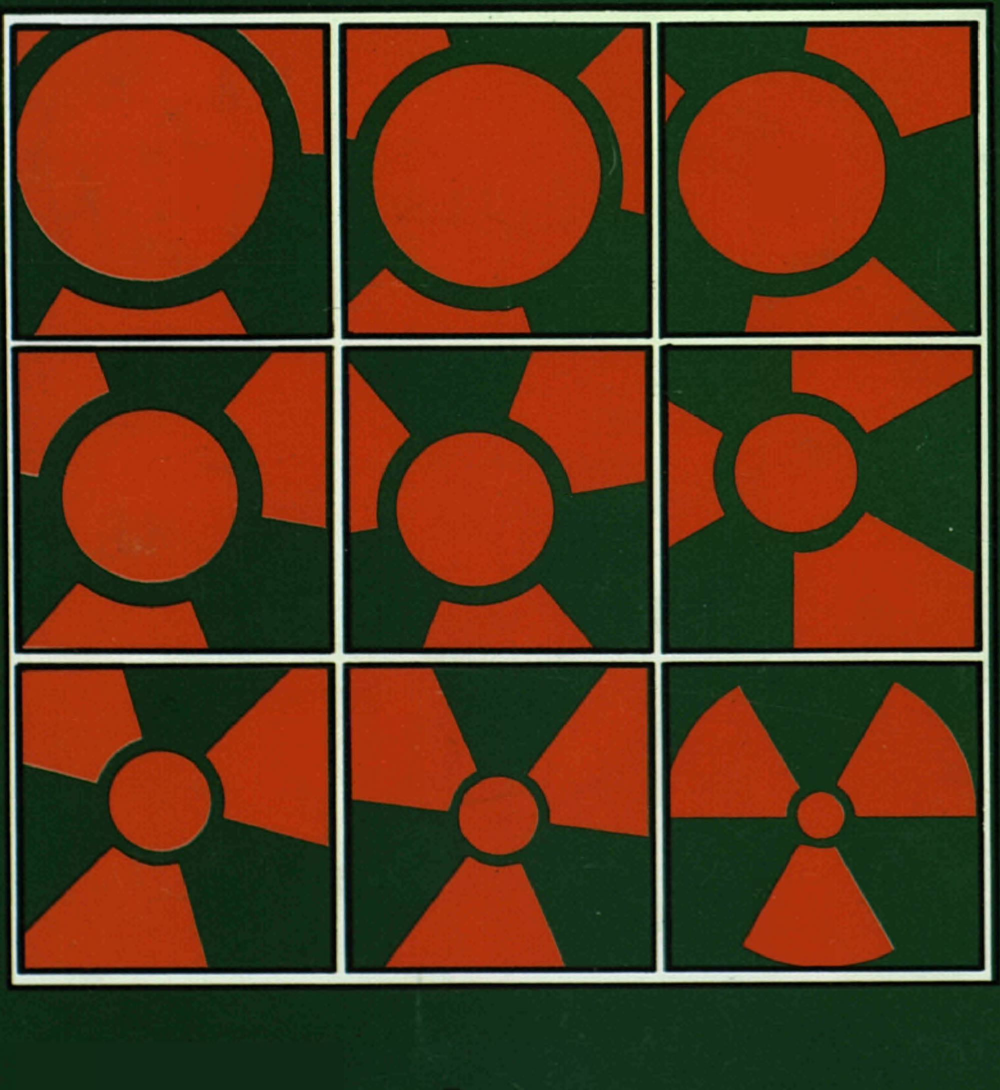
nuclear science and technology

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

Shared cost action

Annual progress report 1989

Volume 1



Report

EUR 12761/1 EN

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Directorate-General
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Foreword

The Council of the Ministers of the European Communities adopted through its decision on March 12, 1985 (1) a five year R&D programme on "Management and Storage of Radioactive Waste" for the period 1985-1989. This R&D programme is being carried out on the competent public organisations and private firms within the Member States. At the end of 1989 over 256 contracts had been concluded with some 70 bodies within the European Community (43 % national bodies and research centres, 36 % private industries, 21 % universities and institutes). The Commission's contribution to the cost of the programme amounts to 62 million ECU (for the five year period).

In the management of the programme, the Commission is being assisted by the Management and coordination advisory committee "Nuclear fission energy - Fuel cycle/processing and storage of waste" (see for list of members pageVII, Vol. 2).

The launching of specific coordinated research projects within the programme has promoted the co-operation between various teams within the Member States. Half of the contracts concluded are dedicated to such projects. The exchange of fresh scientific information on the progress and results of the work carried out in the framework of the programme is assured at operational level by periodical progress meetings of working groups for the various projects. The final results of the research contracts are published in the EUR series which publication are e.g. listed in the six monthly news letter, EC FOCUS. In addition the Commission is publishing annual progress on the overall programme. This report, covering the year 1989, is the fourth of this type, the previous being published under no EUR 11089 for the year 1986, no EUR 11482, for the year 1987 and EUR 12141 covering the year 1988. For each contract the objectives, working programme and a summary of progress and results obtained have been given as prepared by the contractor, under the responsibility of the project leader. The Commission wishes to express its gratitude to all scientists who have contributed to this report. The overall results of the five year programme will be presented, as usual, to the worldwide scientific community at the third European Conference on Radioactive Waste Management to be held September 17-21, 1990 in Luxembourg.

S. ORLOWSKI
Head, Nuclear Fuel Cycle Division

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VOLUME 1

CONTENTS

PART A

WASTE MANAGEMENT STUDIES AND ASSOCIATED R & D ACTIONS

TASK No 1

SYSTEM STUDIES

TASK No. 1: SYSTEM STUDIES

A. Objective

To characterise the various overall management schemes for some waste categories with a view to evaluating their feasibility and availability and optimising 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
- Alcaline liquid wash waste, arising during spent fuel reprocessing operations

C. 1985-1989 programme

The system studies 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 being developed to provide a rational base for comparative evaluations. In particular, two subjects are 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

For the system studies, groups of contractors (six for reactor waste, five for hulls, and four for the reprocessing - direct disposal comparison) cooperate closely in assessing different possible management routes.

ASSESSMENT OF MANAGEMENT ALTERNATIVES FOR REACTOR WASTES

CONTRACTOR : BELGATOM S.A. rue de la Loi, 75 B-1040 BRUXELLES

CONTRAT N° : FI 1W-0124

DURATION OF CONTRACT : November 1987 - January 1990

PERIOD COVERED : January 1989 - December 1989

A. OBJECTIVES AND SCOPE

The objective of the contract is to constitute a contribution to a joint study aiming at assessing management routes for Light Water Reactor Wastes on the basis of economic and radiological criteria and by drawing up the basic options emphasizing the collect - treatment - conditioning - packaging - storage and transport aspects.

The reference scenario considered is the following :

- Installed nuclear power : 20 GWe ;
- All P.W.R. - Grouping of reactors by 4 units ;
- Lifetime : 30 years ;
- Location : Inland sites with stringent discharge limits.

A management route is defined as each set of coordinated actions by which the management of L.W.R. wastes from their production to their disposal is implemented.

B. WORK PROGRAMME

The evaluation of the management routes for LWR-wastes is based in the frame of our contract, on the execution of the following sequence of tasks :

1. Definition of typical primary waste inventories resulting from normal operation of 900 MWe-PWR's (gaseous, liquid and solid wastes).

2. Definition of discharge limits, waste acceptance criteria and transport regulations.

3. Drawing up of basic management routes taking into account treatment and conditioning variants.

4. Sensitivity studies on each basic management route.

6. Costing of the basic management routes as well as the variants evolved from sensitivity studies.

7. Assessment of the related occupational exposure

8. Assessment of the related radiological impact to the public (short and long term).

BELGATOM have to execute partly the tasks 1, 2 and 6 and wholly the tasks 3, 4, 7 and 8 for one basic management route based on the Belgian concepts and practices.

C. PROGRESS OF WORK AND OBTAINED RESULTS.

C.1. State of advancement

Point 1 : Already completed and reported

Point 2 : Already completed and reported

Point 3 : The descriptions of Belgian management routes for solid Waste and for liquid and gaseous effluents are completed.

Point 4 : In preparation
The proposed scope of work is the following :

- Comparison of the liquid waste management through a fixed installation or by means of a mobile unit working on several sites ;
  Estimation of influence of this choice on the investment costs and on the operating costs ;

- Comparison between two ways for the solid waste treatment :
  - . through incineration of the combustible part of the solid waste and compaction of non-combustible part ;
  - . by means of supercompaction of all the technological waste ;

  and the related influence of these two ways on the investment and operating costs

Point 6 : This point is now completed by supplying TASK/KAH with the data related to equipment costs and operating costs of
- the gaseous effluents (off-gases and ventilation) treatment
- the liquid effluents treatment
- the solid waste treatment

Point 7 : The study of this point begins in February 1990

Point 8 : This study was performed and nearly finished

A complete separate document will be supply in march 1990.

C.2. Progress and results

Point 1 : See annual progress report Nov. 87 - Dec.88

Point 2 : See annual progress report Nov. 87-Dec.88

Point 3 : The descriptions of the basic management routes used in Belgium for gaseous and liquid effluents so as for solid Waste are given in two types of documents.

- Firstly the "General descriptions" where are described the basic flow -sheets of each treatment chain including mass and activity balances and

- secondly the "Technical descriptions" which give the detailed flow-sheets of all processes and the specific equipment characteristics including instrumentation and control in order to allow an evaluation of the equipment cost.

There are three "General descriptions" for
- Gaseous effluents (off-gas + Ventilation)

- Liquid effluents

- Solid waste

There are three corresponding "Technical descriptions" however, the Technical description of the gaseous waste treatment is splitted into off-gas treatment and ventilation air treatment due to specificity of each effluent stream. During the reported period some of these seven documents were revised to take into account specific requests of CEC specially related to the costing study and activity flow-charts. The Technical description of the ventilation has been completely new written.

Point 4 : In preparation
The report of this point is foreseen at the end of the first semester of 1990.

Point 6 : Two allow a costing study, BELGATOM has also supplied two types of documents :

- one for the equipment costs

- another for the operating costs and this related to the liquid effluents, the gaseous effluents and solid waste.

The costing study of the equipment costs related to the gaseous effluents is splitted into off-gases and ventilation equipment costs.

- with regard to operating costs : the gaseous and liquid waste are treated together because the operation of this part of the plant is performed by the same personnel.

- in order to take into account the actual situation in Belgium, the solid waste related operating costs is splitted into :

  * on-site installation which treats I.E.R; filter cartridges, evaporators concentrates and flocculates, and,
  * central treatment unit which receives not only the so-called technological waste but also other solid waste coming from other waste sources than nuclear power plants.

Point 7 : In preparation
The corresponding report is foreseen at the end of the first semester of 1990

Point 8 : The corresponding report begins with a discussion of the source term, a description of the waste processing system (gaseous and liquid effluents) and a calculation of the liquid and gaseous waste releases.

On this base, an assessment of Radiological impact to the public is performed separately for liquid and gaseous releases each for an Inland Site and for a Coastal Site and for both real and design cases.
A calculation gives also the collective doses due to noble gases releases, to particulate (aerosols) releases and to liquid releases, each for both Inland and coastal Sites.
See table "Radiological Assessments"

All the results are given in several tables with a splitting per isotope and for several organs of the human body, and under a normalized form to allow extrapolations.

RADIOLOGICAL ASSESSMENTS

The radiological assessments (doses to critical individuals and collective doses) are summarized hereafter for the real and design cases.

1. LIQUID EFFLUENTS	REAL CASE		DESIGN CASE	
	INLAND	COASTAL	INLAND	COASTAL
DISCHARGES (Ci/y)	1,74 H3 = 6.10^{2}	1,74 H3 = 6.10^{2}	6,8 H3 = 6.10^{2}	6,8 H3 = 6.10^{2}
DOSES TO CRITICAL INDIV. µSv/y 1. TOTAL BODY	1,0	0,23	2,0	0,35
2. MOST EXP. ORGAN.	3,6 (Thyroïd)	2,6 (Thyroïd)	10 (Thyroïd)	7 (Thyroïd)
COLLECTIVE DOSES - Man.Sv/y 1. Total Body	$3,1 . 10^{-1}$	$3,2 . 10^{-4}$	$3,7 . 10^{-1}$	$6,9 . 10^{-4}$
2. THYROID	$4,5 . 10^{-1}$	$3,4 . 10^{-3}$	$8,1 . 10^{-1}$	$9,7 . 10^{-3}$

2. GASEOUS EFFLUENTS (*) (INLAND)	REAL CASE		DESIGN CASE	
	10.000 Nm³/y 30 Ci/m³	6.000 Nm³/y 30 Ci/m³	24.000 Nm³/y 300 Ci/m³	10.000 Nm³/y 300 Ci/m³
RELEASE (Ci/y) NOBLE GASES	$1,1.10^{3}$	713	$3,91.10^{5}$	$1,75.10^{4}$
IODINE (**)	0,31	0,27	1,72	0,563
AEROSOLS	$3,7.10^{-4}$	$2,5.10^{-4}$	$8,5.10^{-5}$	$4,3.10^{-5}$
DOSES TO CRITICAL INDIV. 1. Total Body - Noble gases (µSv/y)	0,16		52	2,5
2. Total Body - Iodine + particulates (µSv/y)	1,2		1,4	1,2
3. Most exposed Organ (Thyroïd) (µSv/y)	14		$1,9.10^{2}$	16
COLLECTIVE DOSES (Man.Sv/y) Noble gases + Aerosols + iodine 1. whole body	$1,2 . 10^{-2}$		1,3	$7,1 . 10^{-2}$
2. Thyroïd	$7,5 . 10^{-1}$		9,5	$8,4 . 10^{-1}$

(*) In the case of the atmospheric releases, the doses to the critical individual are the same for in-land and coastal sites. The collective doses of a coastal site are evaluated to 50 % of corresponding values for an in-land site.

(**) Including I131 + I133 releases.

DRAWING UP OF MANAGEMENT ROUTES FOR REACTOR WASTE BASED ON INDUSTRIAL PRACTICES IN ITALY AND THE F.R.G.

Contractors : GNS, Essen, F.R.G. and FRAMATOME, Paris, France
Contract No. : FI1W/0130
Duration of contract: January 1988 - April 1990
Period covered : January 1989 - December 1989
Project leaders : R. Geiser, Y. Huet

A. Objectives and scope

During the last few years, reactor waste management practices have taken advantage of many improvements as far as processes, organization and safety are concerned. Within the framework of the 3rd EC Waste Management programme, GNS and FRAMATOME are taking part in the present joint study, the purpose of which is to characterize various overall management schemes resulting from these new developments. The complete description and anlysis of each scheme will consist in evaluating its industrial feasability, costs and radiological impact on workers and public. The following sensitivity studies will point out the impact of some important parameters on processed waste product characteristics and quantities, costs and radiological impact.

The assessment of the different European management alternatives will make up basic data for the study. Each national scheme will be applied to a hypothetical site with 20GWe capacity consisting of light-water cooled reactors (PWR's and BWR's) and to low and intermediate radioactive waste generated during normal operation. After having analysed each basic case, sensitivity analysis will be carried out, varying the most important parameters such as waste characteristics, treatment methods, discharge limits and disposal criteria affecting both cost and radiological impact.

GNS and FRAMATOME have taken charge of providing the assessment of German and Italian approaches. Both of these management schemes will comprise regulations, waste inventories, regulations, treatment, conditioning, packaging, interim storage, transport and final disposal operations, cost evaluations and radiological impact on workers and public. Sensitivity studies will then be performed.

B. Work programme

2.2. Definition of typical primary waste inventories resulting from normal operation of PWR's and BWR's.
2.3. Definition of discharge limits, waste acceptance criteria and transport regulations.
2.4. Drawing up of basic management routes, taking into account treatment and conditioning variants.
2.5. Sensitivity studies for each basic management route.
2.6. Assessment of the related occupational exposure.
2.7. Assessment of the related radiological impact on the public (short and long term).

In this regard, FRAMATOME/GNS will be partly responsible for tasks 2.2., 2.3. and 2.7. and wholly responsible for tasks 2.4., 2.5. and 2.6. for two basic management schemes relying on the German and Italian philosophy and practice.

C. Progress of work and results

No contribution has been received at the edition's deadline.

DRAWING-UP OF MANAGEMENT ROUTES FOR REACTOR WASTES BASED ON INDUSTRIAL PRACTICES IN FRANCE AND SPAIN

Contractor : SGN - St. Quentin-en-Yvelines, France
Contract No. : FI1W/0132
Duration of contract : September 1987 - March 1990
Period covered : January 1989 - December 1989
Project leaders : B. de Wavrechin, C. Laouen

A. Objectives and scope

The objective is to contribute to the implementation of a joint study on management options for LWR wastes by drawing up two basic routes emphasizing the treatment/conditioning and packaging aspects. A management route is defined as each assembly of coordinated actions by which the management of LWR wastes from their production to their disposal is implemented. Usually, these actions comprise treatment, conditioning, packaging, interim storage, transport and disposal operations. The assessment of management routes on the basis of economic and radiological criteria is based on the French and Spanish concepts and industrial practices.

Basic information and data, related to the operating experience in France and in Spain, is made available by EDF and INYPSA respectively, who cooperate with SGN as contractors. More specifically, the contribution of INYPSA applied to the study of the BWR waste management options is based on the Spanish experience.

B. Work programme

1. Definition of typical primary waste inventories resulting from normal operations of PWRs and BWRs.
2. Definition of discharge limits, waste acceptance criteria and transport regulations.
3. Drawing up of basic management routes taking into account treatment and conditioning variants.
4. Sensitivity studies on each basic management route.
6. Costing of the basic management routes as well as the variants evolved from sensitivity studies.
7. Assessment of the related occupational exposure.
8. Assessment of the related radiological impact to the public (short and long term).

based on the French and Spanish concepts and practices.

C. Progress of work and obtained results

State of advancement

During the reference year 1989, the following tasks were performed:

- Modification of typical primary waste inventories.
- Costing of the basic management routes.
- Assessment of the related occupational exposure.
- Assessment of the related radiological impact to the public.

The remaining task "Sensibility studies on each basic management route" will be completed by the end of March 1990. This part of the study will examine the impact of using mobile conditioning units on capital and operating cost.

<u>Progress and results</u>

1. Modification of typical primary waste inventories.
   The inventory of liquid and gazeous primary waste already given in 1988 was changed further to be comparable to the French PWR actual performances. Lower values of the activity present at the TEP and TEG units were adopted:
   - Gazeous 20 Ci/Nm3 instead of 200 Ci/Nm3 (TEG - ventilation excluded)
   - Liquid 0,1 Ci/Nm3 instead of 1 Ci/Nm3 (Tritium excluded) (TEP)

   together with a slight adjustment of their spectrum.
2. Definition of discharge limits, waste acceptance criteria and transport regulations.
3. Drawing-up of basic management routes taking into account treatment and conditioning variants.
4. Sensitivity studies on each basic management route.
   To be performed in 1990.
6. Costing of the basic management routes as well as the variant evolved from sensitivity studies.
   - Based on the information given to TASK by SGN in 1988 for the cost assessment of the management routes, the cost assessment was up-dated. Its results show concordance with data given by EDF for PWR in France.
   - In addition transport costs were provided based on the following assumptions:
     - Transport by truck (unlike the French case where most of the waste packages are transported by rail).
     - Average distance covered = 500km (instead of 660km in France).
     - Payload : 26 t of packaged waste per truck.

     which leads to an average transport cost of about 100 ECU/t.
7. Assessment of the related occupational exposure.
   In addition to the data given in 1988 for the radiological impact, the mean individual dose equivalent integrated by the operators of the Effluent treatment units of a two 900 MWe unit is assessed to be equal to 0.5 rem/year.
   The collective dose of the 19 operators becomes approximately 10 man.rem/year.
   The dose equivalent rates are calculated on the basis of the French experience (EDF) that does not allow determination of a specific value per treatment unit so far.
   However, it can be noted that the dose equivalent integrated by workers arises primarily from the Solid Waste Treatment System (TES) where most operations are performed manually.
8. Assessment of the related radiological impact to the public.
   In addition to the data given in 1988 for the radiological impact, the following information on released activity and related radionuclide spectrum was provided and discussed:
   - Gaseous release to the stack : 150,000 Nm3/hr/unit
     + 6,000 Nm3/yr/unit
     including, C-14 : 0.001 Ci/yr/unit
     Iodine : 0.067 Ci/yr/unit
     Noble gases : 728.317 Ci/yr/unit
     Aerosols : 4 x 10^{6} Ci/yr/unit
     Total Activity : 728.385 Ci/yr/unit

- Liquid effluents to the river (or to the sea) -
  12,000 m3/yr/unit
  i.e., 3.33 Ci/yr/unit (H3 excluded)
  Tritium - 600 Ci/yr/unit.

The spectrum accounted for the releases is assumed, conservatively, to be the same as the one taken for the primary wastes (secondary liquid effluents).

COST EVALUATION OF ALTERVATIVE MANAGEMENT SCHEMES FOR LWR WASTE

Contractors : TASK Ricerca 1 Sviluppo S.r.l. - Kraftanlagen AG
Contract No. : FI1W/0125
Duration of Contract · October 1, 1987 - January 31, 1990
Period covered : January 1, 1989 - December 31, 1989
Project leaders · G. Thiels (TASK R&S), F. Stenersen (KAH)

A. Objectives and scope

A joint strategy study is being performed to assess a number of schemes for the treatment, conditioning, packaging, interim storage, transport and disposal of LWR wastes on the basis of economic and radiological criteria. In this context, TASK R&S and KAH are contributing towards the costing of five basic management routes and their variants evolving from the sensitivity studies.

The scope of the work is to assess the capital and operating costs of the various unit operations incorporated into each basic management scheme on the basis of the detailed process descriptions provided by the other participating organisations. Moreover, the plant and transport costs will be actualised to the operational start-up date of the plant utilising the "Present Worth" method, finally yielding a cost per unit volume of primary waste treated. The costing of the waste disposal itself does not form part of the study.

TASK R&S and KAH will also contribute to the sensitivity studies. Their aim is to evaluate the impact of different basic parameters (e.g. discharge limits, process variables, duration of interim storage, plant capacity) on the overall management costs.

B. Work programme

2.1. Scope of the programme
2.2. Cost evaluation
  2.2.1. List of possible intermediate management stages
  2.2.2. Cost assessment procedure
  2.2.3. Results
  2.2.4. Sensitivity studies

C. Progress of work and obtained results

State of advancement

TASK R&S and KAH have performed the cost evaluation of three management options for LWR waste. For this purpose, general procedures have been established for the cost assessment and cost scaling of the envisaged management schemes.
The implementation of these procedures has been limited to the PWR routes due to the delays encountered in the programmes of the other partners of the joint strategy study, responsible for the engineering of the BWR management routes. As a result, the cost assessment procedure has only been applied to the PWR routes (PWR1: SGN; PWR2: GNS-Framatome; PWR3; Belgatom).

Progress and results

2.2.1. Management options to be costed

The engineering and process development of the basic management routes by the other partners of the joint strategy study have undergone delays, thereby also retarding the costing study.

2.2.2. Cost assessment procedure

For the cost assessment of the various management options a number of cost elements have been defined, which are utilised to determine the overall plant cost. Several assumptions concerning the plant siting and process technology have been established. Using this framework, the capital cost in 1988 is derived from the material cost of the Major Equipment or "Base Value"; all the other capital cost elements, except the Civil Works, are expressed as a fraction of this Base Value. For the operating cost the annual consumption of Process Materials, Utilities and Maintenance Materials and the costs associated with the Direct Labour and Overheads are taken into account to obtain the annual cost of the different cost elements in 1988.

Both the capital and annual operating costs are actualised to the start-up date of the plant using the "Present Worth" method. Finally, the actualised values are converted into an annual cost per unit volume of waste treated by employing the "Annual Value" method.

To evaluate the capital and annual operating costs related to the transport of the conditioned LWR waste, the type and amount of transport casks and the transport distance were defined in collaboration with the other participating organisations. On the basis of this data, the transport costs in 1988 by road or rail are elaborated. Subsequently, they are actualised employing the cost assessment procedure and transformed into an annual cost per unit of volume of waste treated.

2.2.3. Results

The cost determination procedure was applied to the three PWR management routes. The costing of PWR2 route is based on the costs provided by GNS-Framatome, whereas that of PWR1 and PWR3 has been derived by TASK R&S - KAH from the engineering data given by SGN and Belgatom. It should be noted that the interim storage has either a capacity of 1 year (PWR1 & PWR2) or 10 years (PWR3). The results thus obtained are shown in Table I.

Concerning the transport, the national practice was adopted, i.e. the transport is either performed by road (PWR1 & PWR3) or rail (PWR2). Moreover, the distances covered vary from 2 x 100km (PRW3) to 500km (PWR1 & PWR2). The results are given in Table II.

2.2.4. Cost scaling

A general procedure has been developed to scale the costs with changing plant capacity. It is based on the "six-tenths rule" and derived formulas available in the literature, which are normally applied in the chemical industry. This procedure is applicable to a reference capacity of 20 GW(e).

However, in the case of the PWR management routes the basic data refer to plant capacities ranging between 1.3 and 1.8 GW(e) (i.e. 1 module). Therefore, it has been suggested to perform a linear cost scaling using as reference the costs for 1 module.

Table I

Actualised capital and annual operating costs together with the corresponding total plant cost for 30 years of operation and constant annual cost for the three LWR waste management routes. The costs do not include the transport of the treated waste.

Actualisation data: 01.01.92

ROUTE	ACTUALISED CAPITAL COST (MECU)	ACTUALISED ANNUAL OPERATING COST (MECU a^{-1})	TOTAL PLANT COST FOR 30 YEARS OF OPERATION (MECU)	CONSTANT ANNUAL COST (MECU a^{-1})
Route LWR1 (PWR)	666.459	50.976	1 370.492	125.199
Route LWR2 (PWR)	1 360.120	61.304	2 206.794	201.599
Route LWR3 (PWR)	867.266	42.363	1 452.344	132.677

Table II

Actualised capital and annual operating costs together with the corresponding total transport cost for 30 years of operation and constant annual cost for the three LWR waste management routes.

Actualisation date: 01.01.92

ROUTE	ACTUALISED CAPITAL COST (MECU)	ACTUALISED ANNUAL OPERATING COST (MECU a^{-1})	TOTAL TRANSPORT COST FOR 30 YEARS OF OPERATION (MECU)	CONSTANT ANNUAL COST (MECU a^{-1})
Route LWR1 (PWR)	0.091	1.048	14.565	1.331
Route LWR2 (PWR)	1.125	1.259	18.513	1.691
Route LWR3 (PWR)	0.000	3.134	43.284	3.954

COST AND RADIOLOGICAL IMPACT OF REACTOR WASTE IN BELOW-GROUND VAULTS

Contractor	: INITEC, S.A., Madrid, Spain
Contract No.	: FI1W/0127
Duration of contract	: December 1987 - December 1989
Period covered	: January 1989 - December 1989
Project leader	: M. Sanchez Delgado

A. Objectives and Scope

As part of the joint study aiming at assessing management routes on the basis of economic and radiological criteria, INITEC focuses on the cost and radiological impact assessment for the final disposal phase of reactor wastes in below ground vaults.

The main goals of this project are:

- Determine the radiological impact both short term and long term associated to a storage facility of the below ground type for reactor wastes. The following main release pathways have been taken into account: ground water migration of radioactive elements, surface water releases and atmospheric releases. Three different stages in the life of the installation have been considered: operation of the facility, institutional control phase and free use of the land after termination of the licence. Different scenarios have been assumed for each one of the different stages, including normal operations scenarios as well as accidental scenarios.
- Determine the radiological burden to the facility operators.
- Cost assessment related to the disposal of the LWR waste products in below ground vaults, including capital and operating costs.

B. Work programme

The following activities were performed in the six month period covered by this report.

B.1. Cost assessment

The cost estimates have been performed in accordance with procedures applied by the other contractors. Calculation bases are the following:

B.1.1. Capital costs

- . Site works include only acquisition and preparation costs.
- . 20% of civil works in vaults construction is carried out before start up date.
- . QA (quality assurance) and indirect labour calculated as a percentage of direct cost from civil works, vault construction and major equipment and bulk materials.
- . Architectural and Engineering devices are taken to represent 16.2% of the direct capital cost.

B.1.2. Operating costs

- . Expected life of the facility 30 years.
- . 120 m^3 of wastes.
- . Salary for operators + 13 ecu/h and higher labour categories = 25 ecu/h.
- . 80% civil work in vault construction is performed along the life of the facility.

- Decommissioning cost has been converted into a constant annual cost which should be invested at 10% of interest rate.

B.1.3. Actualisation of cost was based on the following values:

- Date of actualisation: 01.01.93 (start up).
- Construction period 3 years (1990-1993).
- Annual rate of interest 8% a
- Annual rate of inflation 3% a
- Return on inversion (provisions for decommissioning) 10% (nominal).
- Money borrowed at the middle of the duration period of each activity and paid back at the end of the construction period.
- Exchange rate 130,9 pta/ecu.
- The cost determination scheme provided by KAH applied.

B.1.4. Costs

Breakdown of costs in ecus per m^3 of waste is provided below:

- Capital cost 899
- Operating cost 1505

Capital cost structure was found to be:

Site works	17%
Civil works	2%
Vaults construction	4%
Major equip. + bulk mat.	5%
O.A.	2%
Indirect construction	1%
Laboratory and health physics	1%
Architectural and Engineering Services	5%

Operating cost structure was found to be:

Direct labour	32%
Overheads	6%
Vaults construction	11%
Decommissioning	9%
Utilities	3%
Materials	2% (maintenance and process).

B.2. Occupational exposure assessment

Occupational exposure was calculated for the waste disposal facility of the type Below Ground Vaults.

The approach adopted for estimating the occupational exposure is based on a per shipment basis and most significant data have been obtained from relevant literature and adapted to the specific design.

Major tasks and operations have been established and workers and times required for completing them, as well as representative distances between workers and waste have been estimated for calculating the doses received by workers during disposal of two types of waste packages: drums and containers.

The results of these calculations show that projected annual collective doses range from 0.21 to 0.65 person-Sv/year and from 5.24-5 to 1.64-4 person-Sv/m^3 for the sources and packages assumed. Accordingly annual average individual doses range from 1.05-2 to 3.27-2 Sv/year and 2.63 to 0.10-5 Sv/m^3.

B.3. Assessment of the radiological impact to the public.

B.3.1. Main assumptions

The main hypothesis used in the definition of the "normal evolution scenario" are:

- It is assumed that the storage will receive during a period of 30 years a total amount of medium and low level waste generated by 20 GWe of installed nuclear capacity, of which 75% corresponds to PWR type reactors and 25% to BWR.
- The calculation of the total activity in the different waste streams for the radionuclides considered is based on the models and normalized data of NUREG/CR-1759.
- The values for the "Annual Lixiviation Fractions" used in the analysis corresponds to those specified as maximum acceptable for concrete imobilized waste in the French acceptance criteria.
- The institutional control period is assumed to extend over 300 years after the closure date, and the cover is assumed to remain effective against infiltration in this period.
- The degradation of waste packages is assumed to follow a normal law, characterized by a mean time (time at which 50% of the packages will be degraded) and the standard deviation.
- Only the degraded packages are subject to lixiviation by percolating water.
- After the end of the institutional control period the lixiviation rate of the degraded packages corresponds to the full values of the acceptance criteria. During the institutional control period, the lixiviation rate of the degraded packages is assumed to be 13% of the full values, fraction that corresponds to the intitial saturation percentage of the clay in the cover.
- Water that percolates and lixiviates the waste packages is assumed to reach the underlying aquifer, where it is transported and diluted with the general ground water flow. The aquifer discharges to a river located at a short distance (1km) from the storage site.
- At a certain distance downstream the discharge area, water is pumped from the river and used for human and animal consumption, as well as for irrigation of a piece of land in which vegetables for human and animal consumption are grown.

B.3.2. Maximum individual doses

The maximum value of annual effective committed dose, 1.14 (-5) Sv/y (1.14 mRem/y) corresponds to the age group of infants, most of it due to the ingestion of Ni-59 in contaminated milk. This maximum value occurs 960 years after the closure of the installation.

The maximum doses to adults are 1.91 (-6) Sv/y (0.19 mRem/y) at 1194 years after the closure of the installation.

The most significant radionuclides on a 1TBq basis are, I 129, Nb94, Cs135, Np237, Pu239 and Tc99, their maximum values 10(-6)-10(-8) Sv/y being reached 332, 1308, 448, 1994, 2934, 332 years after closure of the facility.

B.3.3. Collective doses

Collective doses have been estimated and the final report will be submitted in the near future.

COST AND RADIOLOGICAL IMPACT ASSESSMENT FOR THE DISPOSAL OF REACTOR WASTE BY NEAR-SURFACE DISPOSAL

Contractor : CEN Fontenay-aux-Roses, CEA, France
Contract No. : FI1W/0135
Working period : September 1987 - December 1989
Period covered : January 1989 - December 1989
Project leader : J. Malherbe

A. Objectives and scope

The study is part of a joint study aiming at assessing management routes for LWR wastes on the basis of economic and radiological criteria. A management route is defined as an assembly of coordinated actions by which the management of LWR wastes, from their production to their disposal, is implemented. Usually, these actions comprise treatment, conditioning, packaging, interim storage, transport and disposal operations.

In the framework of this large programme, CEA is mainly involved in the final part of the management routes : definitive storage. In cooperation with INITEC, the contractor will develop, for this reactor, the concept of the Near-surface Disposal (French and Spanish storage).

B. Work programme

2.2. Definition of acceptance criteria, in the case of a Near-Surface Disposal.

2.3. Drawing-up of basic management routes : on the basis of inventories and criteria acceptance, the contractor will define all the subsequent disposal operations by Near Surface Disposal.

2.4. Sensitivity studies : will be performed in order to determine the impact of some important parameters on costs and doses.

2.5. Cost assessment : To perform the cost evaluation, an extensive description of the components entering the capital and operating costs for each main step will be carried out.

2.6. Assessment of the occupational exposure

2.7. Assessment of the radiological impact to the public

C. Progress of work and obtained results

In accordance with an up-dated list of waste packages communicated by SGN, a new evaluation of the Near-Surface Disposal installation has been performed.

An estimation of radiological impact of reactor waste disposal has been calculated on the basis of the radionuclide inventory in report NUREG-CR 1759.

The study is now completed.

2.2. Definition of waste acceptance criteria

This work was completed and has been reported in 1988 Annual Progress Report.

2.3. Drawing-up of basic management routes

This work was completed and has been reported in 1988 Annual Progress Report.

2.4. Sensibility Studies

In this study, the volume of waste has been taken as a parameter. Particularly, Near-Surface Disposal has been evaluated taking into account the volume of low active reprocessing waste and reactor waste or only the latter. A cost reduction of 10% only is achieved in investment and operating costs for a 30% reduction in volume of waste.

2.5. Cost Assessment

On the basis of a nuclear park of 20 GWe operating for 30 years, the total volume of waste to be disposed of by Near-Surface Site has been evaluated to be 280,000 m^3.

A cost evaluation has been done on the basis of this total volume of waste applying the cost determination method proposed by TASK/KAH.

2.6. Assessment of occupational exposure

This evaluation has been performed in dividing the site in 3 zones where annual dose equivalent rates are specified : zone 1 or "surveillance zone" with a rate limited to 0.6 micro Sv/h, zone 2 or "low risk controlled zone" with a dose rate limited to 2.5 micro Sv/h and zone 3 or "regulated zone" with a dose rate of 25 micro Sv/h.

2.7. Radiological impact to the public

In the reactor waste inventory communicated by other contractors in charge of definition of the waste, no long-lived radionuclide has been mentionned. Then, in agreement with INITEC and CEC staff, a list of radionuclides has been taken as given in report NUREG-CR 1759. That led to an evaluation of impact due to reactor waste estimated to be 0.5 micro Sv/y maximum.

DRAWING-UP OF MANAGEMENT ROUTES FOR LWR-HULLS BASED ON THE DIRECT CEMENTATION AND MELTING CONCEPTS

Contractor	: Commissariat à l'Energie Atomique Centre d'Etudes de la Vallée du Rhône (FRANCE)
Contract No.	: FI1W/0131
Duration of contract	• September 1987 - December 1989
Period covered	: January 1989 - December 1989
Project leader	: C. Sombret

A. Objectives and scope

The objective of the contract is to contribute to the implantation of a joint study on management options for hulls and caps by drawing up two basic routes emphasizing the treatment/conditioning and packaging aspects:

- Route No. 1 : Hulls and caps cementation/packaging/interim storage (reference industrial route of the La Hague reprocessing plant).
- Route No. 2 : Hulls melting in a cold crucible, caps melting in conventional crucible/packaging/interim storage (alternative route under development).

B. Work programme

In order to evaluate management routes for hulls and caps, a methodology is applied which consists in performing the following sequence of tasks:

1. Definition of a reference scenario (size of the nuclear park, reactor type, fuel burn-up, cooling time before reprocessing).
2. Definition of basic hypothesis concerning discharge limits and waste acceptance criteria for disposal.
3. Definition of the characteristics and arisings of hulls and caps.
4. Drawing-up of basic management routes taking into account treatment and conditioning variants.
5. Sensitivity studies on each basic management route.
6. Development of computing programmes for itemising and evaluating the different management option.
7. Costing of the basic management routes as well as the variants evolved from sensitivity studies.
8. Assessment of the related occupational exposure.
9. Assessment of the related radiological impact to the public (short and long term).

With respect to the other tasks, CEN/VALRHO takes in charge wholly tasks 3, 4, 5 and 8, partly task 9 to two basic management routes based on direct hulls cementation for the first, and on melting for the second.

C. Progress of work and obtained results

C.1. State of advancement

The reference scenario was defined jointly by the working group and the basic data related to the amount of hulls and ends generated and their characteristics have been fixed. Discharge limits and waste acceptance criteria were also defined.

The drawing-up of the two basic management routes was performed:

- Route No. 1 : hulls and ends cementation/packaging/interim storage.
- Route No. 2 : hulls and ends sorting/melting/conditioning/ interim storage.

For each route flow diagrams and mass balances were determined. A description of the processes, a list of the main equipment and their cost, the conceptual design of the cells and building were given. This data was used by Task R&S and KAH to perform the cost evaluation of these two management options.
Sensibility and safety studies were also done.

C.2. Sensibility studies

The effects of variation of a number of paramters were studied for each route as defined by the working group.

- Radioactive content in hulls and caps : within a large range of activities the cementation process appears to be acceptable for thermal loading.
- Interim storage prior to treatment : a 50 year interim waste storage period prior to the treatment reduces the biological shielding requirement, allows the tritium to decay and lowers the activity level of the waste by about two orders of magnitude. These advantages do not appear sufficient to offset the constraints implied by a long interim storage period.
- Decontamination performance during melting : the active experimentations needed to estimate the decontamination performance are still under preparation.
- Discharge limits : Cementation is not affected by variation of the plant discharge limits, whereas for melting it will be necessary to capture the radioactive gas released during melting and to improve the decontamination efficiency of the liquid waste treatment.

C.3. Safety studies

Assessments of the related occupational exposure and the radiological impact to the public have been performed. The results are presented in Table 1. Compared to the radiological impact of the reprocessing plant, the relative contribution is very low (less than 1%).

Table 1 : Radiological impact

		Cementation	Melting
Public	Seaside plant	-	0,17 man.Sv/y
	Inland plant	-	0,05 man.Sv/y
Workers	-	0,09.man.Sv/y	0,11 man.Sv/y

DRAWING-UP OF MANAGEMENT ROUTES FOR LWR HULLS, BASED ON THE COMPACTION/PACKAGING EXHAUSTIVE DECONTAMINATION CONCEPTS

Contractor : CEN/SCK Belgian Nuclear Research Center, Mol, Belgium
Contract No. : FI1W/0123
Duration of contract : November 1987 - February 1990
Period covered : January 1989 - December 1989
Project leader : M. Klein

A. Objectives and scope

This study is part of a joint study, which aims at the assessment of different management routes for hulls and caps, generated during the reprocessing of spent fuel. The assessment is based on economical and radiological criteria.

The methodology applied for the evaluation of the management routes, consists of the following tasks:

1. Definition of a reference scenario.
2. Definition of discharge limits and waste acceptance criteria.
3. Definition of the characteristics and arisings of hulls and caps.
4. Drawing up of basic management routes.
5. Sensitivity studies on each management route.
6. Development of computing programmes for itemizing and evaluating the different management options.
7. Costing of the basic management routes as well as the variants evolved from the sensitivity studies.
8. Assessment of the related occupational exposure.
9. Assessment of the related radiological impact to the public.

B. Work programme

CEN/SCK covers partly task 3 and wholly tasks 4, 5 and 8 for two basic management routes.

B.1.: Discussion of data concerning amounts and characteristics of hulls and caps, generated in the frame of the reference scenario.

B.2.: Drawing up of two basic management routes:
Route No. 3 : Hulls compaction/packaging/interim storage
Route No. 4 : Hulls decontamination/cementation/packaging/interim storage.

B.3.: Sensitivity studies to study the impact of some important parameters on waste product characteristics and on the total volume of the treatment and conditioning facility buildings.

B.4.: Calculation of the occupational exposure for routine operation and maintenance : annual individual dose and collective dose for 30 years operation.

C. Progress of work and obtained results

State of advancement

A detailed description of the routes No. 3 and 4 was carried out. This comprises:

- engineered flow diagrams (mass balances);
- flow sheets;
- characteristics of the main pieces of equipment;
- manpower requirements.

The transport cost for the route No. 3 was estimated assuming a transport with a TN28V cask which has a nominal capacity of 28 glass type containers.

The sensitivity studies were performed for both routes. For each route, the relevant parameters were defined by the Working Group and are given hereafter for routes Nos. 3 and 4.

Route No. 3 : Compaction/Packaging
1. Discharge limits
2. Volume reduction Efficiency
3. Disposal criteria
4. Type of packaging

Route No. 4 : Decontamination/Cementation
1. Content of dissolver residues in hulls
2. Discharge limits
3. Decontamination efficiency

The assessment of the occupational exposure will be done in the beginning of 1990.

Results

B.1. Discussion of data concerning amounts and characteristics of hulls and caps

The characteristics of the cladding waste produced is based on standard PWR fuel with 3.5% enrichment and a burn-up of 33 GWd/MTHM. Reprocessing and conditioning are foreseen 3 years after reactor discharge. For a 600 THM/a reprocessing capacity, about 171 T hulls and 18 T caps are produced annually.

B.2. Drawing up of basic management routes

Route No. 3 compaction/packaging

The reference route is the CEN/SCK process of compaction of the hulls and packaging of the compacts inside a triple container SS+Pb+SS; the caps are conditioned by the cementation route identical to route No. 1 developed by CEA. This results in the production of 277 glass type canisters for the compacted hulls equivalent to 56 m^3 or 271 tons and 22 drums with cemented caps equivalent to 38 m^3 or 80 tons. The flow sheet of the compaction/packaging process for the hulls is given in Figure 1.

Route No. 4 decontamination/cementation

The major steps of route No. 4 are decontamination of the hulls and cementation of hulls and caps according to the French Process. The reference decontamination process consists of washing of the hulls with cold HNO^3 3 M, which results in 95% alpha decontamination. Application of this process results in the production of 237 drums of cemented hulls and caps, i.e. 403 m^3 or 948 tons. The flow sheet of route No. 4 is given in figure 2.

For both routes, a series of data sheets gives the characteristics of the main pieces of equipment (dimensions, materials, power consumption). The operation time and the manpower requirements were also estimated. For route No. 3, this corresponds to 9900 man.hours/a and for route No. 4 to 11550 man.hours/a. Plant layouts and the related buildings volumes were also determined.

B.3. Sensitivity studies

Route No. 3 Compaction/packaging

1. Discharge limits

The airborne releases are one or several order of magnitudes lower than the authorized releases so that retention of the gases is not to be considered. For the liquid effluent, only the drying of the hulls generates a small volume (8.5 m^3/a) of significantly active effluent which should be recycled in the reprocessing plant.

2. Volume reduction of the compacted product

The reference compacted product has a density of 75% vs the theoretical density of zircaloy. An increase of 10% of the compacted product density results in a decrease of 7% in the number of canisters produced whereas a 10% decrease results in a 16% increase. The removal of the lead lining results also in a 12% decrease of the waste volume.

3. Disposal criteria

For the reference case, the conditioned compacted waste contains 238 GBq alpha/ton or 1095 GBq/m^3 and 629 TBq/ton beta-gamma.
For the sensitivity study, the disposal criteria is varied between 185 and 1850 GBq alpha/m^3; therefore the compacted waste can be accepted in a repository only in the latter case.

4. Type of packaging

The reference case considers packaging in glass type 200 l container. As an alternative, the use of a 400 l standard drum is considered. The total waste volume and weight are decreased respectively by 12 and 20%. The press diameter is multiplied by a factor of 2, which means that the needed force is multiplied by a factor of 4; this will markedly affect the press cost.

Route No. 4 Decontamination/cementation

1. Influence of residues content

In the reference process, the 0.5% residues, essentially Ru, represent 6.5% of the total beta-gamma emitter inventory. A variation of the residues content between 0.5% and 5% will only result in a 60% increase of the canister activity and in a 80% increase of the activities of the liquid wastes produced by the decontamination process.

2.2. Discharge limits

Airborne releases are well below the authorized releases.
The decontamination solutions and the washing aqueous solutions are concentrated by evaporation; most of the distillates can be recycled in the decontamination process, the concentrates are recycled to the reprocessing plant for alpha recovery together with the distillate purges. With this treatment scheme, only 3 m^3/a must be treated as liquid waste.

2.3. Decontamination efficiency

The reference process assumes a 95% decontamination for the alpha's. The purpose of the decontamination process is to remove the activity to such a level that the hulls can be disposed in a near surface disposal site. The acceptance criteria, in France, is fixed at 3.7 GBq alpha/t after 300 years. To reach this value, the alpha decontamination must be higher than 90%. This performance is reached by several decontamination processes.
All the decontamination processes are focused on the removal of the alpha activity but, in fact, the tritium and the strontium activity levels are respectively 2 and 1 order of magnitude higher than the acceptance criteria defined in France.

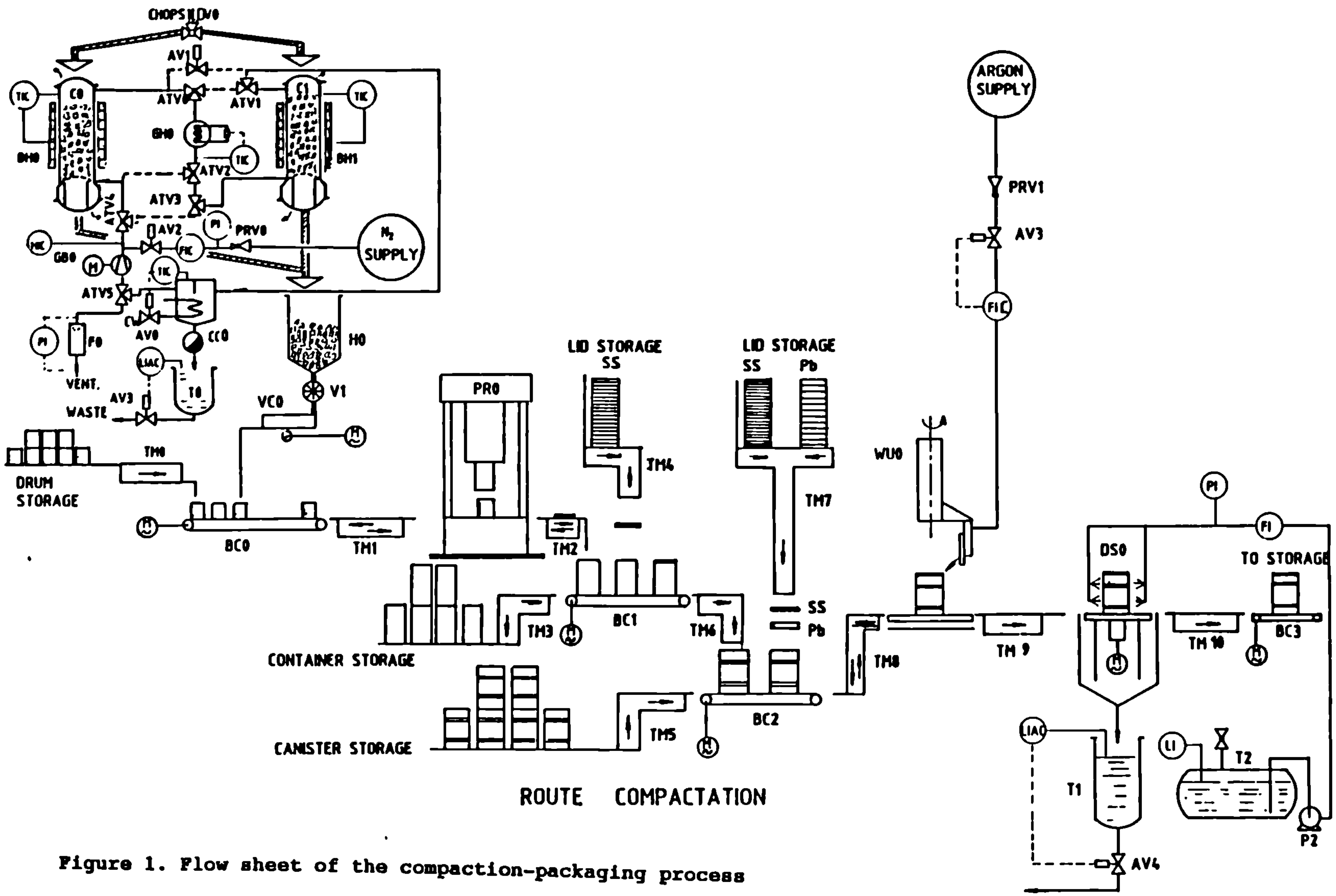

Figure 1. Flow sheet of the compaction-packaging process

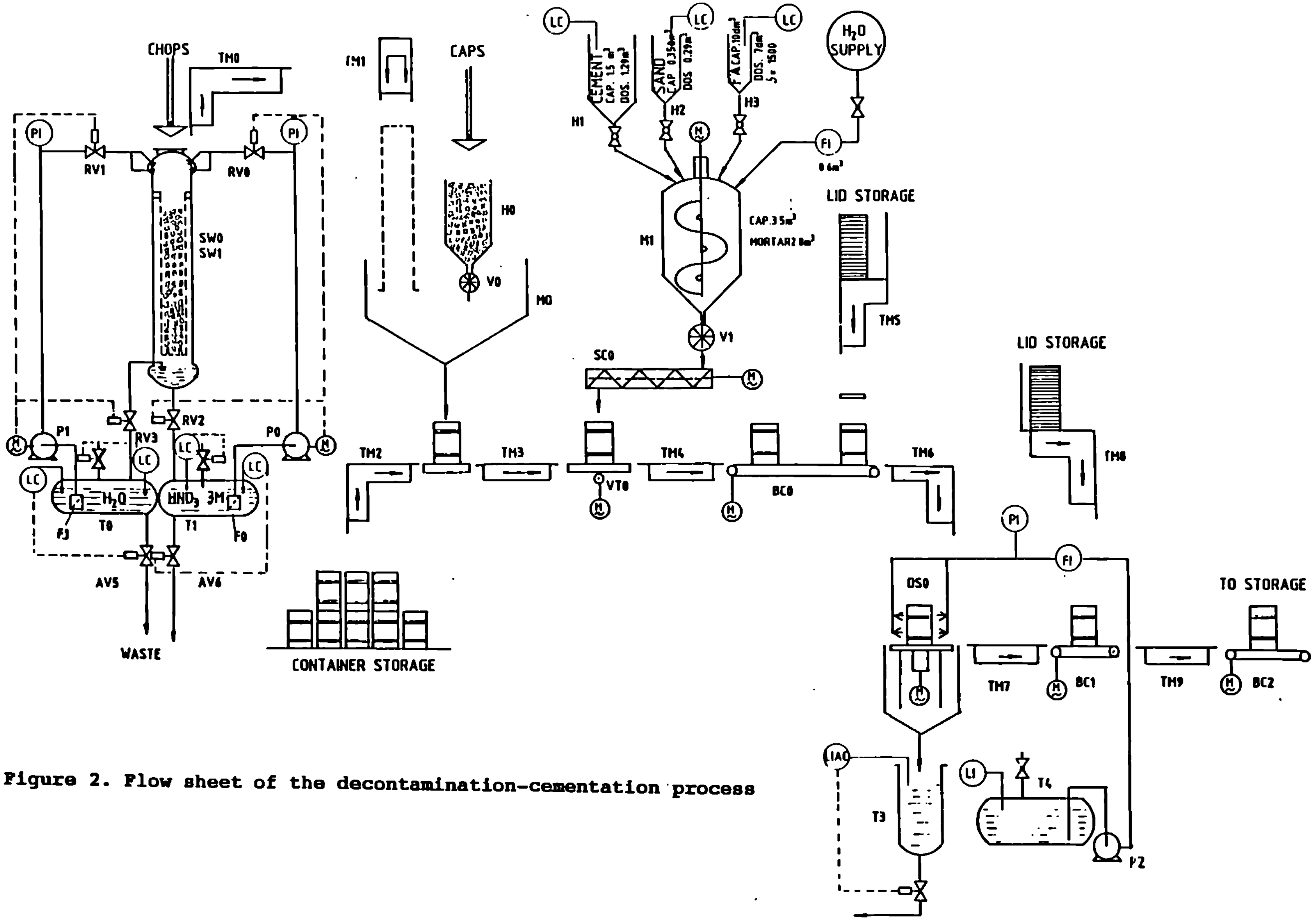

Figure 2. Flow sheet of the decontamination-cementation process

DRAWING-UP OF MANAGEMENT ROUTES FOR LWR HULLS BASED ON COMPACTION/CEMENTATION AND COMPACTION/EMBEDDING IN GRAPHITE CONCEPTS

Contractor : NUKEM GmbH, Alzenau, FRG
Contract No. : FI1W/0137
Duration of contract : August 1987 - October 1989
Period covered : January 1989 - October 1989
Project leaders : O. Mehling, F.H. Wingender

A. Objectives and scope

The objective of this contract is to contribute to the implementation of a joint study on management options for hulls and caps by drawing up two basic routes emphasizing the treatment/conditioning and packaging aspects. A management route is defined as each assembly of coordinated actions by which the management of hulls and caps from their production to their disposal is implemented. Usually, these actions comprise of treatment, conditioning, packaging, interim storage, transport and disposal operations. Since this joint study will adopt the methodology followed in a previous one, devoted to two other specific alpha wastes (solid plutonium containing waste and reprocessing sludges), it will be referred to for the definition of the reference scenario, the basic hypothesis and the procedure to be carried out for assessing cost and radiological impact to the public.
The tasks of NUKEM in this contract are:

- definition of characteristics and arisings of hulls and caps, partly,
- drawing-up of 2 basic management routes taking into account treatment and conditioning,
- sensitivity studies on each basic management routes,
- determination of geological disposal costs at Gorleben,
- assessment of the related occupational exposure.

B. Work programme

2.2. Hulls and caps characteristics and arisings

For this task, it is only asked of NUKEM to discuss the data provided by another organisation participating in the joint study, so that a reference waste composition can be agreed upon within the working group.

2.3. Drawing-up of basic management routes

NUKEM extensively defines two basic routes:

route No. 1 : hulls, caps, compaction/cementation/packaging/
interim storage
route No. 2 : hulls, caps compaction/embedding in graphite etc.

2.4. Sensitivity studies

For both the management routes sensitivity studies are performed by variations of the most important parameters as indicated in the work programme.

2.5. Cost evaluation

As far as disposal of conditioned and packaged hulls in the Gorleben salt dome is concerned, NUKEM will provide data on the related disposal cost. This will be expressed in ECU/m^3 of conditioned waste.

2.6. Assessment of the occupational exposure

For the two basic routes of concern, the occupational exposure will be determined for routine operations including manual operations for repairs and maintenance, packaging, transport and disposal at Gorleben.

C. Progress of work and obtained results

State of advancement

In a supplementary work programme additional work was completed concerning item 2.4. - review and evaluation of different criteria - and item 2.5. - updated cost evaluation.

The study has been completed according to the time schedule. The final report has been supplied to the Commission.

Progress and results

2.2. Hulls and caps characteristics and arisings

A reference waste composition was finally agreed upon in 1988.

2.3. Drawing-up of basic management routes

This item was completed in 1988.

2.4. Sensitivity studies

The parameters which had to be varied were discussed. An increased burn-up of the fuel elements treated would increase in the thermal capacity and dose rates from the containers affected. The compaction efficiency resulting from the implementation of alternative compaction devices can be doubled; hence the number of waste containers for hulls would be reduced by half. A waste acceptance criteria for disposal with an upper alpha activity limit of ca. 2.0 E12 Bq/m^3 will be met. The theoretical ca.2.0 E11 Bq/m^3 alpha criteria would increase the number of waste packages. This increase for route No. 2 would not be achievable in the layout described for the basic scenario due to the through-put difficulties. Packaging of the conditioned waste materials in CEN/VALRHO cemented waste drums and UP3-HLW type canisters can be realized.

2.5. Cost evaluation

An updated cost evaluation of the disposal operations (capital and operating costs) was done. The disposal costs in ECU/m^3 of conditioned waste given in the 1988 Annual Progress Report were confirmed. A mathematical relationship quoting the disposal cost of hulls as a function of their arisings was given.

2.6. Assessment of the occupational exposure

The resulting collective dose uptake in man. Sv/a is listed below (20 GWe nuclear park).

operation	route No. 1	route No. 2
waste treatment	3.9 E-2	1.1 E-1
packaging	3.2 E-3	3.2 E-3
transport	3.0 E-2	2.8 E-2
disposal (at Gorleben)	1.1 E-2	1.1 E-2

COST EVALUATION OF ALTERNATIVE MANAGEMENT SCHEMES FOR ZIRCALOY HULLS

Contractors : TASK Ricerca & Sviluppo S.r.l. - Kraftanlagen AG
Contract No. : FI1W/0126
Duration of contract : October 1, 1989 - January 31, 1990
Period covered : January 1, 1989 - December 12, 1989
Project leaders : G. Thiels (TASK R&S), F. Stenersen (KAH)

A. Objectives and scope

A joint strategy study has been performed to assess a number of schemes for the treatment, conditioning, packaging, interim storage, transport and disposal of LWR hulls and caps on the basis of economic and radiological criteria. In this context, TASK R&S and KAH contributed towards the costing of six basic management routes.

The scope of the work was to assess the capital and operating costs of the various unit operations incorporated into each basic management scheme on the basis of the detailed process descriptions provided by the other participating organisations. Moreover, the plant and transport costs were to be actualised to the operational start-up date of the plant utilising the "Present Worth" method, finally yielding a cost per unit volume of primary waste treated. The costing of the waste disposal itself does not form part of the study.

During the second phase of the work, TASK R&S and KAH scaled the costs for plant capacities ranging from 6 to 60 GW(e).

B. Work programme

2.1. Scope of the programme
2.2. Cost evaluation
    2.2.1. Management options to be costed (provisional)
    2.2.2. Cost assessment procedure
    2.2.3. Results
    2.2.4. Cost scaling

C. Progress of work and obtained results

State of advancement

TASK R&S and KAH performed the cost evaluation of the various management options for Zircaloy hulls. For this purpose, general procedures were established for the cost assessment and cost scaling of the envisaged management schemes.

These procedures were implemented on the six management routes.

2.2.1. Management option to be costed

The engineering and process development of the basic management routes were elaborated by the other partners of the joint strategy study. They regard the following routes:

- Route ZH1 (CEA/CEN Valrhô):
  direct cementation/packaging/interim storage
- Route ZH2 (CEA/CEN Valrhô):
  melting in cold crucible/packaging/interim storage
- Route ZH3 (SCK/CEN):
  compaction/packaging into lead lined containers/interim storage

- Route ZH4 (SCK/CEN):
  hull decontamination/cementation/packaging/interim storage
- Route ZH5 (NUKEM):
  compaction/cementation/packaging/interim storage
- Route ZH6 (NUKEM):
  compaction/embedding in graphite/packaging/interim storage

2.2.2. Cost assessment procedure

For the cost assessment of the various management options a number of cost elements have been defined, which are utilised to determine the overall plant cost. Several assumptions concerning the plant siting and process technology have been established. Using this framework, the capital cost in 1988 is derived from the material cost of the Major Equipment or "Base Value"; all the other capital cost elements, except the Civil Works, are expressed as a fraction of this Base Value. For the operating cost the annual consumption of Process Materials, Utilities and Maintenance Materials and the costs associated with the Direct Labour and Overheads are taken into account to obtain the annual cost of the different cost elements in 1988.

Both the capital and annual operating costs are actualised to the start-up date of the plant using the "Present Worth" method. Finally, the actualised values are converted into an annual cost per unit volume of waste treated by employing the "Annual Value" method.

To evaluate the capital and annual operating costs related to the transport of the treated Zircaloy hulls, the type and amount of transport casks and the transport distance were defined in collaboration with the other participating organisations. On the basis of this data, the transport costs in 1988 by rail are elaborated. Subsequently, they are actualised employing the cost assessment procedure and transformed into an annual cost per unit of volume of waste treated.

2.2.3. Result

The cost assessment procedure was applied to all management routes. The costing of routes ZH1 and ZH2 is based on the costs provided by CEA/CEN Valrhô, whereas that of the remaining routes has been derived by TASK R&S - KAH from the engineering data provided by SCK/CEN and NUKEM. The results thus obtained are shown in Table I The national practice for the type of cases was adopted for this study. The results are given in Table II. The transport cost contributes to a large extent to the overall plant cost.

2.2.4. Cost scaling

A general procedure has been developed to scale the costs with changing plant capacity. It is based on the "six-tenths rule" and derived formulas available in the literature, which are normally applied in the chemical industry. The have been adapted for the present study. This procedure takes into account the different behaviour of the various cost elements, thus reducing the associated error. The scaling can be carried out within the range of normal power production (6-60 GW(e)), utilising the data obtained for 20 GW(e) as reference.

Table I

Actualised capital and annual operating costs together with the corresponding total plant cost for 30 years of operation and annual cost per unit volume of waste treated for the six Zircaloy hulls management routes. The costs do not include the transport of the treated waste.
Actualisation data: 01.01.91

ROUTE	ACTUALISED CAPITAL COST (MECU)	ACTUALISED ANNUAL OPERATING COST (MECU a^{-1})	TOTAL PLANT COST FOR 30 YEARS OF OPERATION (MECU)	ANNUAL COST PER UNIT VOLUME (MECU $a.m^3$)
Route ZH1	25.364	2.130	54.782	26.400
Route ZH2	32.669	3.288	78.080	37.600
Route ZH3	31.114	1.411	50.601	24.400
Route ZH4	22.818	1.614	45.109	21.800
Route ZH5	21.947	1.279	36.611	17.700
Route ZH6	24.740	6.452	113.849	51.000

Table II

Actualised capital and annual operating costs together with the corresponding total transport cost for 30 years of operation and annual cost per unit volume of waste treated for the six Zircaloy hulls routes.
Actualisation date: 01.01.91

ROUTE	ACTUALISED CAPITAL COST (MECU)	ACTUALISED ANNUAL OPERATING COST (MECU a^{-1})	TOTAL TRANSPORT COST FOR 30 a OF OPERATION (MECU)	ANNUAL COST PER UNIT VOLUME (ECU/($a.m^3$)
Route ZH1	3.536	7.402	105.766	50.900
Route ZH2	0.884	1.544	22.208	10.700
Route ZH3	0.000	5.209	71.941	34.700
Route ZH4	3.536	7.595	108.431	52.300
Route ZH5	2.316	1.675	25.450	11.400
Route ZH6	3.088	2.265	34.370	15.400

COMPARISON OF WASTE MANAGEMENT ASPECTS IN DIRECT DISPOSAL OF SPENT FUEL AND REPROCESSSING

Contractor : CEN Fontenay-aux-Roses, CEA, France
Contract No. : FI1W/0134
Working period : January 1987 - December 1989
Period covered : January 1989 - December 1989
Project leader : J. Malherbe

A. Objectives and scope

The overall aim of the whole joint project is to compare, on the basis of the costs and radiological impact of the management and disposal of all the associated wastes, reprocessing of Light Water Reactor fuel with its direct disposal by emplacement in a deep geological formation on land. Three main management routes are considered:

- immediate reprocessing of spent fuel after 3 years of cooling in ponds;
- no reprocessing: immediate disposal after short cooling time and possibly rod consolidation;

In the part of the project covered by this study, the aim is to compare immediate reprocessing and delayed reprocessing.

B. Work programme

The quantity of fuel to be considered will be that arising in a hypothetical 20 GW(e) reactor park consisting of PWRs, over a period of 30 years. The fuel is to be reprocessed either after a short cooling time, or after an interim storage time up to 50 years in a plant whith a 600 MTHM/year capacity. The CEA study will only deal with the reprocessing option. The main items of the programme are as follows:

2.2. Data base and waste inventory:
The 20 GWe nuclear park is assumed to consist of standard PWR reactors, the burn up of the fuel being 33,00 MWd/MTHM.

2.3. Extended storage:
This part takes into account two successive steps: the first one is the storage at reactor (AR) and the second one is a centralised storage (AFR = away from reactor).

2.4. Liquid waste treatment scenarios:
The inventories of reprocessing waste products will be determined taking into account the site characteristics (discharge limits) and the waste treatment scheme selected.

2.5. Final disposal:
Following the main scenarios, the conditioned waste arisings are classified in:

- LLW for which the final storage is in shallow land burial;
- MLW, which will be disposed of in geological formations;
- HLW, which will be disposed of in geological formations after a cooling time of some years up to 50 years.

2.6. Transport:
The casks for transport of the conditioned wastes are those in use by COGEMA.

2.7. Cost evaluation:
The cost data concerning the different scenarios will be composed of costs from existing facilities or estimated costs from various projects.

2.8. Radiological impact:
The radiological impact to the public will be assessed in accordance with the methodology developed by CEA/IPSN.

2.9. Sensitivity studies
These will deal with variation of burn up (up to 45,000 MWd/t), variation of the size of the nuclear park, treatment of MOX fuels, variation of the disposal criteria and discharge limits (coastal and inland sites) and type of packaging.

C. Progress report and obtained results state of advancement

Main parts of this study were performed in 1988 such as collection of the data base, extended storage, transport and sensitivity studies. In 1989, all other parts were performed, including final disposal, cost evaluation and radiological impact assessment.
The study is completed and the final report is being prepared.

Programme and results

2.2. Data base and waste inventory
This chapter was completed and reported in the 1988 Annual Progress Report.

2.3. Extended storage
Description of several types of fuel interim storage was reported in the 1988 Annual Progress Report. Complementary information has been given on the investment and operating cost of these installations.

2.4. Liquid waste treatment scenarios
The characteristics of effluents from liquid waste treatment were given for this data base and for extended storage assessment.

2.5. Final disposal
A description of final disposal of reprocessing waste has led to an estimation of the costs of main installations. Investment and operating costs have been evaluated. Low level reprocessing waste is disposed of by near Surface Disposal, which is used also for reactor waste. This installation was costed in the frame of the study of Reactor Waste Disposal.

2.6. Transport
This part was reported in the 1988 Annual Progress Report. Information has been added on cost estimation of transport of the whole reprocessing waste.

2.7. Cost evaluation
An estimation of all steps in the management of reprocessing waste, transport, interim storage and final disposal has been made.

2.8. Radiological impact
Impact of reprocessing waste disposal has been evaluated for low level waste or medium and high level waste. The peak dose for high level waste disposal is due to Np-237 and has been evaluated a 1 micro Sv/year. The maximum appears at 3.10^6 years.

COMPARISON OF WASTE MANAGEMENT ASPECTS OF DIRECT DISPOSAL OF SPENT FUEL AND REPROCESSING

Contractor: National Radiological Protection Board, Chilton, UK
Contract No: FI1W-0129
Working period: November 1987 - April 1990
Period covered: January 1989 - December 1989
Project Leaders: M D Hill, S F Mobbs (NRPB), and R Dodds (BNFL)

A. OBJECTIVES AND SCOPE

The overall aim of the whole joint project is to compare, on the basis of the costs and radiological impact of the management and disposal of all the associated wastes, reprocessing of PWR fuel with its direct disposal by emplacement in a deep geological formation on land. For the reprocessing case, the wastes to be considered include gaseous and liquid effluents discharged routinely during reprocessing, solid low and intermediate level wastes arising at the reprocessing plant, and vitrified high level waste. The latter will also be assumed to be disposed of by emplacement in a deep geological formation. The study will include an analysis of the sensitivity of the results to variations in key assumptions, such as the time for which spent fuel is stored prior to reprocessing.

Radionuclide inventories will be provided for all the wastes arising from reprocessing, and estimates will be made of the costs of management and disposal of these wastes based on UK experience and studies. Vitrified high level waste will be assumed to be emplaced in a granite formation and solid low and intermediate level wastes in an intermediate depth repository in a clay formation. The radiological impact on the public of the management and disposal of all reprocessing wastes, and of direct disposal of spent fuel in a granite formation, will be assessed. The cost of direct disposal of spent fuel in a granite formation will also be estimated.

B. WORK PROGRAMME

B.1 Agreement of detailed study assumptions with CEC and other contractors: NRPB and BNFL.

B.2 Provision of inventory data for discharges and solid wastes: BNFL.

B.3 Estimation of costs for effluent treatment, vitrification, packaging, storage, transport and disposal: BNFL.

B.4 Assessment of operational radiological impact on workers and the public: NRPB.

B.5 Assessment of post disposal radiological impact on the public: NRPB.

B.6 Sensitivity studies: NRPB and BNFL.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Work on item B.1 was completed during the last reporting period. Work on items B.2 and B.4 is now complete, and that on item B.5 is almost finished. The radiological impacts of routine discharges of liquid effluents during reprocessing, shallow land burial of low level solid wastes, and deep geological disposal of intermediate level solid wastes, vitrified high level reprocessing wastes and spent fuel have been calculated. Work on item B.3 is in progress. The contract was extended for four months and now finishes at the end of April 1990.

Progress and results

B.2 Provision of inventory data for discharges and solid wastes

BNFL has compiled the inventory data for liquid and atmospheric discharges and for all the solid wastes. The radionuclide inventories have been checked for consistency with those produced by CEA under another contract associated with this project.

B.3 Estimation of costs for effluent treatment, vitrification, packaging, storage, transport and disposal

BNFL is compiling the cost estimates.

B.4 Assessment of operational radiological impact

The calculations previously carried out for operational impact of unit discharges of radionuclides in liquid effluents have been scaled by the BNFL inventory for each radionuclide, assuming discharges occur over 30 years. The peak individual doses for the two sites considered, Cape de la Hague and Sellafield, were practically identical except for ^{95}Zr and ^{60}Co, as in the previous calculations, because the same critical group habits are assumed. The integrated collective doses from the two sites varied as a result of the different seafood catch sizes close to the two sites.

B.5 Assessment of post disposal radiological impact

NRPB have calculated the radiological impact of disposal of low level, intermediate level and vitrified high level waste arising from the reprocessing of spent fuel and of direct disposal of spent fuel without reprocessing, using the BNFL inventory data.

The low level waste was assumed to be buried within trenches at Drigg and the calculations were based on a previous assessment of the Drigg site[1], but used an updated BIOS code[2] for the biosphere modelling, with a revised database for seafood consumption. The intermediate level waste disposal assessment was based on a hypothetical deep repository located in the clay formations under Harwell, and closely followed the assessment carried out by UK contractors for the PACOMA project[3]. The vitrified high level waste and spent fuel disposal assessments were based on a hypothetical repository in granite, as in the PAGIS project[4]. In all the solid waste disposal impact calculations both radionuclide release and migration with groundwater, and inadvertent human intrusion into disposal sites, were considered. The results of the calculations are summarised in Tables 1 and 2.

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[2] LAWSON, G and SMITH, G M, BIOS: A model to predict radionuclide transfer and doses to man following releases from geological repositories for radioactive wastes. NRPB-R169, Chilton (1985). (London, HMSO).

[3] NRPB, EWE, AEA (Harwell) and Principia Mechanica, PACOMA - UK assessment of disposal in a clay formation (EUR report in preparation).

[4] VAN KOTE, F et al, PAGIS, Enfouissement dans les formations granitiques. EUR 11777 (1988).

Table 1 - Maximum Annual Individual Risks from Solid Waste Disposal

Waste Type		Individual Risk (y^{-1})	Time after Disposal (y)
LLW	migration	$1\ 10^{-8}$	$4\ 10^{4}$
	intrusion	$3\ 10^{-6}$	800
ILW	migration	$1\ 10^{-11}$	$3\ 10^{4}$
	intrusion	$5\ 10^{-6}$	100
HLW	migration	$2\ 10^{-9}$	$4\ 10^{5}$
	intrusion	$1\ 10^{-8}$	100
Spent	migration	$2\ 10^{-7}$	$4\ 10^{5}$
Fuel	intrusion	$2\ 10^{-7}$	100

Notes

1. Risks are those of contracting fatal cancer.
2. Migration risks are per GW(e) y, intrusion risks are per repository.

Table 2 - EC and World Collective Doses (man Sv) from Solid Waste Disposal

	Integration Time (y)				
	100	10^3	10^4	10^6	10^8
EC Collective Dose					
LLW	0	0	0	200	200
ILW	0	0	0.02	0.1	3
HLW	0	0	0	200	700
Spent Fuel	0	0	0	8000	$2\ 10^4$
World Collective Dose					
LLW	0	0	0	200	200
ILW	0	0	0.7	2	30
HLW	0	0	0	200	700
Spent Fuel	0	0	0	8000	$2\ 10^4$

Notes

1. Results are per GW(e) y.
2. Collective doses less than 0.01 man Sv are reported as zero.

COMPARISON OF WASTE MANAGEMENT ASPECTS OF DIRECT DISPOSAL OF SPENT FUEL AND REPROCESSING

Contractor : NUKEM GmbH, Alzenau, FRG
Contract No. : FI1W/0138
Duration of contract : August 1987 - November 1989
Period covered : January 1989 - November 1989
Project leaders : O. Mehling, H.J. Wingender

A. Objectives and scope

The overall aim of the whole joint project is to compare, on the basis of the costs and radiological impact of the management and disposal of all the associated wastes, reprocessing of Light Water Reactor fuel with its direct disposal by emplacement in a deep geological formation on land. The study includes an alalysis of the sensitivity of the results to variations in key assumptions, such as the time for which spent fuel is stored prior to reprocessing. The study follows the main basic scenario and its variations, as specified for the joint study (20 GWe reactor park consisting of PWRs, etc., ...).

This part of the joint project covers the direct disposal part of the comparison and mainly investigates following areas:

- spent fuel storage in engineered structures with 3 options of preconditioning ((i) disassembled elements preconditioned according to the NUKEM/DWK-PAE process; (ii) disassembled elements preconditioned according to the DWK-process; (iii) disassembled fuel elements, rods cut and preconditioned according to the DWK-process;
- conditioning for final disposal in a salt dome repository;
- disposal of low and intermediate level wastes in the Konrad mine (including radiological consequences and criteria).

B. Work programme

2.2. Spent fuel storage and preconditioning
  a. evaluation of the basic data;
  b. determination of the storage phase prior to the preconditioning;
  c. determination of the preconditioning process (3 options);
  d. determination of the interim storage phase after preconditioning.

2.3. Conditioning for final disposal
  - process flow and handling schemes, building structure, equipment, staff, media supply, secondary wastes characteristics;
  - costs of building, equipment and operation;
  - safety parameters (according to 2.2.c.).

2.4. Disposal of LLW and MLW
  - comparison of waste characteristics with Konrad acceptance criteria;
  - mine structure and handling scheme, equipment, staff, material supply;
  - safety parameters (occupational exposure, effluents, incidents, long term safety.

C. Progress of work and obtained results

State of advancement

In a supplementary work programme item 2.3. and item 2.4. were examined and evaluated in a more detailed way.
The study has been completed according to the time schedule. The final report has been supplied to the Commission.

Progress and results

2.2. Spent fuel storage and preconditioning

The areas covered are : a first interim storage phase of spent fuel, three options of preconditioning processes, and a second interim storage phase.
No substantial difference in secondary waste arisings for each of the three conditioning options were found. Options 3, which involves size reduction of the fuel rods by cutting resulted in a larger annual aerial effluent discharge than options 1 and 2. Potential incidents and consequences as a result of operations were also found to be similar for the three conditioning options. The total annual radiological exposure of personnel does not vary significantly for each of the three conditioning options.
Due to the significantly larger storage requirements (second interim storage) for conditioning option 1 and 2 the capital cost of the conditioning plant were found to be ca. 15% higher than for conditioning option 3. Option 3 involves higher operating costs than options 1 and 2 but the plant is in operation for a shorter period. The capital costs include a supplement for the costs for subsequent decommissioning of the plant.
Total transport costs and dose commitments were not found to vary significantly for options 1 to 3.

2.3. Conditioning for final disposal

Final conditioning of spent fuel for disposal in a salt dome was examined. Two forms of salt dome respository were considered; the difference relates to the storage method used: storage in drifts for the FDC's (FDC = final disposal container) produced by conditioning options 1 and 2, and storage in bore holes for the FDC's produced by conditioning option 3. The underground space requirements were not found to vary significantly for the three options. Handling schemes for the two options do however vary. For option 3 the FDC's require the use of a shielding flask for transport to the final disposal position whereas for options 1 and 2 shielding is provided by the robust FDC itself.
Due to the preliminary layout of the repository, it was not possible to derive detailed costs for the two alternative repository forms or conditioning options.
Dose commitments, effluent discharges and potential incidents were not found to vary significantly for the various conditioning options/salt dome repository types.
Due to the uncertainty in the cost estimates, in particular the disposal cost estimates, the variation between the three conditioning options examined is not considered as being significant. The specific costs for the direct disposal strategy considered are estimated to be around 700 ECU/kg HM (basis 1988).

2.4. Disposal of LLW and MLW

The secondary waste arisings from the conditioning plant were similar for each of the conditioning options and consequently the corresponding disposal costs and safety parameters were of a similar nature. The activity levels of the secondary wastes were well within current preliminary waste acceptance criteria. With the application of a 23 year cooling period for the 400-l drums containing the fuel element end pieces and structural parts, it was found that these wastes would also meet the current acceptance criteria.

COMPARISON OF WASTE MANAGEMENT ASPECTS OF DIRECT DISPOSAL OF SPENT FUEL AND REPROCESSING

Contractor	:	YARD Ltd
Contract No	:	FI1W/0133
Duration of Contract	:	September 1987 to March 1989
Period covered	:	January 1989 to December 1989
Project Leader	:	K A Ware

A. Objectives and Scope

In comparing waste management aspects of direct disposal of spent fuel and reprocessing, a number of radiological and environmental impacts have to be taken into consideration. To assist in performing this comparison, computer models are invaluable for combining and structuring the data and presenting the trade-offs involved in optimisation of various factors.

As part of the work to be undertaken a computer model will be developed which will allow the trade-offs involved in direct disposal of spent fuel and reprocessing to be investigated. The processes that will be taken into account in the model will include storage, transport, conditioning for direct disposal, reprocessing and disposal. The costs and environmental impacts from these processes will be combined through a multi-attribute hierarchy by applying weights to the impacts. The model will allow sensitivity analysis to be performed on these weights and on other parameters such as the time for which spent fuel is stored prior to reprocessing.

The goals of the project are:

- To evaluate the radiological and economic impacts associated with direct disposal and reprocessing of spent fuel. This task will be carried out in conjunction with other contractors.
- To develop a model for investigating the trade-offs between the radiological and economic impacts.

B. Work Programme

B.1 Evaluation of radiological and economic impacts.

B.2 Development of a model for investigating trade-offs.

C. Progress of Work and Obtained Results

State of advancement

A model to assist with the comparison of waste management aspects of direct disposal of spent fuel and reprocessing has been developed. The model has been designed to allow the rapid comparison of different waste management scenarios for direct disposal and reprocessing. The model runs on IBM PCs and compatible machines. The model, documentation and user guide have been delivered to the CEC. The program of work for this contract is now complete.

Progress and results

A computer model of the waste management aspects of direct disposal and reprocessing of spent fuel has been developed. The model called CODDAR (Comparison Of Direct Disposal And Reprocessing) calculates the costs and environmental impacts from storage, processing (pre-conditioning and conditioning for direct disposal or reprocessing), transport and disposal. The options that are modelled are shown in the schematic diagrams in figures 1 and 2.

The model can be used to investigate the impacts of a waste management scenario. The inventory for the spent fuel and the unit costs and impacts for the waste management options being considered, are entered. The model will then calculate the total costs and impacts for the scenario. These costs and impacts are combined through the multi-attribute hierarchy shown in figure 3. The costs and impacts at each level of the hierarchy are weighted and summed to give the impact at the next higher level. The impact at the top of the hierarchy gives an overall measure of the impact of a direct disposal or reprocessing scenario.

Sensitivity analysis can be performed easily using the model. The effect of changes to the inventory and the waste management options can be investigated by defining a new input data set. The effects can be displayed graphically by producing histograms of the costs and collective doses. Reports can be produced which give a description of the data sets used in the scenario and a breakdown of the costs and impacts for the scenario.

The model has been developed around a database so that it can be easily updated in the future. New fields could be added to the database to record extra information if required. The model could also be updated to produce new graphs and reports.

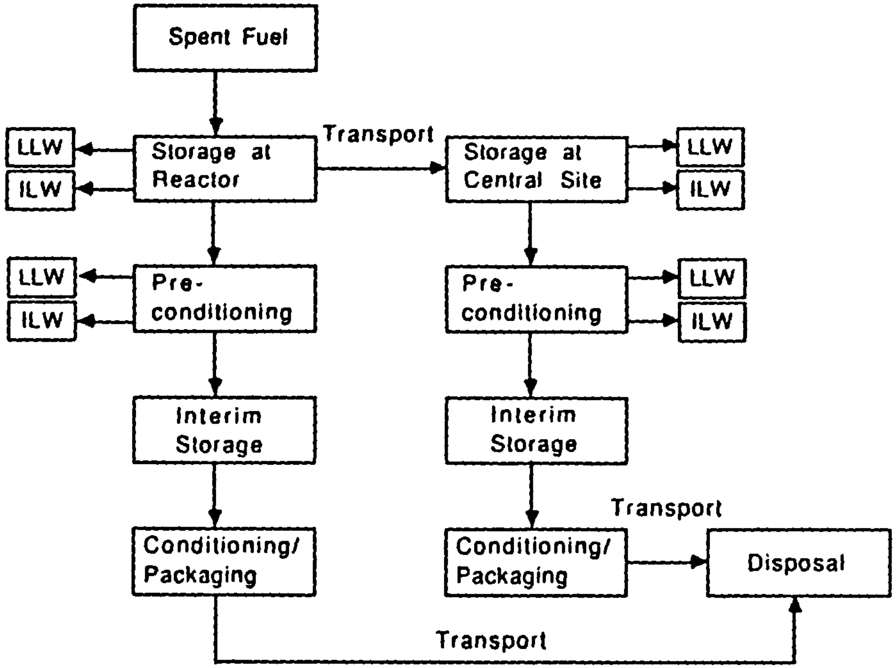

Figure 1 Schematic diagram of direct disposal options

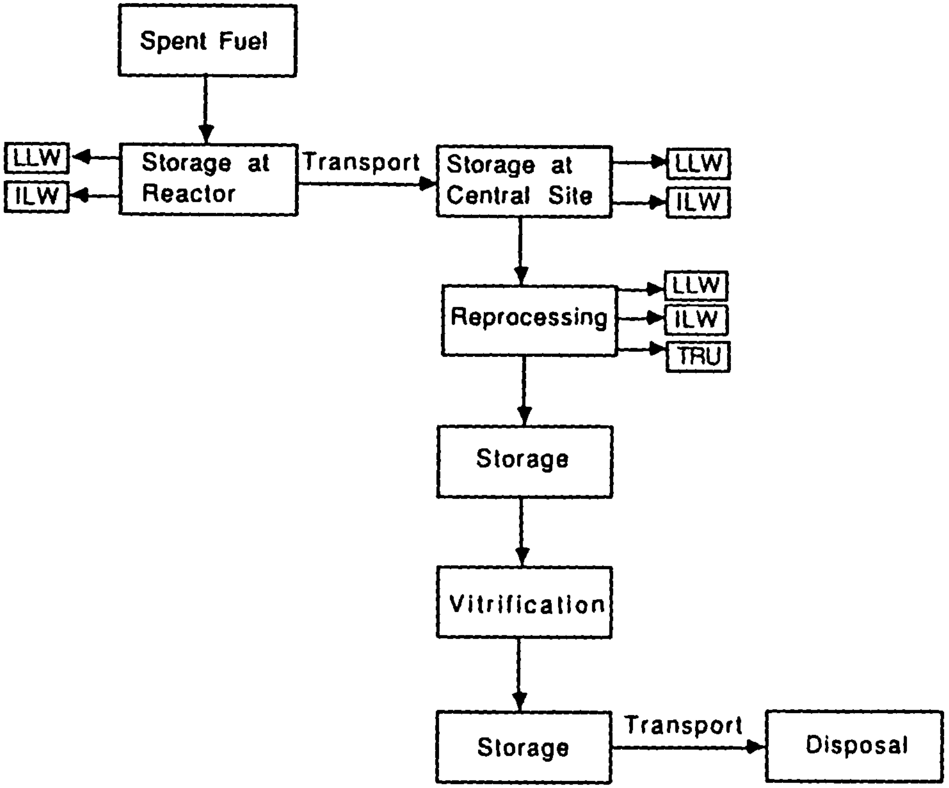

Figure 2 Schematic diagram of reprocessing options

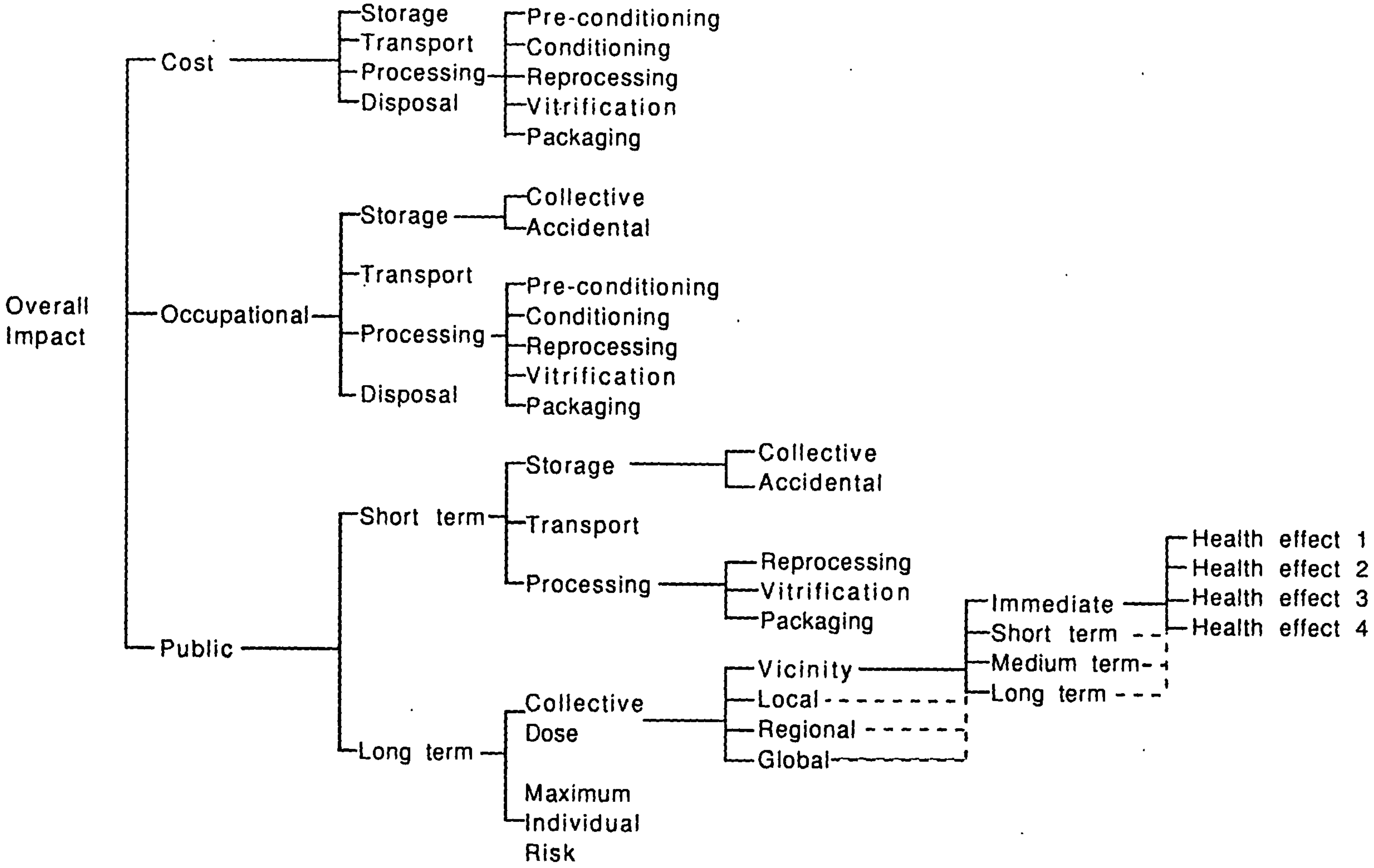

Figure 3 Multi-attribute hierarchy

DERIVATION OF WEIGHTING FACTORS FOR COST AND RADIOLOGICAL IMPACT FOR USE IN COMPARISON OF WASTE MANAGEMENT METHODS

Contractor: National Radiological Protection Board, Chilton, Didcot, UK
Contract No. : FI1W-0128
Duration of contract : 1 August 1987 - 30 June 1990
Period covered : 1 January 1989 - 31 December 1989
Project leader : S.F. Mobbs

A. OBJECTIVES AND SCOPE

Methods of assessing the radiological impact of waste management options have reached the stage where it is possible to make detailed estimates of the doses and risks to workers and the public and, in principle, to quantify the uncertainties in these estimates. It is also possible to quantify the direct financial costs of waste management. However, much less progress has been made on devising ways of weighting financial costs, social costs and the various components of radiological impact so that comparisons can be made between alternative waste management options, on a rational and well-defined basis.

The objectives are to develop a methodology for devising weighting factors for the various components of radiological impact, financial costs and social costs of waste management methods and to demonstrate the methodology by applying it in an example comparison of waste management options.

The research is being carried out jointly by the National Radiological Protection Board (NRPB) and the University of Surrey Psychology Department, acting under sub-contract to NRPB.

B. WORK PROGRAMME

2.1 Identification of the components of financial costs and radiological impact for which weighting factors are to be devised.
2.2 Identification of types of social costs which need to be considered via investigation of the criteria used by experts and decision makers, and of public attitudes, and review of methods of taking these social costs into account.
2.3 Development of a method for deriving weighting factors for the components of financial cost, radiological impact and social cost, and demonstration of the method.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Stages 2.1 and 2.2 of the project were completed in the previous reporting period.

In respect of stage 2.3, three questionnaires have been developed. These are designed to obtain weighting factors for seven attributes relevant to decisions on waste management options. The questionnaires present technical information on the consequences of 12 different waste disposal options, and obtain the information on the weighting factors both by direct and indirect methods. A survey of about 700 people, representing a spread of public opinion (eg nuclear industry workers, general public) has been completed, using a combination of group sessions and individual interviews. The results from this survey are presently being analysed and a report on this work is in preparation. The weights derived from the survey will be used in an example comparison of waste management options.

Due to the time required to undertake the survey, the contract has been extended by 6 months to end on June 30th 1990.

Progress and Results

2.3 Development of the Methodology

In the previous reporting period seven attributes were identified for which it was hoped to obtain weighting factors, and the consequences of 12 waste disposal options (6 for reactor decommissioning wastes and 6 for vitrified high level waste) had been calculated. During this reporting period, questionnaires based on these attributes and the supporting technical information were developed and the full survey carried out.

In developing the questionnaires, it was decided to concentrate on psychological approaches and to examine several possible measurement methods. The results from the different methods could then be compared with one another, both within and across different samples of respondents (eg those employed in the nuclear industry compared with the general public). The types of variation in the measured weights which were considered most useful to assess included:

a) sample characteristics, including age and sex, industrial experience, 'green' membership, and pro-anti nuclear attitudes

b) experimental design (eg ordering of questions, level of information provided)

c) types of measure: conventional scales (0-9), direct relative weighting of attributes, and derived weights from disposal option preferences

In order to achieve this, three different forms of questionnaire were devised. The first ('option preferences') required respondents to indicate, directly, the acceptability of various waste disposal options on a scale of 0-20. To help them achieve this, they were given relevant information concerning the consequences (both radiological and monetary cost) of each of the disposal options. Values for the implied relative weights for each attribute may be obtained from the responses using regression analysis.

The second questionnaire ('direct weighting') required respondents to weight the seven attributes directly. To enable respondents to try out different weighting schemes, a metal clipboard with 21 magnetic counters was used; respondents could allocate as many counters as they liked (up to 21) to each attribute, and alter the spread between attributes until they were satisfied with the relative weightings.

The design of the first two questionnaires inevitably implied a complex and time-consuming task for participants. This was warranted because of the complexity of the issues involved and the fact that information from simpler 'opinion poll' designs already exists. However, the importance of sampling from the full range of views was also recognised, and therefore, the need to interview large numbers of respondents. This would not be possible using the first two questionnaires and so a third, more straightforward questionnaire was developed. This included questions concerning respondents' general attitudes as well as specific questions on the disposal options. It also enabled respondents to list factors, other than the seven identified in the study, which they considered important for decisions on waste disposal. Using this questionnaire, comparisons of sample characteristics could be made, and, in addition, the value of implied weights from this questionnaire could be compared with those obtained from the more complex questionnaires.

Following pilot studies, during which the questionnaires were amended, a full survey was carried out. Respondents were asked either to complete all three questionnaires, or just the third. For those completing the first two questionnaires, a record was kept of the order in which they were asked to complete them. In addition, some respondents were told what each disposal option was, whilst others were only provided with technical information on the consequences. The influence of these factors on the implied weights will be analysed.

A commercial company was contracted to interview 450 individuals (from a wide range of backgrounds) using the third questionnaire. The first two questionnaires (together with the third) were mainly administered to groups of individuals, selected from different sectors of society (eg nuclear industry workers, pressure groups, general public). About 240 respondents were obtained for these.

The questionnaires were met with a good response, and all respondents successfully completed them. The results of this survey are now being analysed. A report on this work is in preparation and will be avaliable by the end of the contract period.

ACCOUNTING METHOD FOR RADIATION DOSES DUE TO LONG-LIVED NATURAL RADIONUCLIDES AND DAUGHTERS

Contractor	: Dornier GmbH
Contract No.	: FI1W/0136
Duration of contract	: October 1987 - March 1989
Period covered	: January 1989 - March 1989
Project leader	: Armin-Dietmar Karpf

A. Objectives and scope

The study was aimed at developing a method to evaluate radiation doses occurring in the very far future from possible current fuel and waste management practices. This method is to be applied to facilitate decisions on different management schemes.

For the distant future it is justified to assume that the radioactive waste will have been mobilised and will have found many pathways to mankind. But only the most long-lived radionuclides can contribute to these pathways. This excludes most of the fission products with their shorter half-lives. The remaining long-lived ones, however, are far less in number than the natural radionuclides which have been discarded earlier in the course of the fuel cycle. Hence for the distant future the latter should also be taken into account when assessing future doses.

As no absolute scales exist for the effects of radioactivity to man, one always has to resort to a comparison with some natural source of radioactivity. In the present case the most related source would be the natural long-lived radionuclides in their original and undisturbed environment and their natural mobilisation by erosion and ground or surface waters.

Both the mobilisation of waste as well as that of natural radionuclides will result in a multitude of different pathways to man which all have to be considered if due account of all influences is required. Hence, this task cannot be solved with individual doses and one has to turn to collective ones.

B. Work programme

i. Assessment of natural scenarios: Abundance of natural radionuclides, mechanisms of deposition, mechanisms of mobilisation, pathways to population and collective doses, future development, validation.
ii. Assessment for use of natural radionuclides: Total needs, produced waste, fuel cycle scenarios, failure of repositories, hazards to population.
iii. Global comparison of natural and used uranium: Collective dose comparison.
iv. Time display of annual collective doses and comparison.

C. Progress and results

A method to evaluate radiation doses occurring in the very far future from current nuclear fuel production and waste management practices has been developed. The method may be applied to compare possible nuclear fuel and radioactive waste management schemes; here, it has been used mainly to evaluate the additional radiological impact from a global nuclear power production programme as compared to exposure to natural radionuclides in undisturbed formations.

The main results of this study are that the highest possible increase of the radiological impact of natural uranium and decay products through anthropogenic activity is around 1%. This additional impact is of the same order of magnitude as the non-uranium-related natural background exposure.

The final report is available as report EUR 12509 from the Office of Official Publications of the EC at Luxembourg.

TASK No 2

IMPROVEMENT OF RADIOACTIVE WASTE TREATMENT AND CONDITIONING TECHNOLOGIES

TASK N. 2

2.A. WASTE FROM LIGHT WATER REACTORS

IMMOBILISATION IN CEMENT OF ION EXCHANGE RESINS ARISING FROM THE PURIFICATION OF REAGENTS USED FOR DECONTAMINATION OF REACTOR CIRCUITS.

Contractor: UKAEA - AEE Winfrith, UK
Contract No: F1 1W 0006 UK(H)
Work Period: January 1989 - July 1989
Project Leaders: 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 Purolite C100, 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 Investigate the effects of decontamination reagent's components on cement hydration.
B.5 Investigate the effect of additives to improve the properties of the cemented product.
B.6 Examine the properties of active cemented ion exchange resin using the ISO leach test.
B.7 Establish waste volume reduction factors.
B.8 Compare and contrast methods used by other LWR Operators in Europe for decontamination of their reactor circuits and disposal of the solutions.
B.9 Establish a satisfactory process flow sheet for encapsulating ion exchange resins in cement.

C. STATE OF ACHIEVEMENT

Previous work has shown that Purolite C100 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 produced from a 9 to 1 blend of ground granulated Blast Furnace Slag (BFS) and Ordinary Portland Cement (OPC) containing 28% ion exchange resin in the water saturated form. If 6% Microsilica is added to the blended cement the waste loading can be increased to 36 w/o. Results obtained from testing small scale samples show that acceptable products can be produced. Recent work has shown that various types of anion resin have no adverse effect on the properties of the cemented waste.

This work has now been scaled up to show that 200 litre monoliths of cemented ion exchange resin (mixed anion and cation) can be produced. These samples exhibit acceptable compressive strengths and dimensional stabilities. Destructive examination has shown that these samples are homogeneous and monolithic. A number of samples have been stored under water, this appears to have no detrimental effect on the dimensional stability and elastic modulus of the product when compared to samples stored in air. Finally, leach test work has been initiated using waste ion exchange resin treated with LOMI from the reactor at Winfrith. This work has been performed in accordance with the ISO leach test procedure.

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 decontamination agent LOMI. Using a strong cation exchange resin like Purolite C100, most of the activation products, eg, ^{59}Fe, ^{51}Cr, ^{54}Mn, ^{65}Zn and ^{60}Co, plus the vanadium from the LOMI and some of the fission products ^{137}Cs and ^{90}Sr, can be removed from solution. Results also showed that some of the picolinate and formate from LOMI were also trapped in the resin.

DETERMINATION OF ION EXCHANGE RESIN LOADING

Previously reported data (1) expressed resin loading in terms of 'damp' resin containing 30 w/o free water. Damp resin loadings of 50% by weight were achieved. In this report, resin loadings are expressed as water-saturated material (no free water). In this case, 36 w/o water-saturated resin loading is equivalent to 50 w/o damp resin loading. The use of oven dried resin loading was considered to be unrealistic.

IMMOBILISATION OF ANION EXCHANGE RESIN IN CEMENT

Previous work has shown that cation exchange resin in the sodium form can be successfully immobilised in blended cement. The formulation derived for cation resins was used as a starting point for work on anion resin.

Two different anion resins were tested. Both were polystyrene polymer crosslinked with divinylbenzene, A400 containing the functional group - $(CH_3)_3N^+$, A200 containing the functional grout - $(CH_3)_2\ (C_2H_4OH)N^+$.

A number of small scale mixes were undertaken using a 9:1 blend of BFS and OPC with a waste loading of 36 w/o to examine the effect of anion resins on the compressive strength, dimensional stability and elastic modulus of the cement matrix.

All products appear to have satisfactory long-term properties with all the samples being intact with no sign of physical deterioration. Results of compressive strength and dimensional stability measurement show that there is little difference between cemented products containing anion or cation resin.

The conclusion of this work is that the inclusion of anion resin into cement does not appear to have any detrimental effect on the physical properties of the product.

IMMOBILISATION OF MIXED RESINS IN CEMENT, LARGE SCALE

If this process is to be used commercially it has to be demonstrated that the process can be scaled up to at least 200 litres. A scale of 200 litres was chosen for reasons of convenience and economics. At present 500 litre packages are the preferred size for disposal of intermediate level waste in the UK, with scale-up from 200 litre to 500 litre not expected to cause any problems.

Two 200 litre mixes (88/035 and 88/067) were prepared using the in-drum mixing technique by adding 109 kg BFS, 13 kg OPC and 7 kg microsilica to 105 kg of mixed ion exchange resin suspended in 65.4 kg of water (waste loading 36 w/o water-saturated resin). The powders were added to the resin at a rate of 15 kg/min with a paddle speed of 80 rpm.

Both mixes were set within 24 hours and produced no free water (bleed). Mix 88/035 was fitted with thermocouples and vibrating wire strain gauges to monitor the properties of the 200 litre block. The thermocouples showed a temperature rise from 18°C to 25°C over the first 36 hours followed by a slow return to room temperature. The vibrating wire strain gauges showed that the matrix expanded slightly over the first 2 days followed by a slight shrinkage. After 180 days the gauges showed an average shrinkage of 100 microstrain. This compares to a slight expansion of 80 microstrain observed for prisms cast from the mix. These results show that there is little significant dimensional movement in the first 180 days for these cemented ion exchange resin formulations.

Mix 88/067 was sectioned and cored after 90 days; sectioning showed that the mixing process produced a homogeneous product with no cracks. The cores produced were trimmed to standard length and crushed to determine compressive strength or tensile strength. The values obtained were in close agreement with those obtained for cast samples from the same mix. Further tests on samples up to 180 days have produced no evidence of sample deterioration (2).

UNDERWATER TESTING OF CEMENTED RESIN

Concern has been expressed about the stability of cemented ion exchange resin when stored underwater for long periods of time. To examine this effect the dimensional stability and elastic modulus of a number of samples stored underwater was periodically measured. When these results were compared to those obtained form samples stored in the normal way, no significant differences were observed.

ISO LEACH TESTING OF CEMENTED ION EXCHANGE RESIN

If the cementation of ion exchange resin is to be accepted as a suitable process for the long-term storage of radioactive waste, it must be possible to show that it impedes the flow of radioactivity into the biosphere. To demonstrate this, samples of ion exchange resin treated with LOMI solution from the reactor at Winfrith were immobilised in cement and leach tested.

Incremental leach rates were determined using the ISO method (3) on cemented ion exchange resin contaminated with spent LOMI from the reactor at Winfrith. As expected, incremental leach rates for ^{60}Co fell rapidly over the first 28 days from 5.53×10^{-4} to 2.68×10^{-6} cm d^{-1} for the sample with the highest waste loading; from 28 to 259 days only a slight decrease in the incremental leach rate was observed. This behaviour is expected as the sample reaches equilibrium with the leachant.

The determination of cumulative fraction of ^{60}Co leached (see Fig 1) indicates that approximately 0.2% of the total ^{60}Co present has leached out of the sample after 259 days. This demonstrates that most of the ^{60}Co is not easily removed by leaching.

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Immobilisation in Cement of Ion Exchange Resins arising from the Purification of Reagents used for the Decontamination of Reactor Circuits. Third Semestrial report, July - December 1987. AEEW - M 2513.

2. C. G. HOWARD, C. B. JOLLIFFE, D. J. LEE.
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3. Long-Term Testing of Solidified Radioactive Wasteforms, First Edition 1982. ISO 6961.

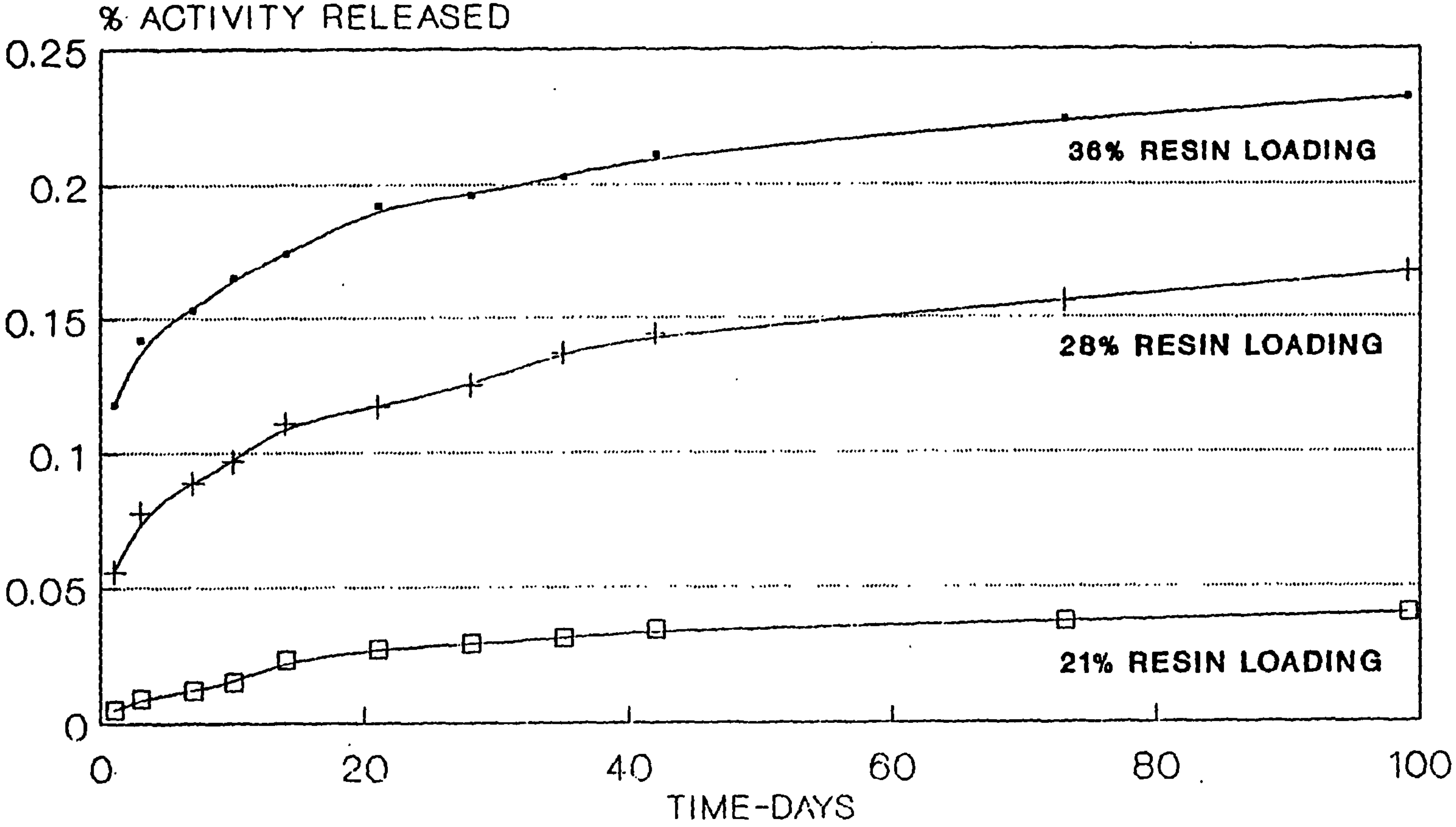


FIG. 1 CUMULATIVE Co-60 ACTIVITY LEACHED FROM CEMENTED RESIN

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 : 36 months (from June 1, 1986 to May 31, 1989)
Project leader : R. Roofthooft
Fourth annual report (1988) : period from January 1 to May 31, 1989

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 flocculation and settling system in the nuclear station of Chooz.

The centrifugation should lead to a more compact system. Before the centrifugation a batch type flocculator 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 Characterisation of the flocs.
B.4 Influence of chemical composition on the flocculation.
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

State of advancement

In the first semester of 1989 the study has been brought to an end by semi-industrial testing of the process developed in the previous years.

A comparison has also been made with other procedures developed by the UKAEA.

The second semester 1989 has been used for final reporting.

Progress and results

During the tests on the pilot plant different parameters have been examined :

- flow rate of the centrifuge
- concentration of polyelectrolyte
- effect of a delay line
- time between openings of the bowl
- quality of the supernatant between the openings
- opening and closing time of the bowl.

Turbidity measurements have been improved.

The tests have shown that the efficiency of the centrifuge (suspended solids and activity) is higher than 95 %.

The centrifuge should be operated at flow rates above 400 l/h to avoid deposits of suspended solids.

The time between 2 openings of the bowl is calculated by the formula :

$$T = \frac{V \times 6 \times 100}{Q \cdot C_{MS}}$$

V = volume of the bowl

Q = flow rate

C_{MS} = concentration of suspended solids

Normally the percentage of solids is measured by decantation. The tests have shown however that they can be measured by a lab centrifuge in a 2 minute test at 5400 rpm.

A polyelectrolyte has to be dosed to obtain good results (about 1 ppm is sufficient).

A delay line improves the decontamination factor.

The water quality decreases slightly after an opening of the bowl.

During continuous testing it has been shown that the injection of polyelectrolyte is essential for the efficiency of the system.

The sludge has also been measured from the point of view grain size. Fig. 1 and 2 show the results before and after centrifugation.

The activity distribution in the effluent before and after treatment is shown in fig. 3 and 4.

The balance of a treatment is shown in table I.

The results of comparative testing are shown in table II.

Table I : Summary of a treatment

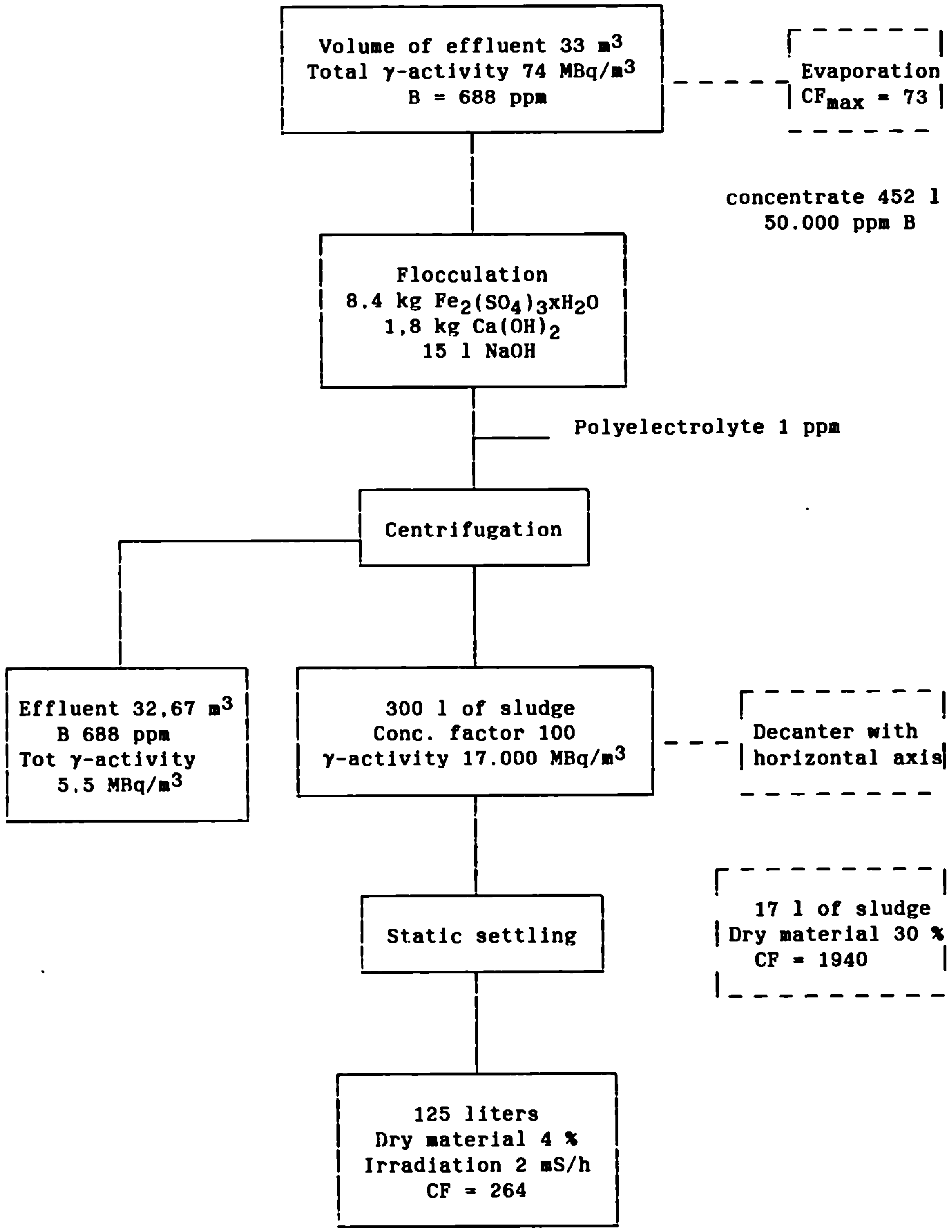


Table II : Comparison of different procedures
Results in MBq/m^3

Isotope	Effluent	UKAEA procedure precipitation + UF	UKAEA procedure EIX (1)	LE procedure centrifugation
^{58}Co	18,1	0,04 - 0,87		0.23
^{60}Co	24	0.018 - 0,2		0,06
^{54}Mn	2,8	0.0006 - 0,11		0,02
^{95}Nb	5,9			
^{65}Zn	0,6			
^{95}Zr	2,8			
^{134}Cs				0,02
^{137}Cs		0,023 - 0,044		0,04
^{131}I				0,03
^{40}K		0,14 - 0,34		0,18

(1) DF$_{max}$ on total γ activity 375
Detected isotopes are ^{58}Co, ^{60}Co, ^{54}Mn, ^{95}Nb, ^{65}Zn, ^{40}K

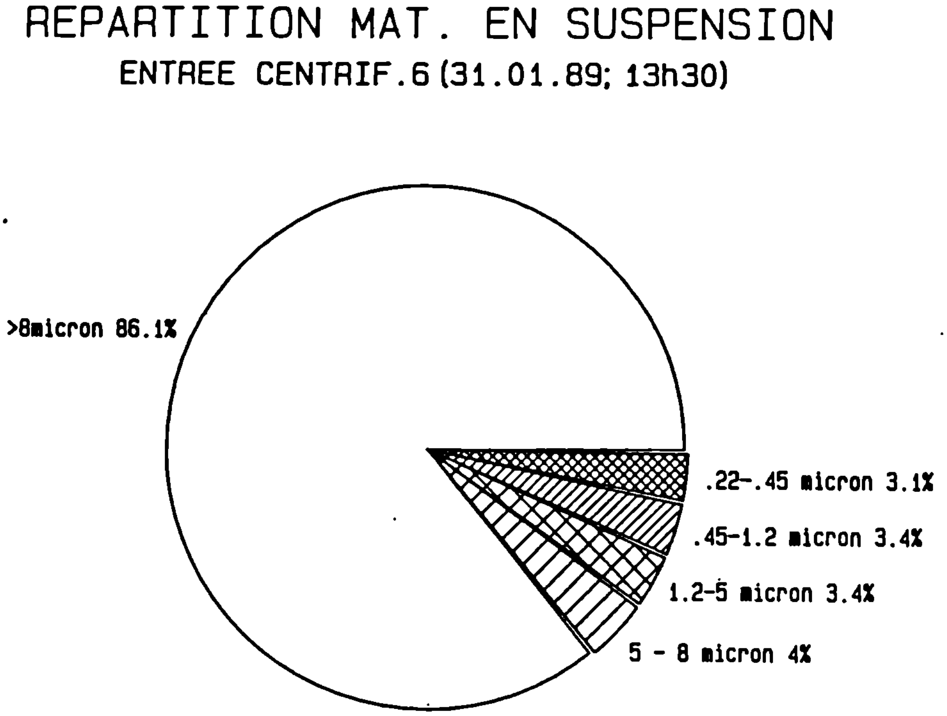


Figure 1

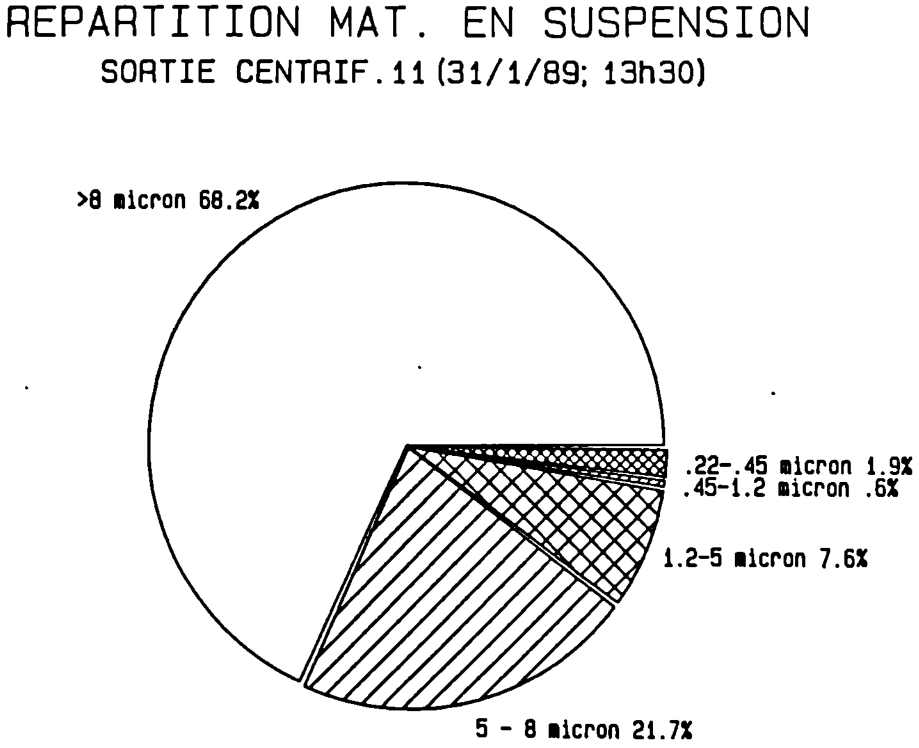


Figure 2

EFFLUENT A TRAITER

TEU B14 AVANT FLOCULATION

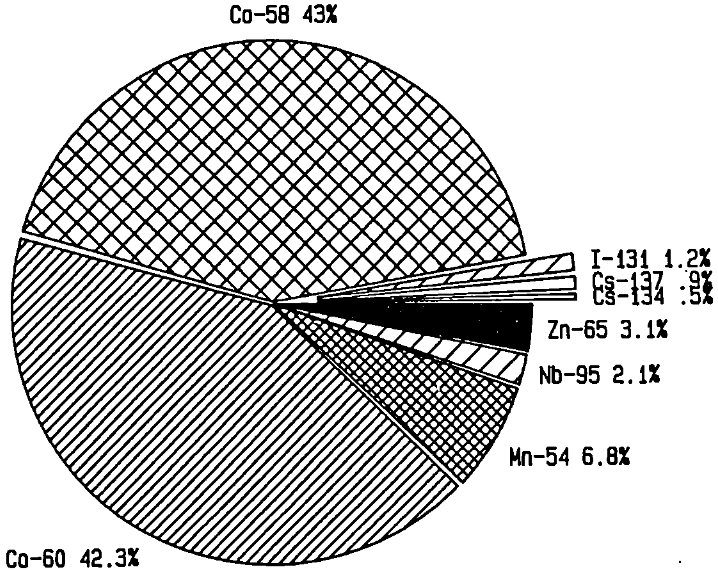


Figure 3

SORTIE CENTRIF.HYDROCOLL.5

REPARTITION DES ISOTOPES

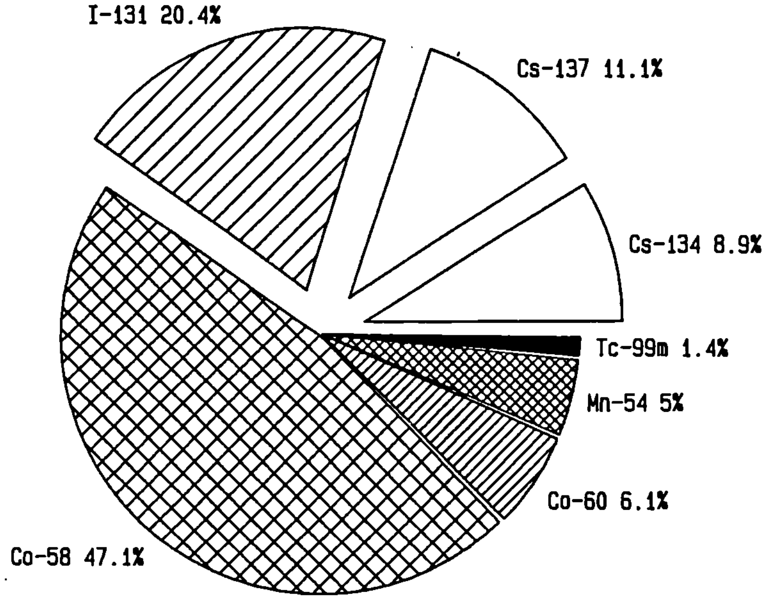


Figure 4

TITLE: "Cement solidification of spent ion-exchange resins arising at nuclear power plants".

Contractor: CIEMAT, Madrid, Spain.

Contract Nº: FI1W/0142.

Duration of contract: From September 87 December 89.

Period covered: January - 89 - December - 89

Project leader: S.J. Ortiz.

A. OBJETIVES AND SCOPE

The characteristics and performance of spent ion exchange resins are being studied, in order to decrease their swelling and the cracking of cement matrices where the ion exchange resins are incorporated.

A study of the selected ion exchange resins is being made to know their differences of size and performance in function of the nature of chemical species, saturation degree, etc. ....

Dewatering experiments of inactive ion exchange resins will be carried out using different techniques (vacuum filtration, pressure filtration, etc.) to evaluate the water content and its possible effect on the swelling.

The main objetives of this R+D project will be the study the ion exchange resins swelling and how to increase the loading of IX into cement matrices.

B. WORK PROGRAMME

B.1. Bibliografic review.

B.2. Identification of Spanish spent IX resins.

B.3. Dewatering experiments.

B.4. Properties of various resins-cement mixtures.

B.5. Interaction between cement and IX materials.

B.6. Freeze/thaw stability.

B.7. Leaching tests.

B.8. Encapsulation of inorganic ion exchangers (zeolites).

B.9. Full-scale tests.

C. PROGRESS OF WORK AND OBTAINED RESULTS

C.3. Dewatering experiments.

Hydration and dehydration tests of DUOLITE ARC 9351 resin have been realized with different techniques, vacuum filtration, pressure filtration, heating, adding hydrophobe substances and irradiation with microwaves. Also, hydrated and dehydrated resin have been add at the end of the cement immobilization tests to study the feasible influence of order mixture on the final samples.

C.4. Properties of various resins-cement mixtures.

Cement immobilization test with DUOLITE MB-200 powder resin have been realized. Virgin and saturated resin with Li_3BO_3 has been used. Water/cement 0,5 ratio and resin/cement 0,08 ratio have been studied.

Cement immobilization of powder resins gives worse results that bead resins V-35 and blast furnaces cements give good results for the immobilization of powder resins.

Two cements are been selected (P-350Y and blst furnace cement) for the immobilization of bead resins.

C.4.1. Compressive and flexion strength.

Ca^{++} solutions have been used to try improve water immersion stability of DUOLITE ARC 9351 satured with Li^+, when this resin is immobilizated with P-350Y cement.

C.4.2. Fluidizes adition.

Two new fluidizing agents (Sikament and Reoplast) have been studied to obtain samples with better characteristics and to increase the amount of immobilized resin.

2.4.3. Water immersion.

Test specimens obtained using V-35 cement and powder resin. P-350Y and blast furnace and bead resins were immersed 28 days in water after 28 days of curing time. Chemical compositions of water has been studied.

Figures 1 and 2 show compressive strength values for resins satured with several ion and the influence of water immersion on compressive strength for some kind of samples.

C.4.4. Hydration heats.

Hydration heats have been determined for mixtures of four cements and three resins with different water content:

C.6. Freeze/thaw stability.

Performance tests in function of thermal cycles have been realized with different mixtures of four cements of three resins used on this project.

C.7. Leaching tests.

Mixtures P-350Y and blast furnace cements with DUOLITE ARC-9351 resin saturated and labeled with Cs-137, Co-60 and Sr-90 have been studied. Figures 3 and 4 show the leaching tests of Cs-137 and Sr-90.

Also has been studied the leaching of mixtures V-35 and blast furnace cements with DUOLITE MB-200 resin satured and labeled with Cs-137, Co-60 and Sr-90.

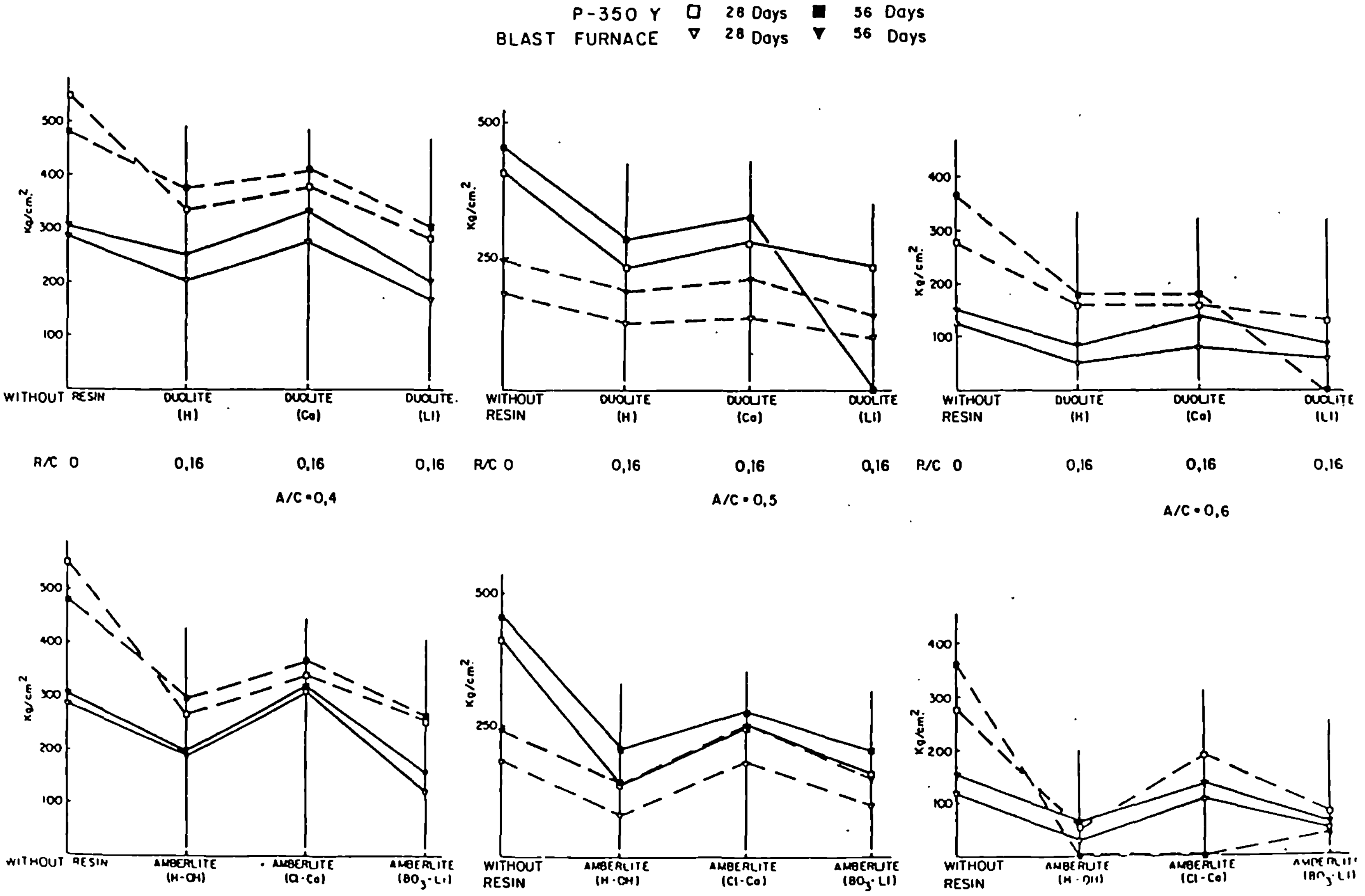


FIG. 1 - COMPRESSIVE STRENGTH DUOLITE ARC-9351 AND AMBERLITE IRN-150

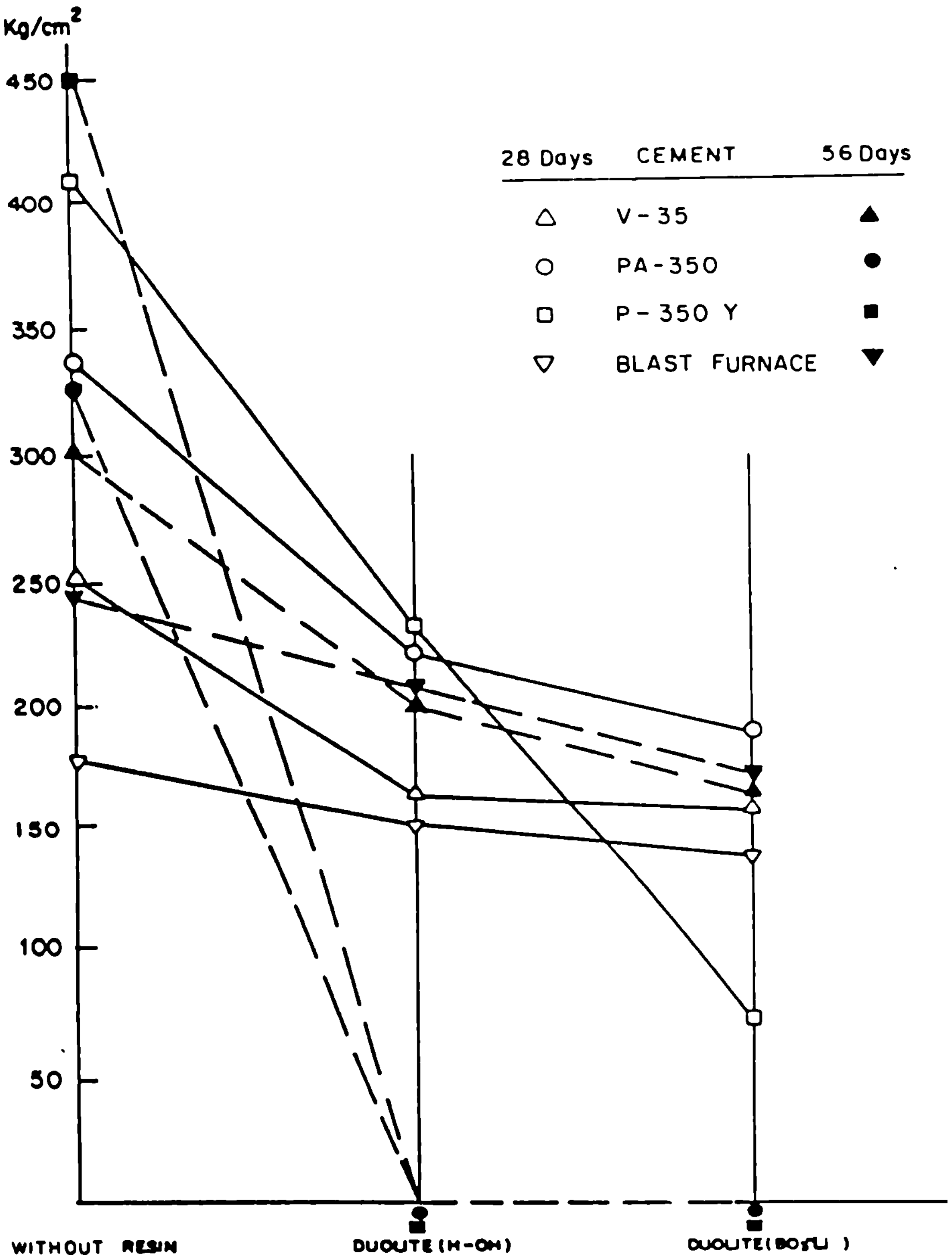


FIG. 2 .- COMPRESSIVE STRENGTH DUOLITE MB-200

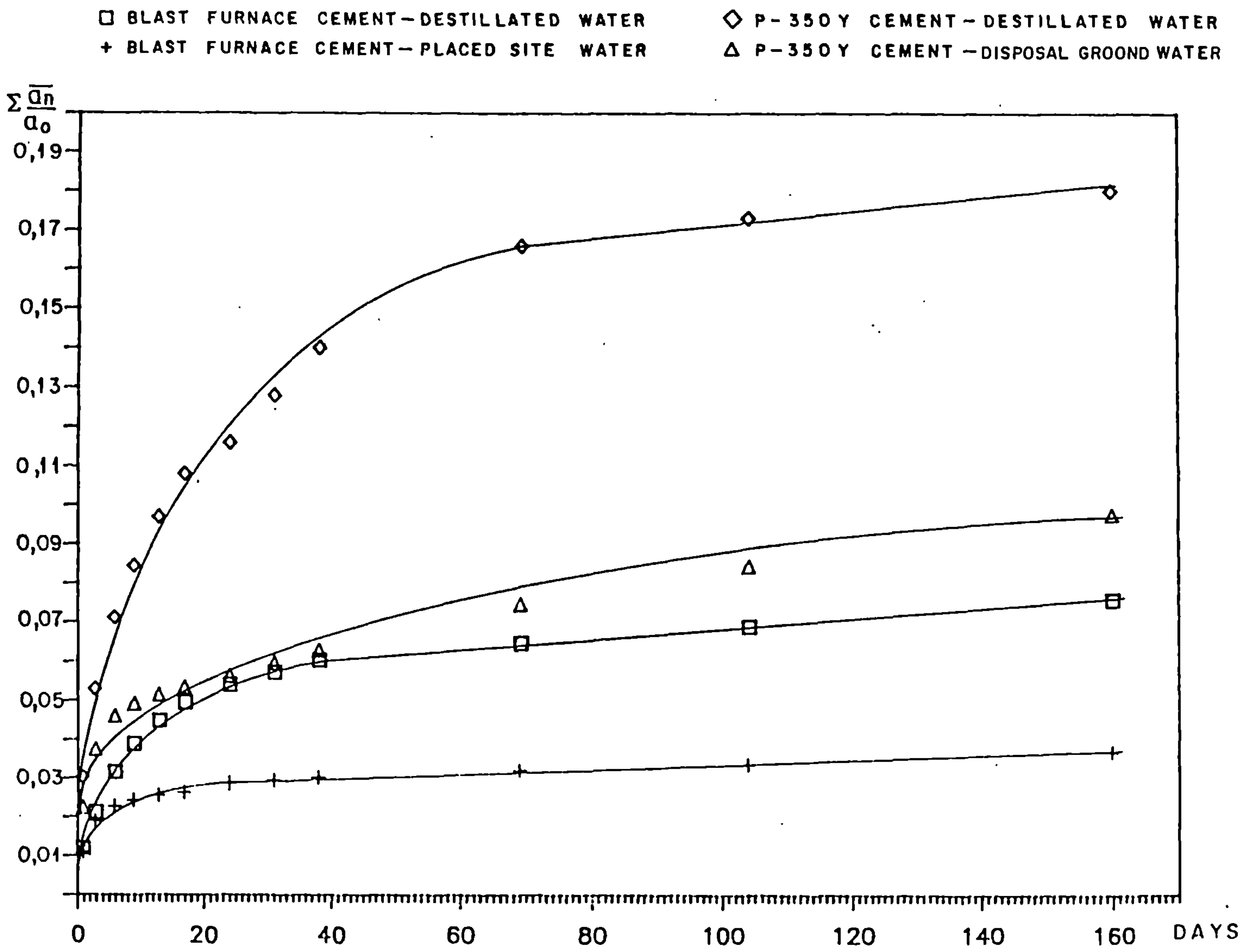


FIG. 3 – CUMULATIVE FRACTION Cs-137 LEACHED

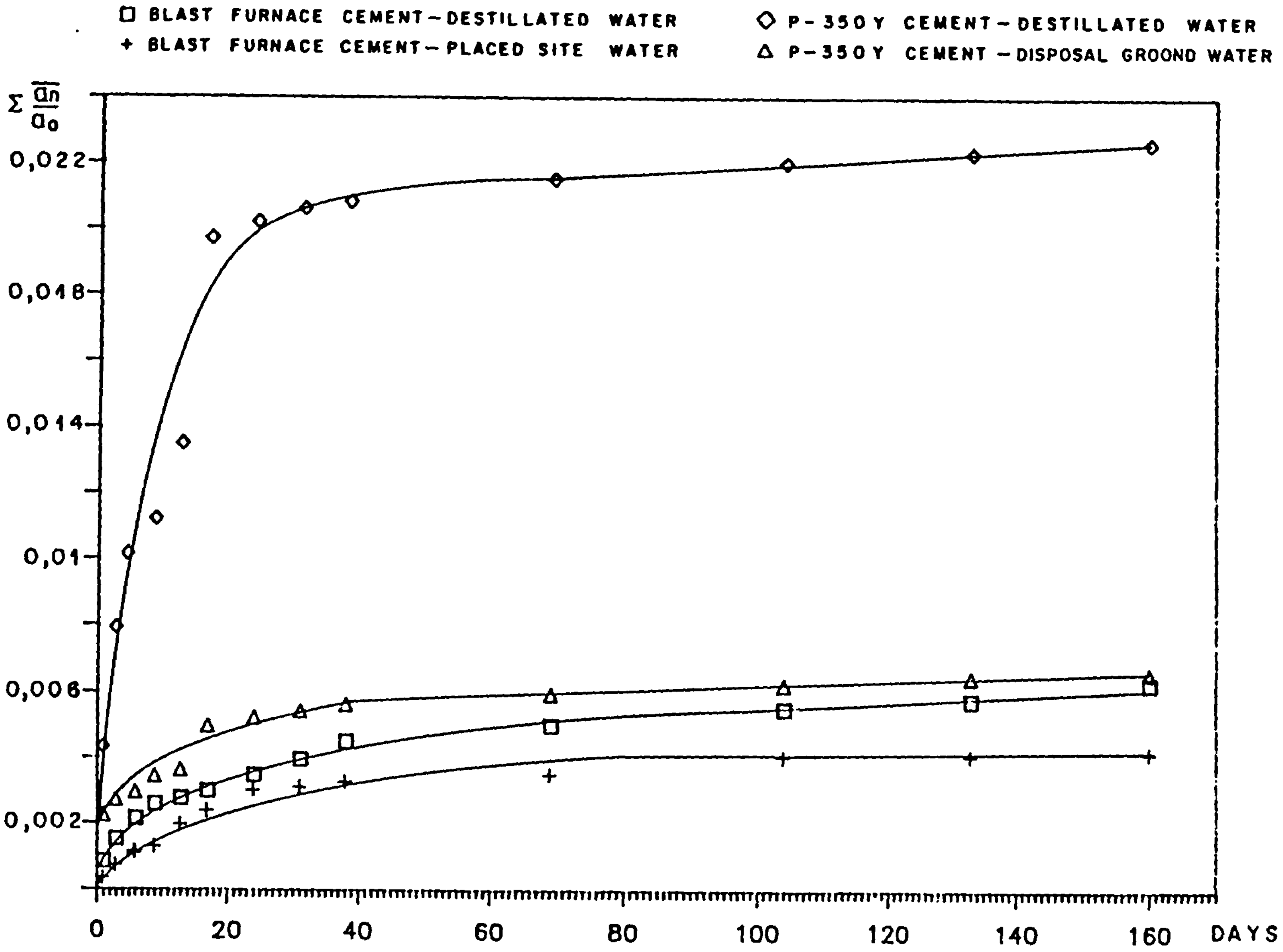


FIG. 4.- CUMULATIVE FRACTION Sr-90 LEACHED

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. - 31.12.89

Project leader : B. Ganser / R. Lang

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

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

2. Construction of a pilot plant

3. Laboratory experiments

- Testing of process parameters
- Characterisation of final products

4. Performance of full scale test

5. Documentation

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement:

Within the first half of 1989 we completed the work for our contract. The experiments with the LINN-furnace could be performed and the results were used for the technical conception of a "hot" facility.

For the completion of our work the results for the entire project are summarized as follows.

Progress and results:

In this project we developed a melting process for radioactive ashes. For this a literature survey was performed to define the state of the art of the melting technique and to get actual data about ash compositions. Based on this results the in-can-melting-process was elected for further development.

Based on the literature data of ash compostions inactive simulates were compiled and mixed. Additives for melting point reduction (net work formers and - transformers: $Na_2B_4O_7$, B_2O_3, Na_2CO_3, Na_3Po_4, glass frit) were systematically investigated. An addition of 50 % by weight of $Na_2B_4O_7$ (concerning ash weight) was found to be sufficient for the melting of all used simulates at 1000° C, only 30 % at 1300° C. Samples of these products were investigated for their leach resistance of waste elements (Cs, Co, Eu etc.) and matrix elements (B, Al). They showed similar low leach rates like vitrified HAW.

With two different melting furnaces full scale melting tests were performed. The Naber-furnace showed sufficient technical operation, but the products had partially unhomogeneous surfaces because of a significant temperature gradient. In the opposite the products of the LINN-furnace showed an excellent homogenity, but the technical function was unsufficient and susceptible. Some products created acid off gases during the melting. An alkaline particle deep bed filter was necessary. The homogeneous products showed leach rates like the lab products (D_e for B: E-17 up to E-19 m^2/s), compressive strenghts of 65 - 160 N/mm^2, porosities of < 0,2 Vol.% (vitrified products) respective 5 - 30 Vol.% (others).

Based on the experiments a concept for a "hot" facility was designed. A cost estimation showed for the melting process prices of about 19 DM/kg ash compared with 15 DM/kg ash for cementation and highforce compaction.

TASK N. 2

2.B. WASTE FROM REPROCESSING PLANTS PLUTONIUM FUEL FABRICATION PLANTS AND RESEARCH CENTRES

EVALUATION OF MATRICES FOR INCINERATOR ASHES

Contractor : CEA
Contract n° FI1W/0005
Duration of contract : from 01.06.89 to 30.06.90
Period covered : January 89 to December 89
Project leader : C.J. KERTESZ

A. OBJECTIVES AND SCOPE

In order to qualify a solidification process for α incinerator ashes coming from solid burnable wastes of a MOX fuel fabrication plant the embedding properties of three matrices have been checked. These matrices are :

1) A cement containing blast furnace slag and flying ashes.
2) An epoxide resin.
3) A polymer - cement compound.

The goals of the project are the following :

- definition and choice of the best α embedded waste form, for the obtention of a long term resistant α packaging according to the criteria defined by ANDRA, responsible in France of waste storage and disposal,

- study at the laboratory scale, giving the main characteristics of the different α incinerator embedded forms,

- conception, design and starting up of a pilot plant, allowing to make the transposition tests from the laboratory study to the industrial scale.

B. WORK PROGRAMME

Started in 86, the studies relative to our contract contain several steps :

1) Formulation study, at the laboratory scale. Determination of the feasibility field for ash embedding in a cement, in an epoxide, in a cement-polymer matrix. This work is made with non radioactive waste.

2) With real active α incinerator ashes, fabrication of 3 samples embedded in each considered matrix : 1 year leaching test, for plutonium release evaluation : sample scale 100 ml.

3) Fabrication of special samples containing a high α activity of ^{238}Pu : these samples were made with 2 objectives :

- an α radiolysis study, with radiolytic gas identification and measurement,

- a leaching test for the evaluation of the combined effect of water immersion and α radiolysis.

4) Confirmation of the behaviour of the best choosen embedded form : change of the sample volume (from 100 to 400 ml), fabrication of a serie of samples : Leaching test.

5) Starting up of a pilot plant, allowing the producing of 200 l incinerator ash embedded form.

For the considered period of time, i.e. from July 87 to June 88, point 3 and part of point 5 were reported.

C. PROGRESS OF WORK AND RESULTS

STATE OF ADVANCEMENT :

- Leaching test on α irradiated samples :

A 1 year leaching test has been done on 100 ml samples, doped with 238 plutonium dioxide.

The date on these samples are the following, α activity of the embedded ash forms :

Cement	1.7	Ci	(1.10^4 Ci.t^{-1})
Epoxide	3	Ci	(2.1 10^4 Ci.t^{-1})
Epoxide cement	3.3	Ci	(2.10^4 Ci.t^{-1})

One of the main results is the fracture of the cemented ash form after 180 days of water immersion (α integrated dose 5 10^8 rad). The two other embedded forms do not show any failure at the same time : after 1 year of water leaching these two forms save their integrity.

The characteristical data, gained after this 1 year leaching test, i.e the cumulated released fraction L_R and the leaching rate E_{ML} and the (expressed in g.cm^{-2}.d^{-1}) are shown in the following table : .

Leaching results	Cement	Epoxide	Epoxide - Cement
L_R 360		1,2 10^{-3}	2 10^{-4}
F_{ML} 360 f.cm^{-2}.d^{-1}	broken (180 d)	4 10^{-6}	1 10^{-6}

Radiolysis gas study :

On the same kind of 238 Pu doped samples a radiolysis study has been done : the samples were placed in tight stainless steel containers, under argon atmosphere, and the radiolytic gas flow was measured by sampling of the inert atmosphere once a month during 1 year.

- Integrated dose :

cement	1 10^9 rad
epoxide	2 10^9 rad
epoxide-cement	2 10^9 rad

- Number of samples :
  2 for each embedded form
- Volume of the samples : 100 ml
- Gas flow analysis (gas chromatography)

Embedded form	Gas volume in ml (t = 1 year)				
	H2	02	N2	CH4	CO
Epoxide	315	80	41	-	11
Epoxide-cement	380	-	15	10	50
Cement	599	208	12	-	-

Observations :

After this 1 year test under inert atmosphere, the following visual observations were made :

- epoxide samples : 2/2 - are without any apparent damage.
- epoxide-cement samples - 2/2 - idem.
- cement samples - 1/2 - show some fractures.

- Mechanical resistance evolution of α irradiated samples.

A compression test was performed on one of the two α irradiated embedded forms. The results of this experiment were compared to those obtained before α irradiation.

Embedded ash form	Without α irradiation	After irradiation	dose
Cement	22 MPa	30 MPa	1.5 10^9
Epoxide	125 MPa	> 200 MPa	3 10^9
Epoxide cement	64 MPa	60 MPa	2.5 10^9

N.B. The test has been performed 1.5 year after the fabrication.

- Water immersion behaviour :

Using the leaching test samples, allowed to measure the influence of the water immersion on each embedded ash form.

a) Samples made with α bearing ash (activity = 50 $Ci.t^{-1}$)
For three embedded forms, and for each sample, metrology measurements were done = no change either in height or diameter was observed.

b) Samples doped with 238 plutonium dioxide
On epoxide samples, and on epoxide cement, the samples do not show any variation of their dimensions : on the other hand, the cemented ash form was broken. After 1.5 year, 40 % of the total weight is divided in less than 1 cm^3 pieces.

- Leaching test on sample, after radiolysis test.

This 90 d leaching test was launched in the second semester of 89. The results will be shown at the beginning of 90.

- Full scale tests on 100 and 200 l packagings on the PICC (pilote de conditionnement des cendres d'incinérateur).

Several embedding campaigns were done in order to define :

. The final operating mode of fabrication of the 100 and 200 l embedding ash form by the epoxide cement process.
. LOPOX epoxide and INJEPOX epoxide products were compared.
. Cleaning tests of the GUEDU mixer were performed allowing to determine the right chemical to be used and also to choose a high pressure cleaning device. The mixer is now being equipped with a BARTHOD high pressure pump giving satisfactory results.

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

Contractor : ENEA-CRE CASACCIA, Rome, ITALY
Contract No : FI1W/0012
Duration of contract : July 1986 - March 1990
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

NO CONTRIBUTION HAS BEEN RECEIVED AT THE EDITION'S DEADLINE

DECONTAMINATION OF SOLID ALPHA WASTES AND RECOVERY OF THE PLUTONIUM (PROLIXE Facility)

Contractor : CEA, CEN-FAR France
Contract No : FIW/0013
Duration of the contract : October 1986 - December 1989
Period covered : January 1989 - December 1989
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 $\alpha\beta\gamma$ emitters for hot-cells studies and with α emitters only for gloveboxe 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 named ELISE for the treatment of α active solid wastes,
b/ a hot-cell (PROLIXE facility) for the treatment of $\alpha\beta\gamma$ active solid wastes.

In these facilities we will develop leaching processes in order to :
1/ decontaminate these wastes especially in 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

2.1 WASTES ANALYSIS to determine their composition and the nature and activity of the radiocontaminants.
2.2 WASTES CRUSHING : characterization of the size of particles obtained after the crushing of the wastes according to their nature.
2.3 PRETREATMENT : in the specific case of the treatment of ashes produced in other facility, the pretreatment procedure to eliminate chloride ion will be defined.
2.4 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.
2.5 EQUIPMENT DESIGN : the electrolyser for the generation of reducing or oxidizing agents will be defined.
2.6 SECONDARY WASTES : an optimization of the management of secondary wastes (gazeous wastes, distillates) will be realized. The opportunity to recover some chemicals like silver will be considered.
2.7 RECOVEREY AND PURIFICATION OF ALPHA EMITTERS : the study of the recovery of alpha emitters, especially the plutonium using extraction chromatography technique will be realized.

2.8 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 two facilities, ELISE and PROLIXE, are operating active runs since February 1987 (ELISE) and March 1988 (PROLIXE).

In 1989, 2236 Kg (= 17,3 m^3) of active wastes have been treated in ELISE : these wastes were subjected to the sorting and crushing operations. In PROLIXE, 356 Kg (= 2,06 m^3) of $\alpha \beta \gamma$ solid wastes have been treated during the year.

Lixiviation campaigns were performed = 1 (10 Kg of PCW) at 60°C in ELISE and 13 at romm temperature in PROLIXE amounting to 213 Kg of solid wastes. In PROLIXE, an electrolyzer for the generation of AgII was installed and used in two lixiviation campaigns and, for the first time, the goal of the "exhaustive" decontamination of solid wastes in α emitters was reached.

At the laboratory scale the following studies have been performed :
1/ AgII OXIDIZING DISSOLUTION : two studies have been realized : a) the determination of conditions for the exhaustive decontamination of stainless steel boxes contaminated in PuO_2 to be used in the MELOX facility, b) the decontamination of the zircaloy hulls, solid wastes produced in the reprocessing of LWR fuels.
2/ STUDY OF APPARATUS : two apparatus have been studied during this year : a) the AgII electrolyzer b) a cyclone concentrator with an improved capacity (10 l/h).

Progress and results

1. Wastes crushing (B.2)

In the two facilities, ELISE and PROLIXE, both equipped with the same crusher, numerous crushing campaigns have been done without any difficulties : in ELISE, 2236 Kg of α active solid wastes have been treated and in PROLIXE 356 Kg of $\alpha \beta \gamma$ solid wastes were crushed.

2. Leaching tests (B.4)

2.1 Laboratory studies

New application of the AgII lixiviation method for the decontamination of solid wastes have been developped.

AG-NET : In the course of the design of specific treatment for the decontamination vs plutonium of solid wastes to be produced in the MELOX facility, a special case is related to the management of the stainless steel boxes which initially contained PuO_2. A special apparatus named AG-NET was designed and used to decontaminate these wastes with electrogenerated AgII. Successful runs were done using 7 different boxes and the final α contamination was found lower than 0,1 Ci/t of the non conditionned waste.

Zircalloy hulls : The Zircalloy hulls constitute a major solid active wastes to be managed in the back-end of the fuel cycle. These hulls are slightly contaminated with plutonium. Experiments have been realized to check the possibility of an exhaustive plutonium decontamination of these hulls by AgII treatment.

2.2 ELISE experiments

One lixiviation campaign involving ≈ 10 Kg of PCW has been realized at elevated temperature ≈ 60°C. No real improvement of the performances of the nitric acid lixiviation was observed in comparison with experiments done at room temperature.

2.3 PROLIXE experiments

About 213 Kg (≈ 1,2 m³) of αβγ solid wastes have been processed during 13 lixiviation campaigns. A total of ≈ 200 Ci of emitters composed essentially by ^{244}Cm and ^{241}Am were recovered in the leachates. After the installation of the AgII electrolyzer into the PROLIXE hot-cell, two treatments of solid wastes with AgII were realized. In the case of an experiment, using 20 Kg of metallic (stainless steel essentially) wastes, highly contaminated with αβγ emitters, produced during the dismantling of the hot-cell named RM2 (CEN-FAR), the goal of the exhaustive decontamination of the wastes was achieved for the first time at that scale. An alpha residual contamination of 3,4 mCi/t of the non conditionned wastes was obtained.

3. Equipment design (B5)

A cyclone evaporator with an improved capacity ≈ 10 l/h was successfully conceived, realized, and installed. It comprises 5 heating resistances with a total power input ≈ 8,2 kW. The vacuum double-jacketed compartment allows an energy efficiency close to 85 %. Liquid effluents with organic solutes and foaming agents can be successfully treated with this apparatus, giving high decontamination factors of the distillates.

4. Secondary wastes (B6)

A cyclone evaporator (5 l/h), made in metallic material, was installed into the PROLIXE hot-cell. A total of 250 litres of active effluents, contaminated by ^{244}Cm and ^{241}Am were successfully concentrated. From the concentrates, ^{244}Cm recovery campaigns were done for the reuse of ^{244}Cm to the preparation of neutron sources.

CONDITIONING OF NUCLEAR CLADDING WASTE BY HIGH TEMPERATURE MELTING IN A COLD CRUCIBLE

Contractor:	CEA, CEN-Valrhô, SDHA, F
Contract No:	FI1W-0014
Duration of Contract:	October 1986 - December 1989
Period Covered:	January 1989 - December 1989
Project Leader:	JACQUET-FRANCILLON

A. OBJECTIVES AND SCOPE

Conditioning of zircaloy and stainless steel hulls by high temperature melting in a cold crucible is being developed by the CEA 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 measuring 18 cm long and 5.7 cm in diameter weighing about 3.5 kg.

The objectives of this program are:

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

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

B. WORK PROGRAM

B.1 Definition of standard working conditions involving either stainless steel hulls or zircaloy hulls. Development of suitable operating methods for characterization of ingots and slags.

B.2 Realization and characterization of inactive stainless steel and zircaloy ingots.

B.3 Realization and characterization of active stainless steel ingots.

B.4 Realization and characterization of active zircaloy ingots.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Inactive ingot characterization confirmed that corrosion of the metal matrix elements was negligible.

Characterization of the glass containing the inactive slag has now been completed.

Work began on producing a second series of radioactive stainless steel ingots. Two ingots have been drawn and are now being characterized.

The activity distribution in the third stainless steel ingot from the first series (test CI05) showed 92.9% α and 8.1% β decontamination efficiency.

The general work progress status is as follows:

- B.1: Completed.
- B.2: Completed
- B.3: Two new radioactive stainless steel ingots remain to be drawn. Active ingots CI02 and CI06 from the first series are now being characterized. The flux will be vitrified in the *Vulcain* cell.
- B.4: Work began to compile the molten zircaloy/water interaction test results in order to obtain clearance from the safety authorities to produce zircaloy ingots.

Progress and Results

1. Inactive Reference Tests (B.2)

The ingot characterization work is finished.

Leach tests continued at 100°C in double-distilled water using Kumagawa-type pyrex Soxhlet vessels with three metal samples (stainless steel, zircaloy 4 and a zircaloy-steel-inconel mixture). The solution ion analysis results did not reveal any significant corrosion of the metal matrices.

Devitrification studies were conducted on R7T7 glass samples containing 2% and 4% CaF_2-MgF_2 flux and % and 4% CaF_2-BaF_2 flux to determine the lower crystallization temperature, the liquidus temperature, and the temperature range within which each of the crystalline phases is present. The same types of crystals were observed as in previous R7T7 glass samples, but with some shifts in the crystal occurrence ranges.

The lower crystallization temperatures were about the same order of magnitude as in R7T7 glass for glass samples containing 2% and 4% CaF_2-BaF_2 flux, and slightly lower for samples with 2% and 4% CaF_2-MgF_2 flux. Thermal stability studies showed the same crystalline phases as those described in the devitrification study.

Compared with the R7T7 reference glass, these samples showed greater bulk crystallization (crystallization was essentially limited to the edges of the reference glass specimen). The samples containing CaF_2-MgF_2 appeared more crystallized than those containing CaF_2-BaF_2. These results confirm the effect of magnesium on crystallization already revealed during the preceding tests.

2. Realization and Characterization of Active Stainless Steel Ingots (B.3)

Four additional radioactive ingots were to be produced by melting stainless steel hulls from Phénix; two ingots (CI07 and CI08) have now been drawn. The test objectives are:

- to obtain more precise results concerning radionuclide volatilization and decontamination;
- to complete the feasibility study for the upper portion of the ingot;
- to test the effects of the flux-to-hull mass ratio, notably on the ingot α decontamination efficiency.

2.1 Ingot Fabrication and Appearance (Ingot CI07)

A suitable molten bath was obtained only after 70 minutes, although the flux melted within 3 minutes. The drawing operation was interrupted when the ingot became jammed, and the test lasted a total of 128 minutes instead of the planned 45 minutes.

The resulting ingot was shiny and visually satisfactory (Figure 1) with no shrink cavities. Only a small tongue was observed at the top.

2.2 Material Mass Balance (Ingot CI07)

As for the previous tests, the recovered slag mass increased by about 14% for the active tests (compared with 13% for the inactive ingots) probably from dissolution of oxides or elements adhering to the hulls.

2.3 Volatilization (Ingot CI07)

The total volatilization (excluding tritium) was around 6.3% of the initial β activity and 0.5% of the initial α activity. The β activity was primarily attributable to cesium; 99.99% of the activity was trapped by the crucible head and dust separator.

All the volatilization figures were calculated from the mean clad activity as measured during the reprocessing operations.

2.4 Ingot Decontamination

All the results for the slag obtained during production of the four ingots are not available at the time of this writing. The activity distribution for ingot CI05 (the third ingot in the first series) is shown in Table I. The decontamination efficiency was 92.9% α and 8.1% β (82.6% for Sr and 91.3% for ^{137}Cs).

2.5 Ingot Characterization

Samples were taken from the midsection and the upper end of ingots CI02 and CI06 for examination.

Specific Gravity Measurements

The measured values were clustered around 8; higher values were found at the core and in the upper part of the ingots.

Metallographic Examination

Macrographic images (Figure 2: X5 magnification) and micrographic images (X100) revealed the following features:

- a dendritic solidification structure with large (> 10 mm long) dendrites, often a large grain size (> 2 mm dia), and significant solute concentrations between the dendritic zones which should be quantified by scanning electron microscope X-ray microanalysis;
- very low closed porosity (approximately 400 μm around the edges and 10–20 μm at the center) especially in the samples with the lowest specific gravity;

These examinations will be completed by α, β and γ autoradiography.

	A	B	C	D = A + B + C	F
	VOLATILISATION %	SLAG %	INGOT %	CALCULATED HULL ACTIVITY %	DECONTAMINATION EFFICIENCY $\frac{D - C}{D} \times 100$
90 Sr + 90 Y	1,92	80,65	17,43	100	82,6
137 Cs	65,80	25,52	8,69	100	91,3
134 Cs	69,37	30,63	--	100	100,0
106 Ru + 106 Rh	< 0,04	0,05	99,92	100	0,08
144 Ce + 144 Pr	< 42,86	57,14	--	100	100,0
125 Sb	< 0,26	0,22	99,52	100	0,5
60 Co	< $4{,}3.10^{-3}$	$7{,}4.10^{-4}$	≠ 100	100	0,005
54 Mn	< 40,12	59,88	--	100	100,0
TOTAL BETA	3,68	4,42	91,96	100	8,1
239 + 240 Pu	3,57	90,0	6,42	100	93,6
238 Pu + 241 Am	2,55	91,56	5,90	100	94,1
244 Cm + 242 Cm	--	48,41	51,59	100	48,4
TOTAL ALPHA	2,97	89,92	7,10	100	92,9

Table I : Activity distribution for test CI 05 - Activity (%) as of october 1, 1989

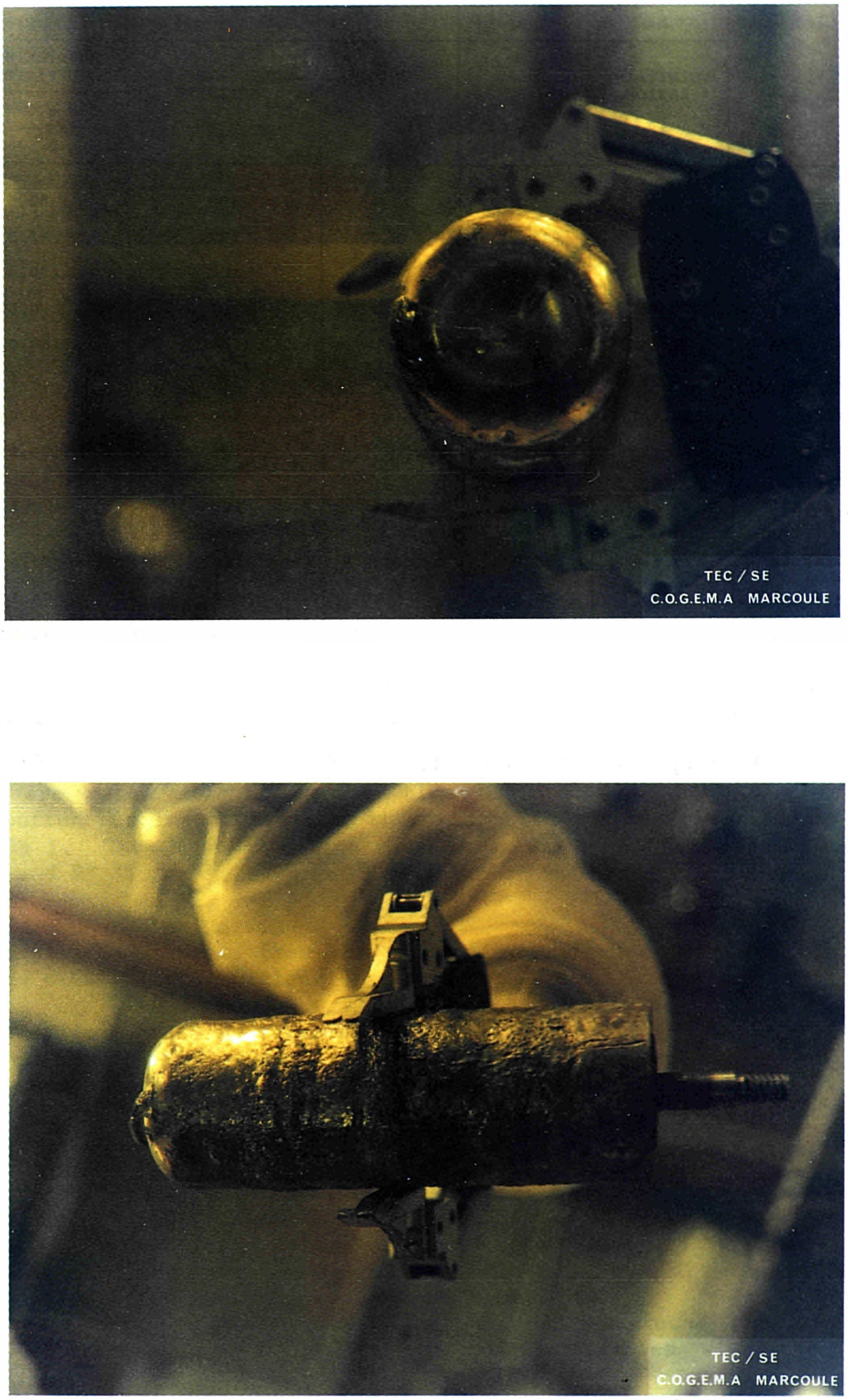


Figure 1 : Ingot CIO7 seen from above and side face

C I 06 A1

Figure 2 : métallography

HOT ISOSTATIC PRESSING OR MELTING OF INCINERATED ALPHA WASTE ASHES

Contractor: CEA, CEN-Valrhô, SDHA (France)
Contract No: FI1W-0015 F CD
Duration of Contract: October 1986 - September 1989
Period Covered: January 1989 - September 1989
Project Leader: A. Jouan

A. OBJECTIVES AND SCOPE

The purpose of this study was to investigate a conditioning process suitable for ultimate storage of incinerated alpha waste ashes. The process would also be applicable to ash chemical treatment residues, β-γ ashes or powder waste of any origin that remains inert at the process temperature.

A multidimensional hot pressing method was chosen in which a vacuum-sealed primary container with the waste ashes is placed in an oven filled with high pressure gas. The resulting product is a type of ceramic that adheres to the container walls without any apical void.

The process has not yet been applied to waste storage. This study was carried out jointly with industrial firms where isostatic presses were available.

Three ash conditioning processes (isostatic pressing, melting and mixed cement-resin embedding) were compared on the basis of four essential criteria: quality of the final product, feasibility, final waste volume and total investment + operating costs.

B. WORK PROGRAM

B.1 Production of representative ashes in industrial pilot facilities or utilization of industrial ashes with similar compositions for technological feasibility tests.

B.2 Determination of pressing parameters at laboratory scale on actual inactive ashes.

B.3 Production of intermediate scale blocks from actual inactive ashes to determine the physical and mechanical properties of the resulting material, and fabrication of a 30 cm diameter block using industrial ashes.

B.4 Fabrication of melted ashes with or without primary glass additives in existing CEA furnaces.

B.5 Preliminary design work for an industrial unit to allow comparison with a melting and an embedding facility.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

The following work was completed during the final contract period:

- investigation of the physical properties of actual pressed ashes in containers with a mean diameter of 140 mm;
- evaluation of industrial feasibility with large (300 mm diameter) containers using incinerated domestic waste ashes;
- comparison of leaching resistance and compression strength properties of three materials: pressed ashes, melted ashes, embedded ashes;
- operation and layout analysis for the cement-resin embedding process.

The three processes were then compared on the basis of technical and economic criteria.

Progress and Results

B.1 Production of Representative Ashes in Industrial Pilot Facilities:
Completed in 1987.

B.2 Determination of Pressing Parameters at Laboratory Scale:
Optimized in 1988.

B.3 Production of Intermediate Scale Blocks:

The physical properties of ashes obtained by pyrolysis and calcining followed by pressing for 2 hours at 800°C under a pressure of 150 MPa in containers 140 mm in diameter were measured by the *Société Française de Céramique*. The results are shown in Table I.

Table II compares the physical quality (compression strength) and chemical quality (leaching resistance) of three materials obtained by melting, pressing and cement-resin embedding. The pressed ashes showed the highest compression strength, but the melted ashes were most resistant to leaching. In both cases, the melted ashes were of better quality than the embedded ashes.

A 300 mm diameter container was manufactured by *Tecphy* to confirm the industrial feasibility of the isostatic pressing process. Recalcined domestic waste ashes were first pressed at room temperature to obtain an initial packing density of 1.81 $g \cdot cm^{-3}$. Optimum conditions for the actual isostatic pressing operation were determined to be 4 hours at 800°C under a pressure of 150 MPa. The calculated density of the final product was 2.4 $g \cdot cm^{-3}$. The container was cut up and the pressed ashes were found to be uniformly compacted.

B.4 Fabrication of Melted Ashes:
Completed in 1987.

B.5 Comparison of Three Conditioning Processes:

As for the other two techniques, the development of the embedding process flowsheet and the resulting layout was assigned to a specialized CEA department.

Figure 1 compares the volume of the three alpha containment structures with the same perspectives. The melting and embedding facilities are of comparable volume, significantly smaller than for the isostatic pressing unit.

Approximately 1700 kg of ashes produced annually by incineration of wastes from the MELOX fuel fabrication plant would represent about 5.7 m^3. Figure 2 illustrates the volume reduction advantage of the melting process.

Investment and operating costs were evaluated as shown in Figure 3. A significant drawback of the isostatic pressing method is the prohibitive cost of unidirectional and isostatic presses.

Figure 4 is an overall comparison of the three technologies according to the four criteria adopted for this study.

LIST OF PUBLICATIONS

The work conducted in 1989 was presented at Madrid on April 20, 1989 and at Karlsruhe on October 12, 1989.

TABLE I: PHYSICAL PROPERTIES OF PRESSED ASHES

APPARENT DENSITY	2.73 $g\cdot cm^{-3}$
OPEN POROSITY	16.3%
COMPRESSION STRENGTH AT ROOM TEMPERATURE	193 MPa
BENDING STRENGTH: ROOM TEMP 1000°C	21 7.5
TENSILE CREEP ON TEST SPECIMEN 32 MM DIA × 50 MM HIGH AFTER 25 HOURS AT 1000°C UNDER 0.2 MPa TENSILE LOAD	0.05%
THERMAL EXPANSION (1000°C)	8%
THERMAL CONDUCTIVITY (425°C)	1.29 $W\cdot m^{-1}K^{-1}$

TABLE II: COMPARISON OF CONTAINMENT MATERIALS

PARAMETER	DIRECT INDUCTION MELTING	ISOSTATIC PRESSING	MIXED CEMENT-RESIN EMBEDDING
MECHANICAL BEHAVIOR (COMPRESSION STRENGTH)	100 MPa	100–200 MPa	65 MPa
CHEMICAL BEHAVIOR (LEACHING RESISTANCE)*	2.16×10^{-4}	7.40×10^{-4}	12.72×10^{-4}

* Mass loss ($g\cdot cm^{-2}d^{-1}$) after 14 days

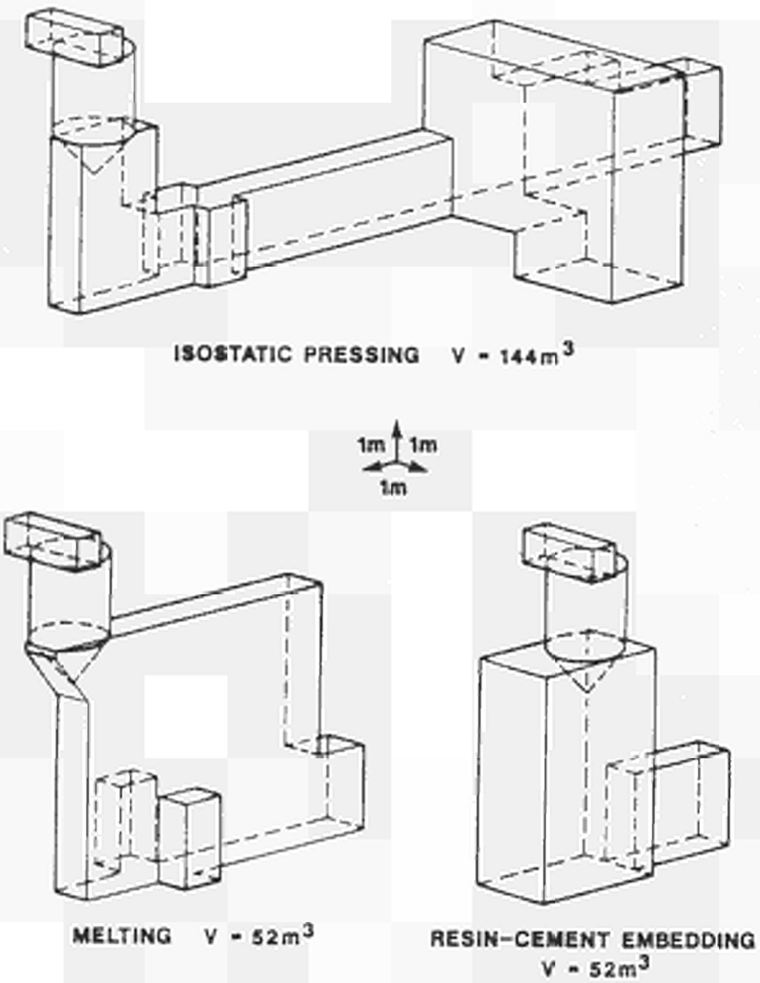


Fig. 1 COMPARATIVE LAYOUT VOLUMES
(α containment)

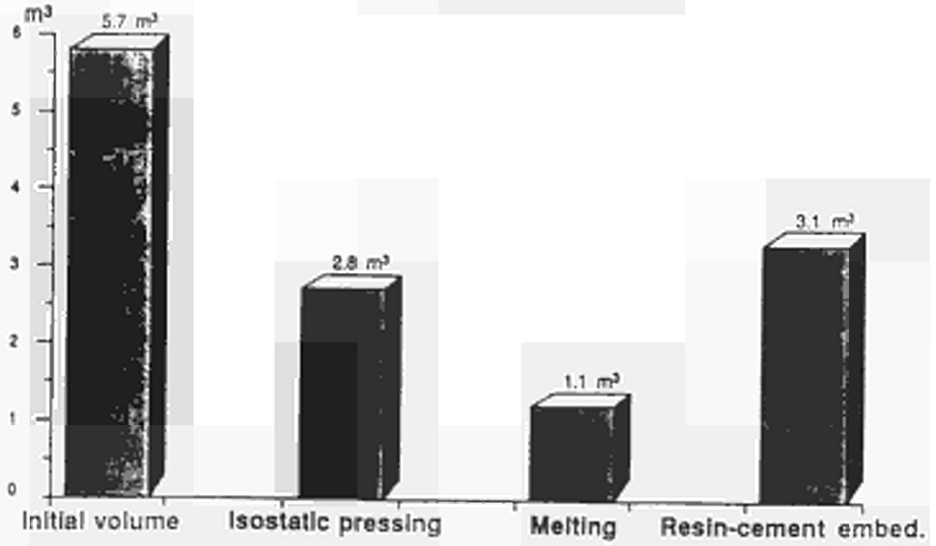


Fig. 2 COMPARISON BETWEEN INITIAL AND CONDITIONED ASH VOLUMES
(Yearly volume produced by the Melox plant)

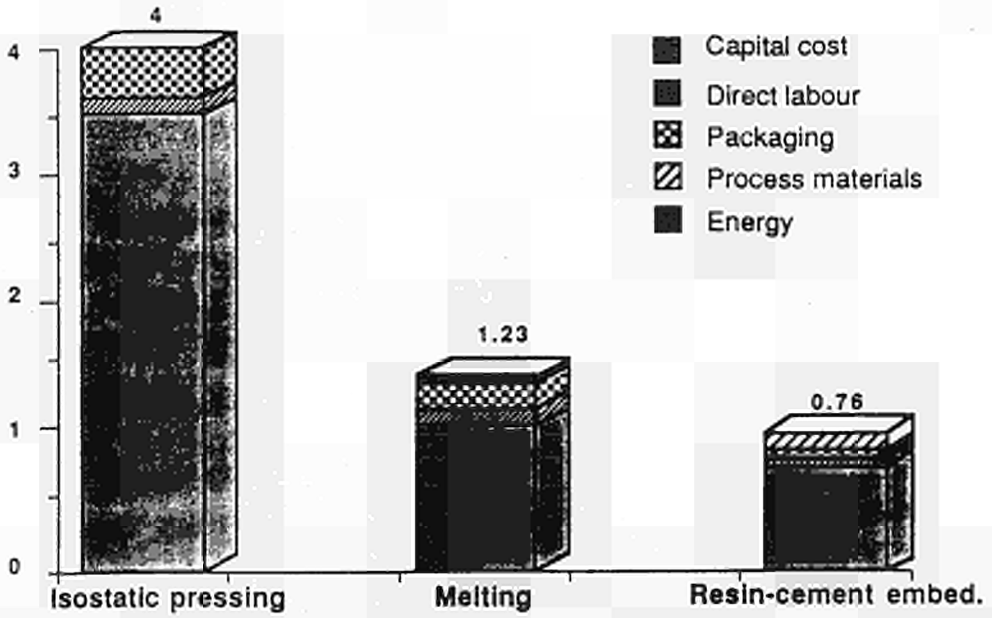


Fig. 3 COMPARATIVE TOTAL ANNUAL COSTS FOR THE 3 PROCESSES
(Millions of francs)

	COST	FEASIBILITY	FINAL VOLUME	PRODUCT QUALITY	TOTAL
HIP	1	1	2	2	6
MELTING	2	2	3	3	10
EMBEDDING	3	3	1	1	8

1 poor 2 satisfactory 3 very good

Fig. 4 OVERALL COMPARISON

Utilisation of liquid membranes for the treatment of reprocessing concentrate

Contractor : CEA, CEN Cadarache, France
Contract n° F II W 1.0016
Duration of contract : January 1987 - December 1989
Period covered : January 1989 - December 1989
Project leader : J.F. DOZOL

A. OBJECTIVE AND SCOPE

Development of nuclear activities at the reprocessing plant of Marcoule must lead to an increase of low and medium activity waste, it is forecast to substitute soon the classical treatment using chemical precipitation by a more efficient treatment by evaporation in order to decrease the activity discharged in the Rhône.

This new process leads to an increase of bituminized wastes to be disposed in deep geological formation, due to the high sodium nitrate concentration in the concentrate. It is the reason why it could be economically interesting to decontaminate this concentrate so that the greatest part will be disposed in shallow land burial and a very small part in geological formation.

Taking into account the radiochemical characteristics of concentrate and to allow a shallow land burial disposal (for instance CSM) cesium stontium and actinides must be removed with DF higher than 50 for fission products and 100 for alpha emitters. The process will be economically interesting if concentration factor exceeds 40.

To decontaminate the concentrates from Marcoule it is intended to use supported liquid membranes. This process allows to transfer selectively nuclides from liquid waste to a stripping solution, so the actinides can be recycled and FP immobilized in glass.

B. WORK PROGRAMME

2.1. Extraction of actinides :

2.1.1. Choice of the component and concentration of the stripping solution.

2.1.2. Interest of using a second membrane. Choice of the NaOH concentration for the second stripping solution.

2.2. Extraction of strontium

2.2.1. Choice of the diluent in order to improve the stability and the life-time of the S.LM and decrease the transfer of acidity through the membrane. The chosen diluent is the decanol.

2.3. Extraction of cesium

2.3.1. Synthesis of B21 C7 derivatives : mono benzo 21 Crown 7 (B21 C7) and tert butyl benzo 21 C7 (tBB21 C7).

2.3.2. B21 C7 is difficult to use due to its low solubility in most of the diluents, tBB21 C7 is easily soluble in many diluents, in particular in the mixture hexylbenzene/decanol.

2.4. Laboratory scale experiments on hollow fibers modules

Devices with one or two hollow fibers modules (one for extraction the other one for stripping) were used.

2.5. Decontamination of a genuine concentrate

2.5.1. Preparation of concentrate from Marcoule genuine liquid waste in Telemac hot cell.

2.5.2. Removal of actinides from concentrate.

2.5.3. Removal of strontium/cesium from concentrate.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement :

- Extraction of 98-99 % of actinides obtained from simulated or genuine concentrate by using a supported liquid membrane (S.L.M) constituted by the mixture CMPO (0.25 M) TBP (0.75 M) in decahydronaphtalene.

- Extraction of more than 98 % of stontium from simulated wastes by using a SLM containing DC18 C6 diluted in hexylbenzene + decanol. Extraction of strontium from genuine concentrate after actinides removal.
- Simultaneous extraction of strontium and cesium with a mixture of crown ethers (DC18 C6 + tBB21 C7) diluted in hexylbenzene + decanol.
- Endurance tests carried out with hollow fibers modules.

D. PROGRESS AND RESULTS

Concentrate was obtained by evaporation of liquid waste arising from Cogema Marcoule in Telemac hot cell. Tests were carried first with simulated concentrate then with genuine concentrate.

Main compounds in genuine liquid waste and concentrate

	mg.l^{-1}		kBq.l^{-1}		
	Liquid waste	Concentrate	Liquid waste		Concentrate
H^+	0,55 N	1,27 N	$^{89+90}Sr$	5600	150 10^3
NO_3^-	37 10^3	280 10^3	^{95}Zr	70	-
SO_4^{2-}	65	< 800	^{95}Nb	65	-
PO_4^{3-}	200	2200	$^{106}Ru+Rh$	5600	160 10^3
Na	2150	58000	^{125}Sb	125	-
Mg	470	13400	^{137}Cs	1600	50 10^3
Al	30	1200			
K	35	760	$^{144}Ce+Pr$	4200	130 10^3
Ca	210	6000	^{238}Pu	35	360
Fe	80	1500	$^{239+240}Pu$	85	740
U	400	1250	^{241}Am	60	1600
TBP	35,2	< 1	^{242}Cm	70	1100
HDBP	5,6	< 1	$^{243+244}Cm$	18	340

The distribution coefficients are about the same for CMPO/TBP and DC18 C6 with genuine or simulated concentrate. But they are low for the tBB21 C7 (0.3 M).

Distribution coefficients $D = \dfrac{[M^{n+}]o}{[M^{n+}]A}$

		Simulated concentrate			Genuine
Extractant		MAR400	MAR400 Al	MAR400 Mg	concentrate
CMPO(0.25M)	$D_{Pu}4+$	1000	1000	1000	1000
CMPO(0.25M)	$D_{Am}3+$	14	35	55	180
CMPO(0.25M)	$D_{Cm}3+$				240
DC18C6(0.5M)	$D_{Sr}2+$	12	18	19	11
tBB21C7(0.3M)	$D_{Cs}+$				0.25

For the actinides extraction, the compounds and the concentration chosen by P.Danesi were used : mixture of CMPO (0.25 M) /TBP (0.75 M) diluted in decalin (decahydronaphtalene. A good stripping of actinides is achieved with sodium citrate 0.5 M, in this case, D.F > 100 are obtained.

An test carried out with genuine concentrate, of which initial acidity is 2 M gave, using a flat membrane Celgard 2500, the following results :

- D.F > 100 for actinides and ^{144}Ce after treatment with S.L.M containing the mixture CMPO/TBP.
- About 80 % of strontium is removed from the concentrate with a SLM containing DC18 C6 (0.5 M) Decanol (0.7 M) diluted in hexylbenzene before a precipitate occurs in the concentrate. An other experience, with an higher initial acidity is being carried out.

tBB21 C7 much soluble than B21 C7 in organic solvents was synthesized.

The synthesis of tBB21 C7 is carried in two stages :

- In pyridine medium, tosylation of hexaethylene glycol :

$HO(CH_2OCH_2)_6H + 2\ TsCl \qquad TsO(CH_2OCH_2)_6\ Ts + 2HCl$

- Then, the washed and deshydrated precipitate reacts with tert butyl catechol, in pyridine medium, in presence of CsF (template effect)

$TsO(CH_2OCH_2)_6\ Ts + OH - C_6H_4$-tButyl   tButyl B21C7 + 2 CsOTs

After evaporation of acetonitrile, the crown ether is extracted by heptane.

To obtain a satisfactory yield (about 65% for each stage) the reagents have to be previously deshydrated and purified.

Tests of stability of supported liquid membranes were carried out with devices containing one or two hollow fibers modules.

These endurance tests showed that a good stability of the S.L.M was achieved in particular when using two hollow fibers modules : the device worked for 350 hours without any difficulties.

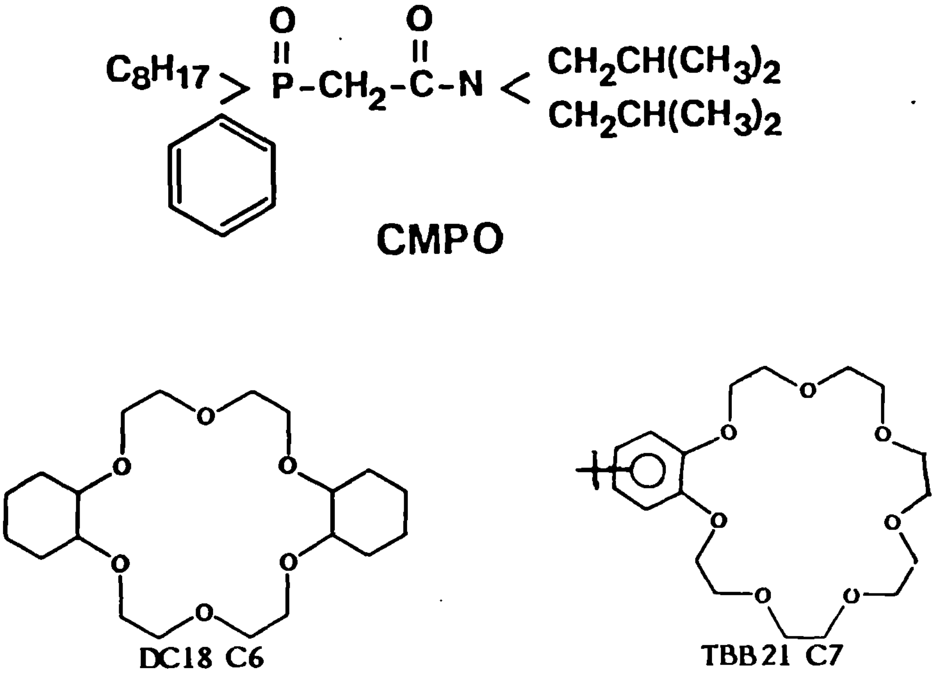


Fig. 1 - Extractants

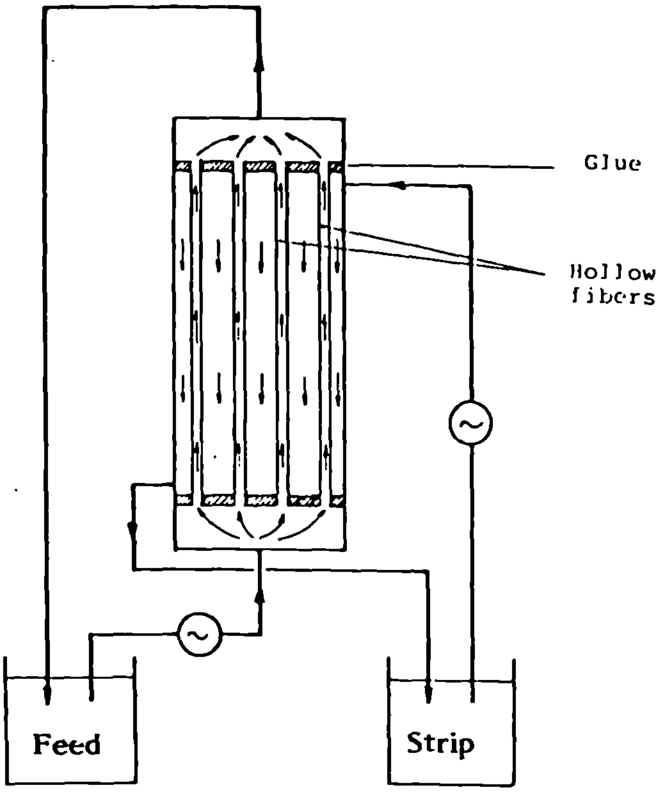


Fig.2 - Hollow fibers module

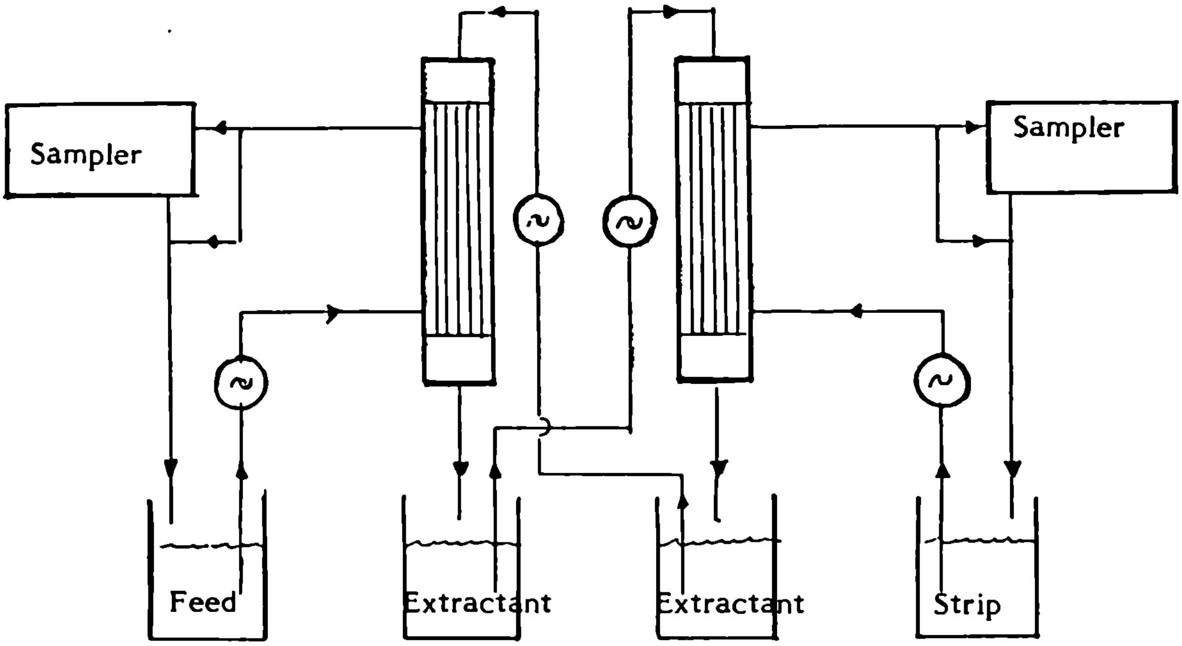


Fig.3 - Double hollow fibers modules

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

Contractor : UKAEA, AERE, HARWELL, UK
Contract No : FI1W/0017 UK (H)
Duration of contract: July 1986 - December 1989
Project Leaders : P. Kavanagh, 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. The plant performance is to be evaluated for improvements in plant throughput and decontamination factor when processing a real radwaste.

B. WORK PROGRAMME

2.2 New precipitation agents
2.3 Tests with alternative membrane
2.4 Tests with electrically assisted process
2.5 Tests with ancillary equipment items
2.6 Design, construction and operation of advanced prototype unit

REQUEST FOR PATENT IN PROGRESS

ELECTROCHEMICAL ION-EXCHANGE/SORPTION FOR MEDIUM ACTIVE LIQUID WASTE TREATMENT

Contractor:	UKAEA, Harwell Laboratory, UK
Contract No:	FI.1W.0018
Duration of contract:	June 1986 - May 1990
Period covered	January 1989 - December 1989
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 interfering ions that adversely affect normal ion-exchange and floc process (eg 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

2.2 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.

2.3 Evaluation of 0.1 m^3/h module performance on the treatment of genuine βγ waste streams. Small scale supporting work on interfering ions.

2.4 Design, construct and commission a 1 m^3/h EIX unit, incorporating any modifications arising from the previous tasks. Evaluate performance on genuine waste.

2.5 Develop high capacity electrosorptive electrodes for the treatment of α bearing wastes. Examine the effect of interfering ions.
Design, construct and commission a 10 ℓ/h module based on these results.

2.6 Evaluate the performance of this unit for the treatment of genuine α containing wastes.

2.7 On the basis of (2.6), design, construct and commission a 0.1 m^3/h plant for the treatment of α wastes. Evaluate performance on genuine waste.

C. PROGRESS OF WORK AND OBTAINED RESULTS

STATE OF ADVANCEMENT

The application of EIX to the treatment of three genuine βγ wastes has been examined. The first was LLLW from the Tihange PWR power station during March 1989, as part of a liquid waste treatment intercomparison exercise. A sequential anion (IRN-78L)/cation (ZrP) EIX treatment reduced the activity levels of the unfiltered stream from 66 to 0.17 Bq/mℓ and also recovered > 94% borate. Selective elution was accomplished into a small volume of water by polarity reversal of each unit in turn. Tests on the Harwell site LLW with a parallel cation (ZrP)/anion (IRN-78L) EIX system gave significantly enhanced performance over cation-only for this relatively high salt content stream - reducing βγ to ∿ 12 mBq/mℓ. By contrast, ZrP-only was sufficiently effective for low conductivity streams - giving DFs > 100 for MTR and Magnox cooling pond water over extended test periods.

Zirconium phosphate EIX electrode lifetimes may now be significantly extended beyond the 6 years previously estimated, by anodic treatment in dilute phosphoric acid. Further enhancement of absorption kinetics has also been demonstrated for modified forms of the absorber.

The five module scaled-up EIX cell (2 m^2 surface area) has now been manufactured and the plant assembled and commissioned. Large scale testing (0.5 m^3/h) will commence after installation of the EIX electrodes to evaluate this modular approach to scale-up.

Significant progress has also been made on the treatment of α containing wastes. Residual α activity in the Harwell LLW was reduced by a DF of > 46 to ⩽ 1.7 mBq/mℓ by a parallel ZrP/IRN-78L cell in which the half cell currents were independently controlled to maintain an effluent pH of 4. Preliminary results with a ZrO_2 absorber have also shown promise in removing U to background levels at pH ∿ 5. An anion-only system was able to reduce α contents to ⩽ 1.7 mBq/mℓ in both high and low salt content wastes. Alternative passive absorption/electrical elution approaches for high salt content streams have, therefore, now been abandoned due to their inferior performance.

Large scale evaluation of these successful removal techniques will be conducted in parallel with βγ tests on LLW.

Preparatory work for the second "round robin" test on Casaccia fuel fabrication wastes, due to take place in March 1990, has now been completed. Conditioning processes prior to EIX treatment have been successfully developed to electrochemically oxidize oxalic acid and electrochemically destroy NH_4NO_3.

PROGRESS AND RESULTS

2.3 TREATMENT OF GENUINE βγ WASTE

2.3.1 Tihange PWR LLW

As part of an intercomparison exercise to test novel liquid waste treatment processes using real waste streams, some trials on EIX were carried out at Tihange PWR station in Belgium during February/March 1989.

The effluent comprised a high concentration of borate (114 ppm B) and sodium (61 ppm) at pH 8.3, as well as 32 ppm suspended solids (including > 5 ppm Fe). The total γ activity was 65.7 Bq/mℓ, of which 42 Bq/mℓ was due to $^{58+60}$Co. A portable test unit (Figure 1) was used to evaluate interchangeable EIX modules of 321 cm^2 surface area. Unfiltered waste was reduced to 0.4-1.6 Bq/mℓ (DF 164-41) at 1-4.3 BV/h by a zirconium phosphate unit at a current density of 5 mA/cm^2. Treatment in a IRN-78L unit not only removed > 94% of the borate at 1 BV/h, 3 mA/cm^2, but the activity was reduced to 0.4 Bq/mℓ. Subsequent treatment by a ZrP unit reduced the activity content further to 0.17 Bq/mℓ - an overall DF of ∿ 380. As > 90% of the initial activity was particulate in nature this demonstrates EIX to be able to remove colloidal as well as ionic contamination. The activity retained on both units could be eluted into a reduced volume for disposal, while Li and borate could be recovered separately for re-use if required.

2.3.2 Harwell low level liquid waste

A unit based on parallel anion and cation EIX electrodes has been successfully demonstrated for the treatment of higher salt content wastes (>10 mM). The feed pH was controlled by the simultaneous absorption of anions in order to optimize the effectiveness of the cation electrode. IRN-78L was chosen as the optimum system in a series of bench-top scoping trials. Subsequent tests with a ZrP/IRN-78L cell on the Harwell site LLW gave a ^{60}Co DF of 7.8 which reduced this nuclide to 12 mBq/mℓ, while ^{137}Cs was removed to background (0.4 mBq/mℓ) - a DF of > 74. This was a significant improvement over the DF of 1.3-1.7 found previously with a ZrP-only system. Sequential anion and combined cation/anion units are expected to give even better results.

2.3.3 Cooling pond water

Excellent performance has been achieved in a zirconium phosphate bench-top flow cell for the treatment of the demineralized water typical of MTR cooling ponds. Cs and Co DFs of 100-200 were obtained at flow rates of 25 BV/h. Subsequent trials in the 0.34 m^2 pilot plant gave a similar performance at 50ℓ/h, declining to a DF of 10 at 0.1 m^3/h. Other wastes falling into this low ionic content category include the effluent from high pressure water jetting and shielding water, both used in decommissioning.

Extended trials on simulant Magnox pond water (100 ppm Na) with a ZrP cell have also shown Cs DFs > 100 over a 25 day test period.

2.3.4 Electrode development

From previous work on zirconium phosphate, it had been estimated that a lifetime of 6 years might be expected due to a slow loss of phosphate arising from hydrolysis. However, it has now been demonstrated that this phosphate can be replaced by anodic treatment in dilute phosphoric acid, to give a further improved performance. Lifetimes can therefore be considerably extended.

Development of the ZrP absorber has identified two systems capable of enhanced kinetics and reduced phosphate loss - based on a ZrP(H)/ZrP(Na) mixture and semi-crystalline ZrP.

2.4 SCALE-UP OF βγ EIX PILOT PLANT TO 1 m^3/h

The construction and installation of a five compartment multi-modular cell of 2 m^2 EIX surface area in the 0.5-1 m^3/h pilot plant has been completed (Figure 2). This has now been commissioned and is ready for the fitting of the EIX electrodes prior to large scale testing. This is primarily to evaluate the modular approach to scale-up.

2.6 ELECTROSORPTIVE TREATMENT OF α WASTES

2.6.1 Harwell low level waste

α removal from the Harwell low level waste by the parallel ZrP/IRN-78L system gave a DF of 4 for identical electrode currents of 3 mA/cm^3 - reducing the effluent to only 7 mBq/mℓ. Performance was further improved to DFs > 46 when the current densities were independently adjusted to ensure that the feed pH was maintained $\geqslant$ 4.

An anion only system (IRN-78L) was also successfully demonstrated for the treatment of both low and high salt content (1M $NaNO_3$) α wastes - giving DFs of 30 and 12 respectively - reducing residual activity to $\leqslant$ 1.7 mBq/mℓ.

Preliminary results with a ZrO_2 EIX system have shown U removal from a low salt content waste at pH 5 to background levels with a DF > 85. While this material ceases to be a cation absorber for Na^+ at pH < 7, it is still able to selectively absorb polyvalent cations as well as anions. However, two alternative approaches to the treatment of high salt content wastes based on passive absorption onto ZrP,ZrO_2 and HTiO followed by electrical elution have now been abandoned, due to insufficient selectivity, and poor performance compared to the anion-only EIX option described above.

2.6.2 Casaccia MLW

Preparatory work has been conducted for the second part of the "round robin" intercomparison exercise. However, only one of the three main Pu containing streams arising in the Casaccia fuel fabrication plant can be treated by EIX without some prior conditioning. One stream is primarily nitric acid (3-7M), a second is a mixture of nitric acid (1M HNO_3) and oxalic acid (0.6M), while the third comprises 11M NH_4OH containing 0.5M NH_4NO_3.

Development work at Harwell has shown that oxalic acid can be electrochemically oxidized with high efficiency in 1M HNO_3 at a gold coated titanium anode between 0.75 and 1.1 V(SCE) with initial current densities as high as 500 mA/cm^2. A portable unit with a 300 cm^2 anode is expected to be able to treat a 2ℓ batch of waste in < 8 h. This waste could then be combined with the other nitric acid stream prior to neutralization with NH_4OH to pH 9 and mixing with the third alkaline waste. Simple filtration is now able to recover the bulk of relatively pure $Pu(OH)_4$, leaving a residue of ∿ 40 Bq/mℓ in NH_4NO_3.

The treatment of this stream will be examined by two alternative routes:- anionic EIX as described above, and conventional ZrP/IRN-78L EIX after destruction of the NH_4/NO_3. This latter process has been successfully achieved by electrolytic reduction at a lead cathode to NH_4NO_2, followed by thermal decomposition to N_2 at 70°C to leave a residual nitrate concentration of only ∿ 1 mM. A cell containing 400 cm^2 of cathode area can treat 2ℓ of 5M waste in < 14 h.

The tests in Casaccia are expected to take place during March 1990.

List of Publications

/1/ TURNER, A.D., BRIDGER, N.J. and JUNKISON, A.R., Electrochemical ion-exchange/sorption for medium-active liquid waste treatment - Annual Progress Report 1988, AERE-G5002.

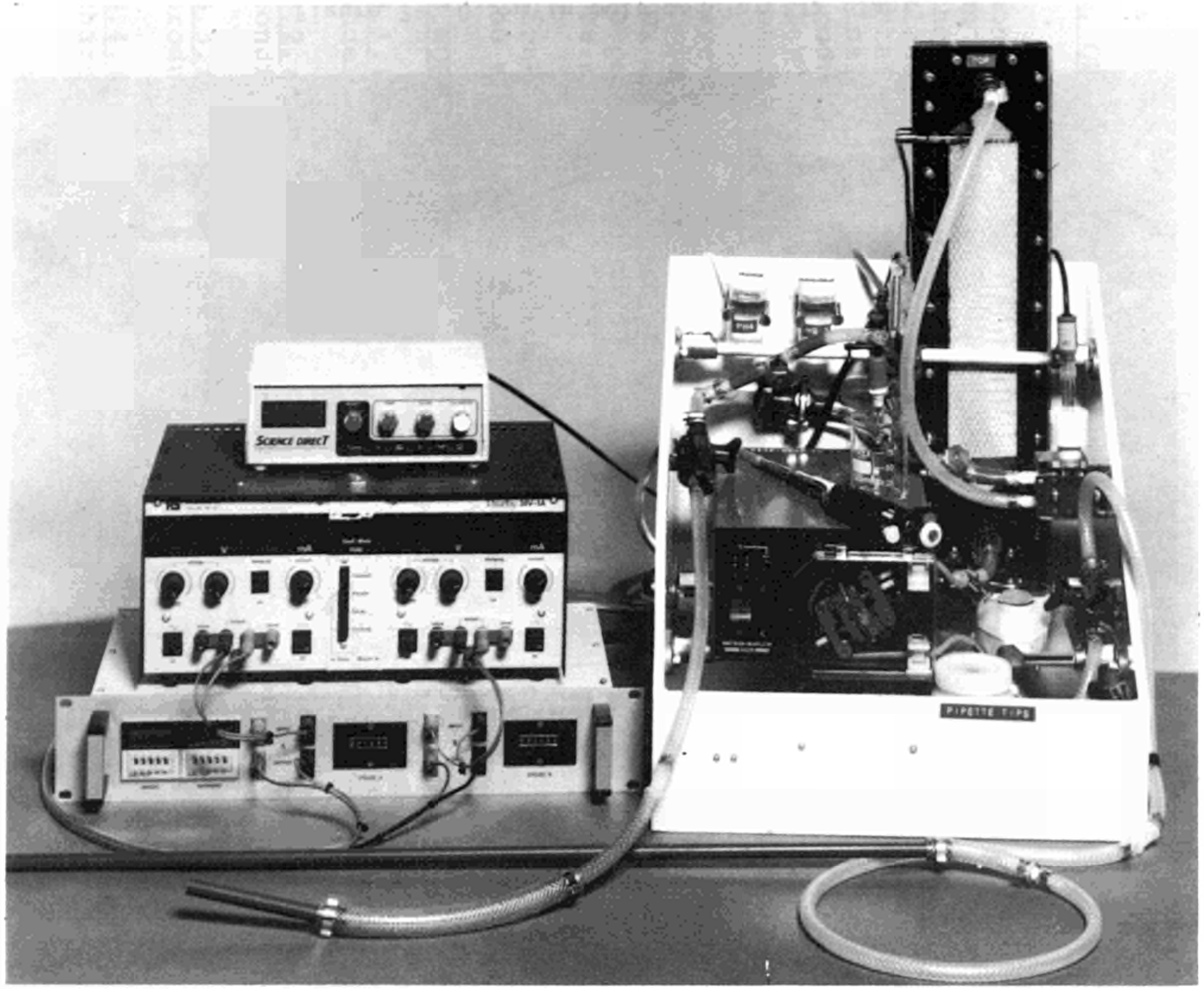


Figure 1 Portable EIX system with FC/9/RR EIX cell

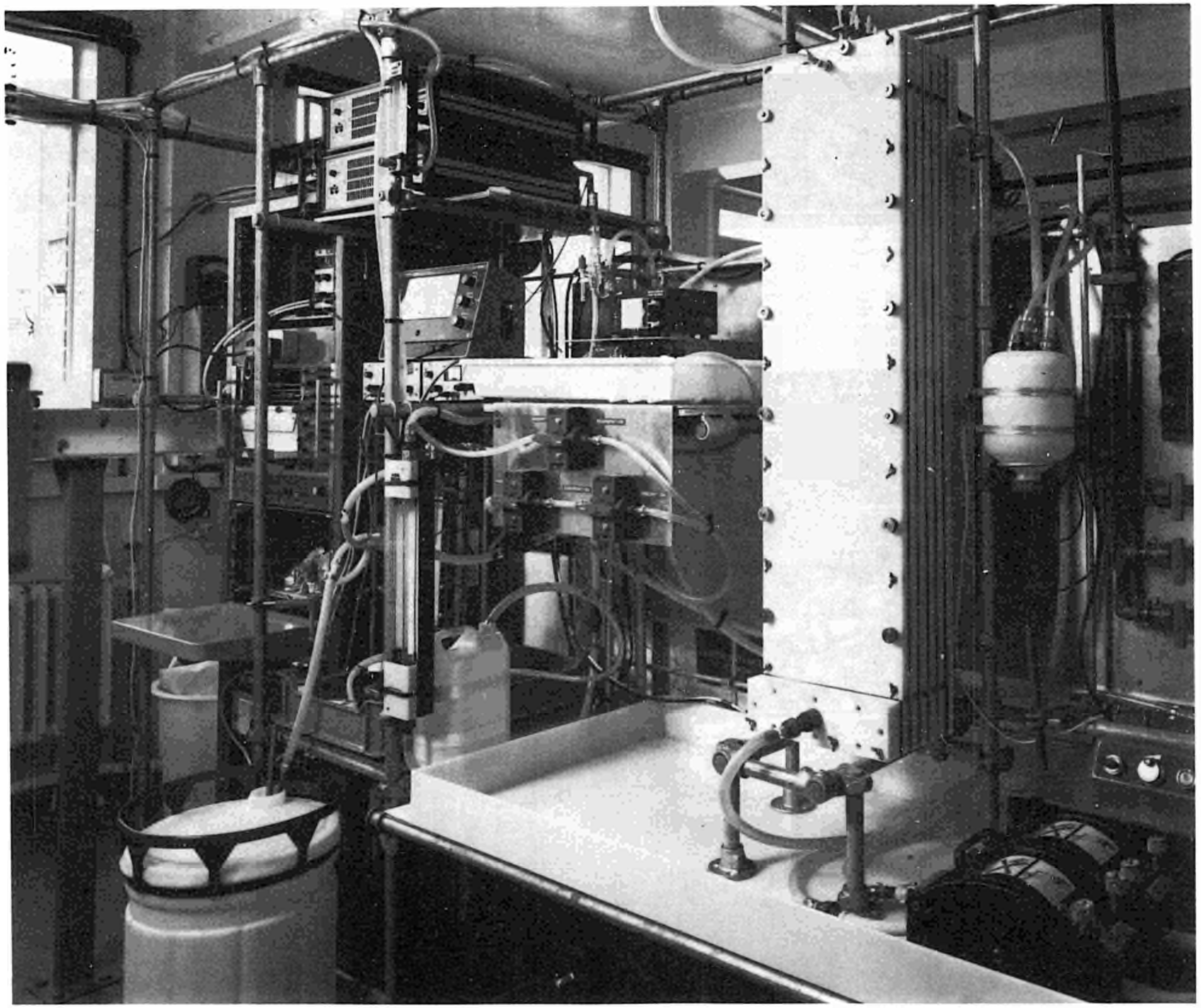


Figure 2   0.5 m^3/h multimodular EIX plant

Immobilization of cladding waste by press compaction and conditioning for final disposal by encapsulation in a lead containment

Contractor :	CEN/SCK Belgian Nuclear Research Center
Contract nr:	FI1W-0019-B
Duration of contract:	from 1.05.1986 to 31.12.1989
Period covered:	January 1989 - December 1989
Project Leader:	M.Klein

A. OBJECTIVES AND SCOPE

The actual research programme proposes an alternative conditioning method for cladding waste.This method is based on cold press compaction of the hulls to about 80 % of the theoretical density of zircaloy, the most representative cladding material for LWR fuels.The important volume reduction obtained is the major advantage of the alternative method.The final conditioning consist of encapsulation of the compaction products in a corrosion resistant container . In view of using clay as final disposal medium for this kind of waste, a seamless lead containment has been chosen as corrosion barrier.

The objectives of the Research Programme are to further develop the conditioning method proposed, on pilot scale, and to demonstrate its feasibility with representative radioactive LWR cladding waste, on the same scale.Special attention will be paid to the characterization of both the compaction products and the conditioned products.

This research is conducted in collaboration with the KernForschungszentrum in Karlsruhe which is responsible for the delivery of about 100 kg of active hulls.

B.WORK PROGRAMME

B.1.:Further development of the press compaction technology 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 , followed by characterization of the compaction products.

B.5.:Conditioning of compacted radioactive hulls in a corrosion resistant container.

C.PROGRESS OF WORK AND OBTAINED RESULTS

STATE OF ADVANCEMENT

During the first semester of 1989, the equipment of the hot cell for the active demonstration of the hulls compaction technology has been completed.The last major action was the functional testing of the ventilation system.

Inactive tests have been carried out in view of the reception of the active hulls in the cell.These tests are based on the preliminary design of the primary boxes for hulls transport.With the cell closed, the manipulator booting installed and the ventilation system in operation, all the manipulations inside the cell were reviewed and successfully tested.

Concerning the reception of the active hulls at CEN/SCK, two new aspects might necessitate changes to the transportation scheme:

- the use of a TN-2 container instead of the GNS-11 ;
- the changes of WAK concerning the design of the primary box.

Difficulties were encountered for the delivery of active hulls.The situation was blocked in Karlsruhe because no hulls were available in the WAK plant.Moreover, even if transportation of active hulls had been possible within the prescribed time, the authorities of CEN/SCK would have opposed the implementation of the active tests on account of the new philosophy on the covering of the dismantling costs .

PROGRESS AND RESULTS

B.1.DEVELOPMENT OF THE PRESS COMPACTION TECHNOLOGY UNDER INACTIVE CONDITIONS.

1.Influence of chop length

The compaction of carbon steel chops of 25 and 50 mm showed that the density of the compacted product is not significantly influenced by doubling the chop length; a density of about 82 % vs. the theoretical density is obtained.

2.Addition of materials

Tests with addition of soft metals for lining of the press die were performed to obtain disks with reduced external surface and better coherence and mechanical characteristics.

The soft metals tested were lead and aluminum.The use of lead granulates, distributed among the hulls in the tin can, did not result in any effect at all.Lead and aluminum sheets with thickness from 0.5 to 3 mm are placed on the bottom and at the top of the can; this resulted in very smooth surfaces but the mechanical characteristics were not significantly improved.

3.Compaction of zircaloy

Tubes, with a diameter of 10.5 mm and a 0.75 mm wall thickness are cut into 50 mm chops.this resulted in a stacking density of 0.81 kg/dm3 in a 750 cm3 tin can for compaction.

In Table I ,the results of the compaction tests are summarized.The density of the compacted disks amounts to 80 % of the theoretical density of zircaloy.This matches very well the target value of 75 %.

The addition of 1 mm lead or aluminum had the same effect as for the carbon steel chops : a decrease in cladding material contents of the compaction products.

An attempt was made to carry out the compaction in successive steps.Only a two step compaction could be realized, in which 75 % of the final pressure of 280 MPa was reached during the first step.A small, but not very significant decrease of the compacted product characteristics was observed .

One feature of the compaction procedure is the compaction time : after compaction, the pressure is maintained for a certain period of time, usually 50 s. An extension of this post-compaction time to 200 s did not have any effect on the product characteristics.

B.2.EQUIPMENT OF A HOT CELL FACILITY

A new hot cell facility shielded with 1.25 m of concrete has been made operational.This consisted mainly in the construction of a SS alpha tight box, the installation of 4 heavy duty manipulators and of a jib-arm for lifting heavy objects up to 250 kg and also the installation of two transfer systems, a small one installed in the intervention door and a 200 dm3 drum discharge port in the floor of the cell. The closed loop ventilation system was also successfully put into operation.

All the equipment necessary for the active demonstration is installed and all manipulation tools are developed. The equipment, adapted for remote control, presently consists of :

- a feeding unit to distribute bulk quantities of hulls into tin cans of 750 cm3.
- a gamma scanning device consisting of a positioning frame, a collimator and a Ge(Li) gamma measuring chain.The frame performs three functions ; rotation between filling and measuring position, rotation of the can and vertical movement.
- a 300 MPa press, with a diameter of 105 mm for compaction of cans of 750 cm3.
- a semi-automatic gas cooled TIG-welding unit for the welding of the triple containment.The container to be welded remains fixed and the welding torch is rotating.For the welding of the lead containment, the torch is oscillating while rotating.The optimal values of the welding parameters were determined in simulated active conditions; they are reported in Table II.
- a leak testing equipment for the inner container.

Inactive reception tests were carried out with the first design of the hulls primary box and all the manipulations inside the cell in simulated active conditions were successfully tested.

B.3.TRANSPORT OF REPRESENTATIVE CLADDING HULLS

The incompatibility between the shipment facilities at KfK and the reception facilities at CEN/SCK has led to the a rather complicated transportation scheme which is shown in Figure 1.

Finally, the transportation scheme had to be reviewed since the GNS-11 transport container initially foreseen , will not be available.The use of a TN-2 container instead of the GNS-11 has been investigated.The final design of the primary box had not yet been received from KfK so that final reception tests could not be realized.

Finally, the situation was blocked at KfK since no hulls could be made available at KfK and since CEN/SCK decided to temporarily stop the programme in the expectation of a revised arrangement taking into account the dismantling costs.

TABLE I : COMPACTION TESTS WITH ZIRCALOY

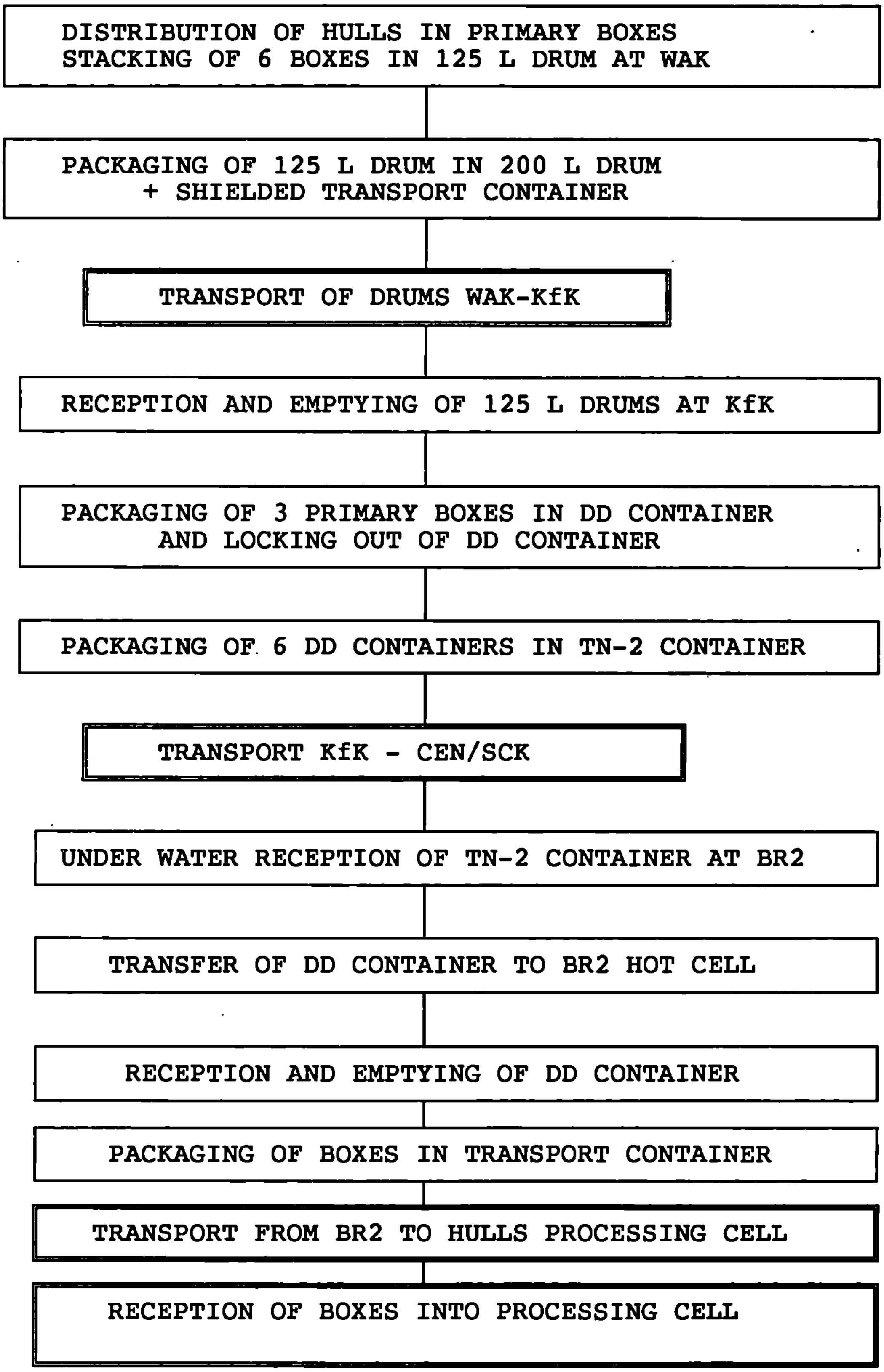
PARAMETER CHANGES WITH RESPECT TO REFERENCE PROCEDURE	COMPACTION PRODUCTS		
	DENSITY % T.D.	VRF	CLADDING MATERIALS CONTENT kg.dm-3
none	79.8	5.32	4.29
1 mm Pb		5.00	4.01
1 mm Al		5.00	4.05
step compaction	78.5	5.20	4.19
200 s post compaction	80.0	5.25	4.23

TABLE II : WELDING PARAMETERS

CONSTANTS: WELDING TORCH DIAMETER 1.6 mm
OSCILLATION FREQUENCY 3 Hz

PARAMETERS	S.S.INNER CONTAINER	LEAD CONTAINER WELDING PASS		S.S.OUTER CONTAINER
		1	2-5	
TORCH DISTANCE mm	1.5	1.5	0.8	1.5
ROTATION SPEED rpm	0.81	0.81	0.81	0.81
WELDING CURRENT A	50	50	50	75
OSCILLATION AMPLITUDE mm	3	7	7-12	3

FIG 1. TRANSPORT OF ACTIVE HULLS



CONDITIONING OF FUEL HULLS AND STRUCTURAL MATERIALS BY HIGH PRESSURE COMPACTION

Contractor: KfK, Karlsruhe, Federal Republic of Germany
Contract No.: FI 1W-0020-D (B)
Duration of contract: July 1986 - December 1989
Period covered: January 1989 - December 1989
Project leader: H. Frotscher

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 REPROCESSINGPLANT (WAK) was 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 large 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 packaged into HLW canisters without matrix.

B. WORK PROGRAMME

2.3.1 Inactive investigations of the behaviour of hulls under high pressure on a laboratory scale.
2.3.2 Inactive investigations of the behaviour of hulls under high pressure in technical scale.
2.3.3 Determination of the surface of inactive compacts as a function of the compacting pressure.
2.3.4 Corrosion behaviour of inactive hulls in Q-brine at 90°C.
2.3.5 Design and manufacture of press-dies and press-punches as prototype tools.
2.3.6 Conceptual design of a press facility for active H + S waste compacting.
2.3.7 Transport of active hulls and active densified products.
2.3.8 Investigations of gaseous activities form active compacts.

C. PROGRESS OF WORK AND OBTAINED RESULTS STATE OF ADVANCEMENT

A major part of the working programme aimed at the development of the radioactive cladding waste technique consists in conceiving a suitable pressing machine. Cold pressing of bulk claddings accompanied by large reduction in volume calls for high pressing forces with long effective path length at relatively low plunger velocities Only so-called force-dependent pressing machines are suited for this purpose. These are, in principle, the hydraulic presses.

PROGRESS AND RESULTS

2.3.5, 2.3.6 Design and manufacture of press-dies and press punches as prototype tools and conceptual design of a pess facility for active H + S waste compacting

The concept of a horizontal 4-cylinder press to be installed in the Hot Cell was selected as the best solution out of several investigated concept variants /1/

This report contains conclusions to the planning engineer about technical details of the selected concept. Its major advantages, namely

- little construction height of the press
- little mounting weight of the press components
- crane hook technique for remote assembly and maintenance
- simple cell block

do not demand particular requirements on the size and equipment of a conditioning cell. It allows the backfitting of an existing conditioning cell. This aspect has become of topical interest after the abondonment of the WACKERSDORF REPROCESSING PLANT and the obligation to take back hull waste from abroad, which has to be conditoned in a suitable way.

A special advantage of the concept is the modular design of the press which is open on all sides (Fig. 1). The using of the crane hook technique presuppose the free accessibility from top.

Fig. 1 shows also the main design details of the press: main-plate (1), mobile head-plate (2), piston-cylinder units (3), extended piston rod (4), press die (5) and ram (6). The press has been designed for a maximum compressive force of 25 MN. The axial ram pressure is about 200 MPa, the necessary oil pressure in each piston-cylinder unit is about 30 MPa.

Fig. 2 shows the functioning principle of the waste form production and the loading of the COGEMA container. The four main functions and the adequate working positions of the ram and the die are shown.

A concept is worked out for the remote replacement of wearing parts of the pressing tools and the maintenance of the four piston-cylinder units. It is planned to use exclusively the crane hook and impact wrench technique for these operations. Sealings of the press piston are replaced outside of the conditioning all. For this purpose, the complete piston-cylinder unit is transferred in a 400 l drum into the service cell which is accessible for personnel. It is planned to demonstrate the most important remote handling operations on a presently built four-cylinder functional model in technical scale.

2.3.7 Transport of active hulls and active densified products

The pressing tests with active WAK hulls at MOL have not yet been performed. The main reason for this delay has been the long phase of shutdown of WAK. SCK/CEN has meanwhile advised us that the active test at MOL are not practicable during this contract duration.

LIST OF PUBLICATIONS

/1/ H. Frotscher, KfK
Presentation of the progress meeting of working group no 2
on October 11-13, 1989, at Karlsruhe (D).

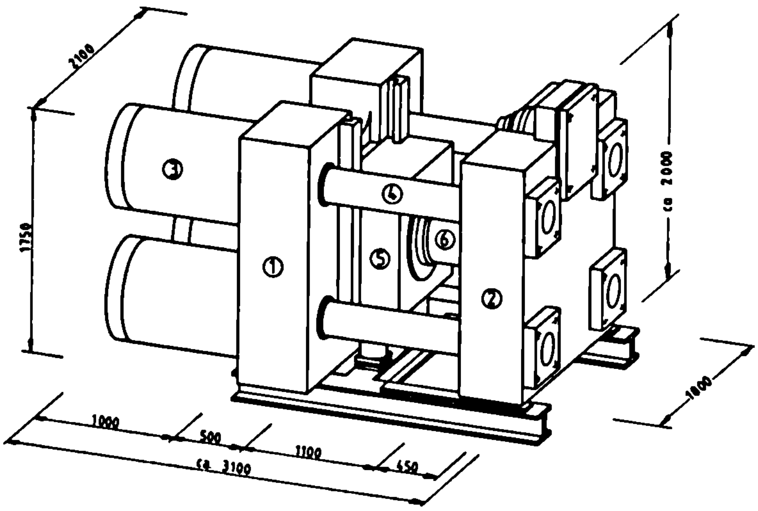


Fig. 1: HORIZONTAL FOUR-CYLINDER PRESS

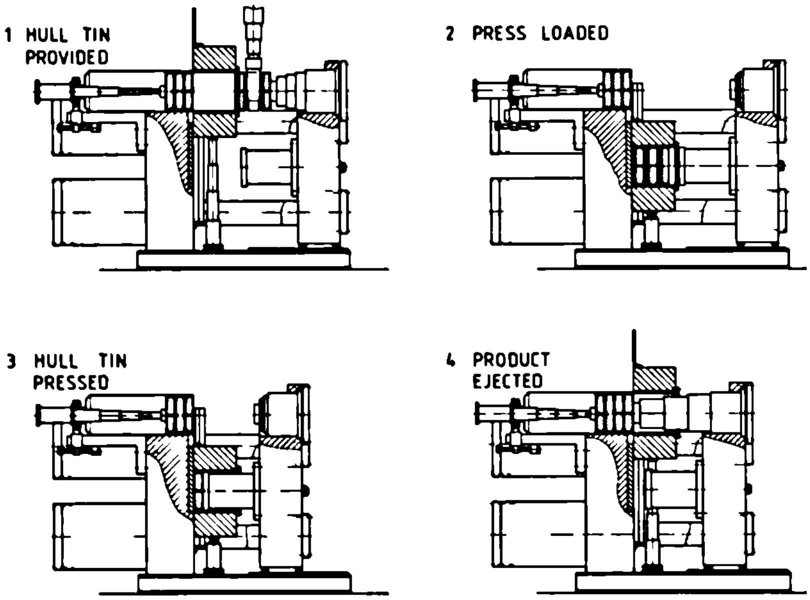


Fig. 2: FUNCTIONAL PRINCIPLE FOR WASTE FORM PRODUCTION AND LOADING OF COGEMA CONTAINER

SOLIDIFICATION OF TRU-WASTE BY EMBEDDING IN A CERAMIC MATRIX

Contractor : Kernforschungszentrum Karlsruhe GmbH / FRG
Institut für Nukleare Entsorgungstechnik (INE)
Contract N° : FI1W/0021-D (B)
Duration of contract : July 01, 1986 - December 31, 1989
Period covered : January 1989 - December 1989
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 alpha-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°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 1 E-7g/cm2d 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

1. : Determination of the maximum waste loading for the alumosilicate ceramic matrix with dissolver residues; characterization of the final products.
2. : Determination of the maximum waste loading for the alumosilicate ceramic matrix with TRU ashes; characterization of the final products.
3. : Determination of the maximum waste loading for the alumosilicate ceramic matrix with sludges, precipitated from acid digestion solutions; characterization of the final products.
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 products.
5. : Ceramization of TRU-waste-mixtures, according 1-4; characterization of the final products.
6. : Development of a technical process for the ceramization of TRU-waste. Construction of a pilot plant.

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

Main item during the year 1989 was the preparation, respectively the characterization of very high TRU-waste loaded alumosilicate-based ceramics KAB 78 containing

- TRU-slurries from simulated filtrate solutions, generated in the frame of the fuel elements fabrication.
- TRU-waste stream mixture consisting of dissolver residues, TRU-ashes, slurries, precipitated from alpha-active solutions.

X-ray powder diffractometry, optical light microscopy and scanning electron microscopy were the mostly applied investigation methods.
R&D-work on the development of a technical TRU-waste ceramization process has been performed in connection with the construction of a pilot plant.

Progress and results

4. Determination of the maximum waste loading for the alumosilicate ceramic matrix with sludges, precipitated from TRU solutions generated during the fuel elements fabrication

Experiments concerning the ceramization of TRU-slurries precipitated from filtrate solutions originated during the fabrication of MOX-fuel elements have been performed using a Pu-doped simulated solution where the TRU-slurries have been precipitated by alkalization and then separated from the filtrate, with a following washing step.
Subsequently five series of ceramic pellets have been produced with a TRU-sludge load from 20 to 60 wt.%, using the KAB 78 ceramic raw materials. In function of the increasing waste loading degree the samples

- densities increase from 3.05(7) to 3.68(7) g/cm^3,
- compressive strenght decrease from 448(46) to 284(20) N/mm^2.
- open porosities remain below 1 Vol.%.

Ceramographic investigations of these series of ceramics have been performed by means of optical light microscopy, alpha-autoradiography and half-automatically working image analysis so far.
The microstructure of these ceramics consists of a very fine grained matrix (grainsize >1μm) and randomly distributed inclusions (sizes up to 100 μm), which might be related to a Fe-rich phase. The (U,Pu)O2-phase was recognized as well.
Leaching tests according to the ISO-draft using Q-brine as leachant yielded plutonium leachrates between 2.5 E-7 and 8.5 E-8 g/cm2d after 50 days of total leaching time.

5. Ceramization of original TRU-waste mixtures, consisting of dissolver residues, TRU-ashes, TRU-slurries, precipitated from alpha-active waste solutions.

Aim of this item was the experimental demonstration on the feasibility to immobilize several waste streams simultaneously by ceramization, which might contribute to reduce the process expenditure and the final product volumes as well.
Dissolver residues, TRU-ashes, TRU-slurries, precipitaed from different alpha-active solutions (as described by items 1-4) have been mixed in equivalent proportions (wt.%). The resulting waste mixture was than homogeneized with the ceramic raw materials KAB 78 in order to produce ceramic products with waste loadings from 20-60 wt.%. The maximum sintering temperature were in the range between 1300 and 1360°C with 20 minuntes holding time.
In funtion of the increasing waste loading the samples

- densities increases from 3.40(6) to 3.90(5) g/cm^3,
- compressive strengths decrease from 355(45) to 150(430)N/mm^2,
- open porosites increase from 3.4 to 8.8 Vol%.

The microstructure of these samples consists of a very fine grained matrix (0<1μm), mostly corundum, mullite, a glassy phase and inclusions sized from several hundred microns down to submicroscopical diameters, which are belonging to the waste related phases.
ISO-draft related leaching tests using Q-brine as leachant yielded plutonium leachrates between 5 E-7 and 1 E-7 g/cm2d after 50 days of total leaching time.

6. Development of a technical process for nuclear waste ceramization; construction of a pilot plant.

The development of a technical process on nuclear waste ceramization has been performed by investigations on the most complicated process steps, using inactive equipments in a (half)technical scale. A twin screw extruder and the related dosing unit, which is able to achieve a throughput of 10-15 kg/h of ceramic green ware containing dissolver residues has been installed. The installation of a (half)technical heat treatment equipment has been performed, too.
Series of experiments focused on the process development have been carried out with emphasis to the process steps (i) "mixing" of ceramic raw materials and waste compounds, (ii) "handling" and transportation of waste streams, (iii) "heat treatment" of the ceramic green ware, including the off-gas-treatment.
Special problems on transporting high concentrated suspensions of dissolver residues could be solved by increasing its viscosity, by adding SiO2-aerosol, which avoids the sedimentation of solid particles.
The suitability on the performance of drying the green ware, respectively the waste suspensions, by passing a heated region of the extruder could be demonstrated principally. The required viscosity of the ceramic green ware to be extruded can be achieved by a following remoisturation. This procedure allows to achieve every desired loading degree of the ceramics, without respecting the amount of solid fraction of the waste slurries.
The final product qualities corresponds to those of TRU-waste ceramics synthesized by lab-scale technique. Transferring the nuclear waste ceramization process into a technical scale might be performed under resonable conditions.

D. PUBLICATION

Loida, A., Solidification of TRU-Wastes by Embedding into an Aluminiumsilicate Based Ceramic Matrix, 91st Annual Meeting of the American Ceramic Society, April 23-27, 1989 Indianapolis; Advances in Ceramic-Nuclear Waste Management (1989).

TREATMENT OF REPROCESSING CONCENTRATE BY EXTRACTION CHROMATOGRAPHY AND INORGANIC ION EXCHANGE

Contractor:	Kernforschungszentrum Karlsruhe, 7500 Karlsruhe, F.R.G.
Contract No.:	FIIW-0022 D
Duration of Contract:	July 1986 - June 1989
Period covered:	January 1989 - June 1989
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 cesium, 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 asses the performances of these alternative treatment processes for decontamination of reprocessing concentrate. The contract deals with the demonstration and feasibility for decontaminating medium level reprocessing concentrate through successive treatment involving experiments in 1, 20, and 100 l scale with simulated in an 1 and 20 l scale genuine ILW solutions.

B. WORK PROGRAMME

2.2 Complementary lab-scale experiments

2.3 Equipment installation for scale-up experiments

2.4 Inacitve testing with 20 and 100 l ILW simulants

2.5 Active testing in a 20 l scale in glass columns

2.6 Hot-cell decontamination and removal of the equipment

2.7 Data evaluation (design and flow sheet)

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The technical feasibility of the partitioning of genuine concentrated nitric acid intermediate level waste (ILWC) has been already demonstrated last year in a 1 l scale and the amount of secondary waste raising from the exchanger materials was estimated to about 300 kg. Whereas for Cs, Am, Eu, and Ce the breakthrough capacities had been determined before, this was in the case of Sb and Ru only possible by performing 10 l experiments with genuine ILWC.

As a final experiment in order to prove the feasibility of the chromatographic system 10 l ILWC from the German reprocessing plant (WAK) have been decontaminated in a hot cell by a filtration step on glass wool, absorption of organics on Bio Beads SM 7, removal of cesium in the suspended bed column using AMP-1 and retention of the remaining nuclides, Sb and Ru, on manganese oxide and dimethylglyoxime on carbon, respectively.

Progress and results

The technical feasibility of partitioning concentrated nitric acid intermediate-level waste (ILWC) solutions from the Purex process into a small volume of high-level waste and a large volume of low-level waste using sorption methods is demonstrated for 11-l batches.

Cesium-134 and ^{137}Cs are selectively separated with a decontamination factor (DF) greater than 1 x 10^5 in a newly developed "suspended-bed" column filled with the microporous inorganic exchanger ammonium molybdophosphate. The ^{125}Sb and the actinides and lanthanides with a 3+ valence state are retained with DFs between 40 and 1000 on metal oxides of antimony and manganese and on an extraction column containing n-octyl (phenyl)N,N-disobutyl carbamoyl methyl phosphine oxide, respectively. Ruthenium-106 and ^{60}Co are removed in a column loaded with dimethyl glyoxime and have DFs greater than 20.

The amount of secondary wastes arising from absorber materials was estimated earlier on the basis of 1 l experiments to be 300 kg for a 350 t/yr reprocessing plant with an ILWC volume of ~ 0.5 m3/t of heavy metal.

One of the main goals of this work was to check out the influence of a "scaling up" from laboratory scale to pilot plant operations. In this frame the comparison of the arising secondary wastes, estimated from the above mentioned 1 l experiments with the larger 11 l active experiments has shown that these wastes will be 1000 kg as calculated on the basis of exact results for the break-through points of ^{125}Sb and ^{106}Ru (Table I).

The second important aim of the work was to reach a decontamination of the ILWC, sufficient to meet the requirements of regulations limiting the dose of a transported containment to 2 mSv/h at a 1-m distance from the surface. Using the values obtained in this work for cementing the LLW effluent into 400-l drums at a 10 wt% loading, lead to a value of ~ 100 µSv/h; thus, this waste can be considered as LLW, which can be handled without any shielding.

Solving the problem of partitioning ILWC into a large volume of LLW and a relatively small volume of HLW raises the question of how to minimize the "secondary HLW" consisting mainly of the column materials used for the separation of the different elements, which are loaded with activity.

The distribution of the gamma-emitting nuclides on the filter and the various columns was determined in single experiments taking samples before and after each separation step. The results are summarized as follows: All the nuclides can be found to some extent on the filter, especially ^{106}Ru and ^{125}Sb (~ 45 %), whereas the Bio Beads SM 7 sorbing the organic contaminants are free from activity. The rest (85 %) of the $^{134+137}$Cs is selectively retained on AMP-1; thus, these isotopes do not reach the metal oxides, which show a very nonspecific sorption behaviour, completely removing the remaining 56 % of ^{125}Sb and adsorbing the other isotopes to a certain degree. The residual actinides and lanthanides (55 %) with a +3 valence and the remaining cobalt and ruthenium (59 and 27 %, respectively) are taken out of the solution in the CMPO and DMG columns, respectively.

It can be concluded from these results that the secondary waste can be treated individually according to the regulations of each country. The AMP-1 can be dissolved in alkaline media and used as a radiation source after solidification in a stable matrix or added to the HLW vitrification process. All the other columns can be considered for cementation or the glass wool filter at the moment. The Bio Beads SM 7 can be treated as LLW.

Tabelle I: Secondary wastes calculated on 11 l experiments

Absorbens		Amount of elements (g/350 t_{SM})	Amount of absorber	(350 t/a)
Material	Element		1 l (kg)	11 l (kg)
Glass wool	precipitate (Ru)	-	70*	92
SM 7	organic	-	50*	128
AMP-1	Cesium	105	2	2
Sb_2O_5/MnO_2	Antimony, Molybdenum	1155	70*	553
CMPO	Am, Eu, Ce	552	30	30
DMG	Co, Ru	5600	70*	252
		Total	292	1057

* estimated values

IMMOBILIZATION OF TRITIATED WASTE WATERS GENERATED DURING REPROCESSING BY SOLIDIFICATION AS ZIRCONIUM HYDRIDE

Contractor: KFA, Jülich, Federal Republic of Germany
Contract No.: FI1W/0139 D (B)
Duration of contract: September 1987 - December 1989
Period covered: January - December 1989
Project leader: H.J. Riedel

A. OBJECTIVES AND SCOPE

At present time it is planned to manage the tritiated waste waters which will be generated at the Wackersdorf reprocessing plant by simple injection into deep geological formations. An alternative management route is the immobilization of tritiated waste waters in a cementitous matrix followed by disposal in deep geological formations. However still another fixation option may be worthwhile further exploration. Zirconium sponge which traps gaseous tritium as zirconium hydride appears to be likely the most promising one, as shown in privious investigations carried out worldwide and also at KFA-Jülich.

These are the goals of the project:

- Identification of the tritiated waste waters which are expected to arise from the Wackersdorf reprocessing plant in order to define a representative waste for the subsequent experimental tests.
- Investigation of the possible electrodes poisoning, using suitable electrolysers. Particularly the nature of the interfering species influencing the lifetime and performance shall be investigated as well as the possible contamination of the generated hydrogen.
- Characterisation of zirconium hydride to demonstrate its suitability.
- Engineering aspects.
- Safety aspects.

B. WORK PROGRAMME

2.4.2. Continuing the experiments on the bonding of protium to zirconium sponge.
2.5 Proposal of a new and simple procedure for the zirconium hydride formation.
2.5.1 Proposal of a suitable waste packaging for transport and disposal.
2.6 Handling of hydrogen and transport - disposal operations in respect of safety.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The experiments on the bonding of protium to zirconium sponge samples were continued up to 100 g and finished. As a result of these experiments a new and simple procedure for the zirconium hydride formation is proposed. Hydrogenation takes place each with 100 g batches of zirconium sponge, so there is no need for a large-scale facility for handling and fixing HT which is only operated sporadically and thus exposed to deterioration during the downtimes.

In respect of safety, since fairly small quantities of tritium and protium (183 Ci of tritium in 22 litres of HT gas) are handled per charge the accidental potential is very low. Accumulation and storage of the approx. 10 m^3 of HT gas is thus dispensed with. The HT gas continously arising during enrichment in the CECE process can be directly fixed on zirconium sponge in batches of 22 litres.

A suitable waste packaging for transport and disposal in geological formations in proposed.

Concerning the transport and disposal operations for packaged wastes the criteria established by the german safety authorities for this waste type are outlined.

Progress and results

Our numerous experiments provided the following results:

The reaction of Zr with H_2 for the formation of $ZrH_{1.8}$ best proceeds with sufficient reaction rate at a temperature of approx. 800 °C. Below this temperature there is a danger that the reaction might be arrested since a passivation of the materials results from Zr hydride formation at its surface and that a post-diffusion of H_2 molecules with less molecular motion at lower temperatures no longer takes place with adequate rapidity. The temperature thus drops further and the reaction for Zr hydride formation comes to a complete standstill. The formation which starts at room temperature and within a short period reaches a temperature of 850°C in the Zr sponge only leads to a through-reaction if a sufficiently high H_2 concentration is supplied. The optimum was determined by us as an H_2 concentration of 5 - 10 % of the total H_2 quantity required for stoichiometric loading. For 50 g of Zr sponge a continuous H_2 pressure of 700 - 800 hPa must be available in the used apparatus in order to achive complete Zr hydride formation. (Table 1 and Table 2). We therefore propose the following procedure: In each case 100 g of Zr sponge is loaded with 0.985 mol HT (22 nl) to $ZrHT_{1.8}$. For the reaction start 10 % (2.2 nl HT) should be immediately admitted into the evacuated hydrogenation vessel where the "activated", i.e. pretreated by annealing for 2 hours at 500°C in a vacuum (10 - 5 hPa), Zr sponge is situated. Hydrogenation may be implemented in quartz glass vessels. Apart from the possibility of visually following the reaction sequence, even at 850 - 900°C quartz glass has an H_2 permeability four orders of magnitude smaller than that of steel.

The mechanical stressing of the glass due to the increase in volume of the Zr sponge during hydrogenation, which could lead to fracturing the glass, is prevented by placing the pieces of Zr sponge in a wire cage (wire thickness: 0.65 mm) leaving a space of approx. 2 mm from the quartz glass walls.

A problem still to be solved is the precise measurement of the H_2 quantity being rapidly fed in. This is important in order to achieve the desired stoichiometric loading. - The zirconium hydride formed is compact and not brittle.

At the end of the reaction when a residual H_2 pressure of 10^{0} - 10^{-3} hPa has been achieved, 11 mCi to 11 μCi of tritium is still present in the hydrogenation apparatus (starting from an HT with 0.32 % T). The apparatus is therefore flooded with protium which is then catalytically oxidized to H_2O and frozen out in a cold trap whereby the residual tritium is removed to such an extent that the hydrogenation vessel can be flanged of in the glove box. Still in the glove box the wire cage with the 100 g of hydrogenated zirkonium sponge is removed and placed in the stainless steel cask until it is full for final storage. This stainless steel cask (volume: approx. 2.8 litres) can be closed by means of a Leybold flange with aluminium gasket and tension chain.

Two container concepts are designed to accomodate ten stainless steele cylinders each containing Zr sponge as the carrier material for binding tritium. Due to the same number and type of Zr hydride cylinders (stainless steel cylinders) contained in the package variants, the stored ^3H activity inventory is always $2.5 \cdot 10^{15}$ Bq (approx. 67,500 Ci) in both final packages. The ten cylinders are placed into positions of a carrier basket contained in the inner canister both are manufactured from corrosion resistant steel. They are similarly designed for both container concepts and thus exchangeable with respect to the package variants. - Since a multi-shell package with double barrier function is envisaged for the safe containment of the radioactive contents, the inner canister is designed as a leaktight enclosure representing the first barrier with respect to activity release. The inner canister bolted with a lid contains several gaskets and test closures as a first sealing barrier for checking the seal function and is designed so as to ensure leaktight containment of the inventory for loads occuring under operating conditions. Consequently, the mechanical designe of the inner canister is based on the following load cases occuring simultaneously:
- Max. acceleration and delay of 10 g in handling
- tightening pressure of bolts to overcome the metal O-ring resistance
- max. overpressure of 0.7 MPa within the inner canister.

The differences between the two container concepts proposed therefore relate only to the outer packages due to the uniform inner canister concept for both variants. However, the outer packages proposed must both exhibit the same safety properties and posses the following protective functions as a second barrier:
- mechanical and thermal protection against operatinal and accident doads
- leaktight containment of the radioactive contents
- corrosion protection.

The variant A outer package will be the standardized type II cast-iron container which is already available in large numbers and has been licensed as a type B package under road traffic law. Moreover, it fulfills the requirements for waste category-II containers stipulated in the provisional conditiones for acceptance at the KONRAD repository. A type B licence is required for both outer packages (variants A and B) due to the high activity inventory. The type B properties still have to be demonstrated for variant B in a type test procedure. - The advantages of the special variant B container adapted to the inner canister result from its weight being lower by a factor of 1.6. Besides lower space requirements for interim storage, the outer package B offers better resistance to external presureloads in a repository due to its smaller diameter. The bolt connections for both outer packages are designed in such a way that the stresses in the fillister-head screws are by a factor of 3.4 to 5.2 below the yield point of 640 N/mm^2 for property class 8.8 screws in the event of simultaneously occuring operational loads such a handling acceleration of 3 g and an internal overpressure of 7 bar. This ensures the safe containment of the radioactive inventory at any time under operating conditions. (Fig. 1 and Fig. 2)

The provisional conditions for acceptance at the KONRAD repository /1/ only permit a max. activity inventory for tritium as HT of 9.6×10^{11} Bq per container. The package concept under consideration does not comply with this limit. The final disposal capability of these packages for the KONRAD repositories will have to be demonstrated in a separate procedure. The relevant procedure is described in Annex III.1, last but one section, of the provisional conditons for acceptance at KONRAD /1/. - The final disposal package concept under consideration emplies with the annual permissible limit of 9.6×10^{15} Bq so that final disposal should be possible via a separate procedure.

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RIEDEL, H.J., Sixth Progress Meeting of Working Group Task No. 2, on Improvement of Waste Treatment and Conditioning Technologies.
Karlsruhe, Germany, 11. - 13.10.1989

TABLE 1

specimen nr.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46
1-2g Zr	0	→			→			→			→		←			←			←			←			←						0	→			←		→		←					12g	9g	9g
3-8g Zr																											0	0	0	0											0	0	0			
annealing 60 min	0	0	0	0																																										
" 90 min					0																																									
" 120 min						0	→			→			←			←			←			←			←		→			→		←			←		→			→		←			←	
loading after 15 min	0	0	0	0	0	0	0	0	0																										0	0	0	0								
" " 30 min										0	0					0		0																0					0	0						
" " 45 min														0			0		0																											
" " 60 min												0	0		0					0	0	0			0	0	0	0	0	0	0	0	0								0	0	0	0	0	0
" " 90 min																							0	0																						
loading one charge	0	→			→			→			→		←			←			←			←			←												0	0	0	0				0	0	0
" batchwise																											0	→			→				←						0	0	0			
pressure·10 mbar																											0_1	→			→				←						0_1	0_1	0_1			
" < 500 mbar	0	→			→			→			→		←			←			←			←			←																					
" > 500 mbar																											0_2	→			→				←		0	0	0	0	0_2	0_2	0_2	0	0	0
H_2 supply < 1.5%																											0_1	0_1	0_1	0_1	0_1										0_1	0_1	0_1			
" " < 2 %																																0_1	0_1	0_1	0_1	0_1										
" " > 2 %																																														
" " > 10%	0	→			→			→			→		←			←			←			←			←		0_2	→			→				←		0	0	0	0	0_2	0_2	0_2	0	0	0
immediate reaction			0			0	0	0	0	0	0		0	0		0		0	0	0	0	0			0	0	0	0	0	0	0						0	0			0	0	0	0	0	0
slow --	0	0		0	0							0			0		0						0	0											0	0				0						
creeping --				0	0										0		0	0					0	0											0	0			0							
no --																																0	0	0												
end-pressure > 10^{0} mbar	0	0	0							0		0			0			0					0	0								0	0	0	0				0							
10^{0} mbar				0	0											0	0			0																0										
10^{-1} mbar						0					0		0	0																										0						
10^{-2} mbar							0	0	0													0			0	0																				
10^{-3} mbar																			0		0						0	0	0	0	0						0	0			0	0	0			
remarks	1															5	5	5	4								2																	3	3	3

TABLE 2

specimen nr.	47	50	51	52	53	54	54 a	55	56	57	57 a	58	59	60	61	62	63	64	65	65 a	66	67	68	69	70	70 a	71	72	73	74	75	76	77
1-6g Zr	0		0																														
10-20g Zr		0		0	0	0	0	0	0	0	0	0	0	0	0	0	0																
50-60g Zr													/					0	0	0	0	0	0	0	0	0							
loading after 15 min		0	0	0	0	0	0	0	0	0	0	0									0	0											
" " 30 min													0														0	0	0	0	0	0	0
" " 60 min	0													0	0	0	0	0	0	0			0	0	0	0							
" batchwise	0	0	0											0	0	0	0	0															
Pressure fixed				0	0	0				0		0																					
" " readjusted			0				0	0	0		0		0	0	0				0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
pressure 100 mbar	0	0	0_2	0	0	0	0		0	0		0	0	0_2		0_2		0_2	0	0	0	50	0	0	0	0							
" 500 mbar								0								0_3	0_2	0_3															
" > 500 mbar			0_1								0			0_3	0_2												0	0	0	0	0	0	0
H_2 supply < 1.5%														0_1	0_1	0_1	0_1	0_1	0	0	0	0	0	0	0	0							
" " < 2 %																		0_2															
" " > 2 %		0	0_2	0	0	0	0		0	0		0	0	0_2		0_3	0_2	0_3														0	0
" " > 10%	0		0_1					0			0			0_3	0_2												0	0	0	0	0		
immediate reaction			0_1				0	0	0		0		0		0		0				0	0		0					0	0	0	0	0
slow --														0_3		0_3		0_3		0			0			0							
creeping --		0		0												0_2		0_2	0	0			0			0	0	0					
no --	0				0	0				0		0		0_2											0								
loading stoichiometr			0					0	0		0		0	0	0			0			0	0								0	0	0	0
" < 10%		0		0			0									0	0		0	0			0	0		0			0				
" ± 2%	0				0	0				0		0													0		0	0					
Temp. Zr < 800 °C		0		0															0					0		0	0	0					
" " > 800 °C.			0				0	0	0		0		0	0	0	0	0	0		0	0	0	0						0	0	0	0	0
remarks											6			2							7	7				8	9 10	10	5 11	5	5	5	5

remarks

1) endpreassure 10^{0}mbar u. < = good stoichiometric loading 2) Index = Charge 3) reaction temp. i. the Zr

4) from specimen 19 onwards in wire gauze cages 5) loading socket not heated 6) Zr- 1250°C

7) loading at 500 °C 8) reaction vessel cooled 9) nr. 71 onwards: 100 g Zr 10) Teflon back-up ring 11) see text

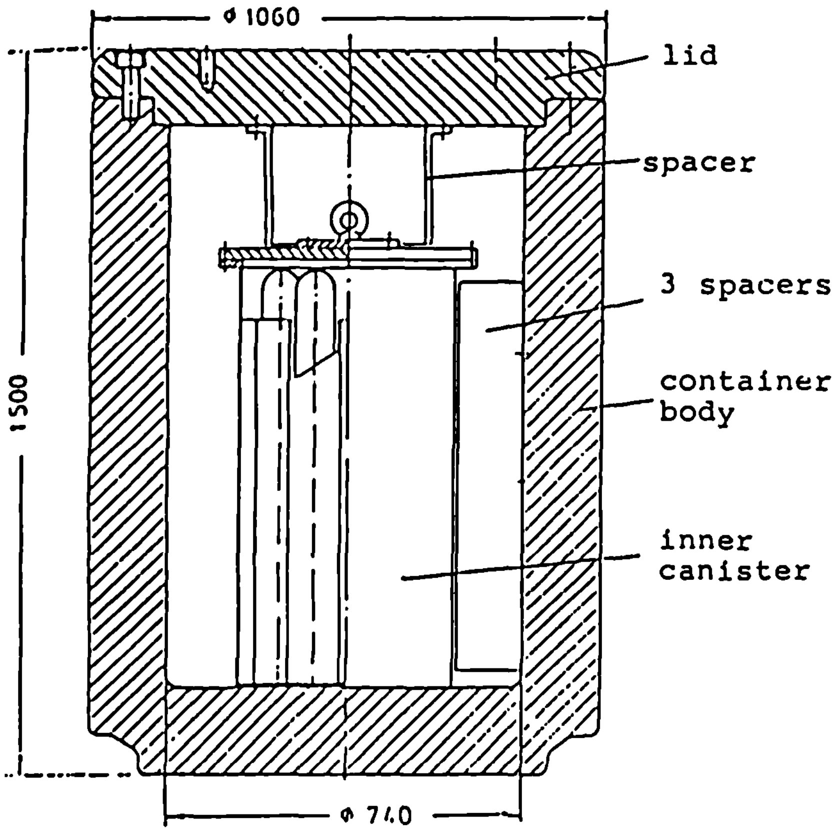


Fig. 1 - Outer packaging variant A with placed-in inner canister

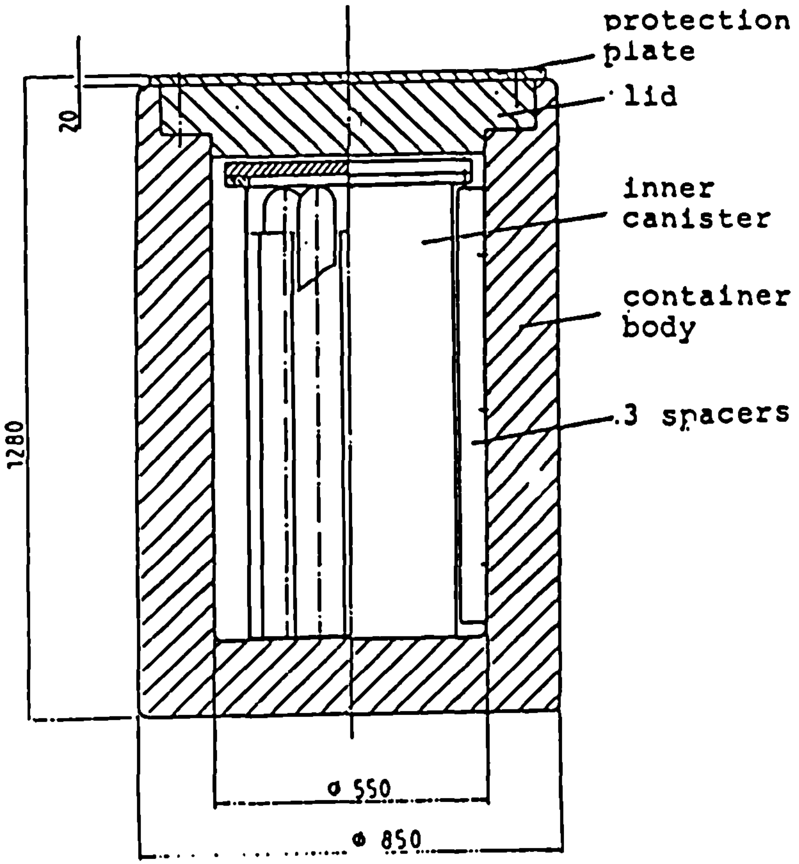


Fig. 2 - Outer packaging variant B with placed-in inner canister

DECONTAMINATION OF Pu-CONTAINING INCINERATION ASHES

Contractor: KfK, Karlsruhe, Federal Republic of Germany
Contract No.: FI1W/0140
Duration of contract: October 1987 - January 1990
Period covered: January 1989 - December 1989
Project leader: K. Gompper

A. OBJECTIVES AND SCOPE

The incineration of Pu containing waste (PCW) is one of the most promising treatment options because of its high volume reduction factor. In this respect, the arisings of Pu containing incineration ashes are expected to increase in the near future. As the Pu content in these ashes may reach high figures (up to 10 wt.-%) their disposal could become problematic in consideration of disposal criteria set up by safety authorities. Likewise, it may be valuable to recover Pu from these ashes for recycling purposes in LWR's. Therefore, the setting up of an effective Pu recovery process appears worthwile.

The main activities of the project are:

- Analysis of literature data on Pu recovery processes
- Evaluation of the experimental results of the ALONA plant for decontamination of the Marcoule alpha ashes.
- Experimental activities for setting up a suitable process.
- Assessment of the perfomance of this new process.
- Preliminary cost evaluation for a plant prototype.

B. WORK PROGRAMME

2.3. Literature survey
2.4. Evaluation of the experimental test performed in the ALONA plant.
2.5. Experimental tests
2.5.1. Characterization of the KfK and Marcoule incinerator ashes.
2.5.2. Ashes pretreatment
2.5.3. Pu recovery from ashes
2.5.4. Pu purification
2.5.5. Evaluation of secondary waste
2.6. Drawing-up of flow sheets
2.7. Cost evaluation

C. PROGRESS OF WORK AND OBTAINED RESULTS

The sulfuric acid/nitric acid system has proved to be generally useful in the treatment of plutonium bearing ashes produced by EURCHEMIC in the ALONA facility. It has been possible to convert into $Pu(SO_4)_2$ up to 99% of the insoluble plutonium. However, it appeared that the concentrated sulfuric acid used in PuO_2 digestion had to be completely replaced as early as after about 0.6 kg ash per liter throughput, on account of its being saturated with dissolved residue. In order to avoid this drawback, the majority of the inactive accompanying substances must be dissolved from the ashes before PuO_2 can be actually digested using sulfuric acid. Nitric acid is examined as an eligible solvent because it is used anyway to oxidize the carbon left in ashes.

The experiments have been continued with two ashes (1-7-88 and 1-8-88) from inactive trial operation of the new KfK incineration furnace. The have served as model substances. To characterize them, the carbon and chlorine contents have been determined and X-ray diffraction diagrams taken of the crystalline phases. The experiments have centered around investigations into the behaviour of the ashes with respect to sulfuric acid and nitric acid in order to obtain information about the solubility of the ash constituents. It has been the target to extend the duration of reaction of sulfuric acid as digesting reagent for PuO_2 by elimination of the soluble ash constituents through pretreatment with nitric acid.

2.5.1. CHARACTERIZATION OF THE KfK INCINERATOR ASHES

The ashes do not contain any chlorine and only 1-2% carbon. The calcite and anorthite crystalline phases and, to a lesser extent, mullite were detected.

2.5.2 ASHES PRETREATMENT

- Behaviour with Respect to Sulfuric Acid

Both ashes (1-7-88 and 1-8-88) were subjected to the conditions of PuO_2 digestion in sulfuric acid. The ash to sulfuric acid ratio was varied from 100 to 500 g/l. The solubility of most of the ash constituents is not dependent on the ash to acid ratio. Only for sodium and calcium the solubility decreases with increasing ash concentration. The two ashes were nearly identical in their solution behaviour despite the slight differences in chemical compositions.

- Pretreatment of the Ashes with Nitric Acid and Digestion of the Residues in Sulfuric Acid

By pretreatment with nitric acid it was possible to dissolve a much higher percentage of the ash constituents than with water. On the whole, the ash 1-8-88 was slightly less soluble in 2-14 molar nitric acid (about 25%) compared with the ash 1-7-88 (about 30%). The best solubility of more than 80% was achieved for calcium. Except for Cr, Fe and Mg, no noticeable influence has been found of the acid concentration. For chromium and iron the solubility slightly increases with increasing acid concentration, whereas it decreases for Mg. The results are similar to those obtained for the ash 1-7-88.

By heating of the residue in sulfuric acid the solubilities of the elements Na, K increased by a factor of 2-3, that of the other ash constituents rose hardly.

2.5.3 PU-RECOVERY FROM ASHES

During the period of reporting the recovery of plutonium from two α-bearing ashes has been investigated. The ashes have been treated in three steps:

Pretreatment includes boiling in diluted nitric acid (step 1). The non-dissolved residue is treated with concentrated sulfuric acid at 250°C in order to digest plutonium oxide (step 2). This step serves to transform plutonium oxide in sulfate which is precipitated almost quantitatively. To dissolve plutonium sulfate the insoluble residue is picked up with diluted sulfuric acid or nitric acid, respectively (step 3). The dissolved plutonium produced in that step can be returned for further processing after it has been purified. The rate of recovery is determined by comparision of the concentration of the dissolved plutonium in step 3 with the plutonium originally present in the ashes.

- Ashes D EUR 1/1

These ashes stemmed from waste produced at EUROCHEMIC, which was incinerated in Marcoule. Their Pu-content was 94 mg/g. 3-5% of plutonium present in the ashes got dissolved during pretreatment with 1 molar nitric acid. 3-7% was measured in the concentrated sulfuric acid after a digestion period of 8 hours. After the last step, i.e. dissolution of plutonium sulfate, between 77 an 90% of plutonium was found in the diluted sulfuric acid, which means that the rate of recovery in these experiments was between 77 and 90% (Figure 1a).

- Ashes 1-8-88Pu

These ashes stemmed from the inactive trial operation of the new KfK incineration facility. They served as model substances for residues from this type of incinerators . It is not intended at KfK to recover plutonium from the α-bearing ashes.

The ashes were added plutonium oxalate and heated to 800°C. The plutonium content of 1.3 mg/g was about 70 times lower than in D EUR 1/1. In order to allow a comparision to be made, the experimental conditions corresponded to those for the ashes D EUR 1/1.

After step 1 only 1-2% of plutonium originally present in the ashes were found in 1 molar HNO_3. The concentrated sulfuric acid used for digestion contained between 44 and 64% because the plutonium sulfate formed due to the low plutonium concentration remained dissolved. Only 6-10% was found in 0.1 molar sulfuric acid. Between 27 and 47% of plutonium remained undissolved in the residue (Figure 1b). Subsequent work has concentrated on the extention of the digestion period. Moreover, the sulfuric acid digesting reagent has been used repeatedly to further reduce the plutonium losses.

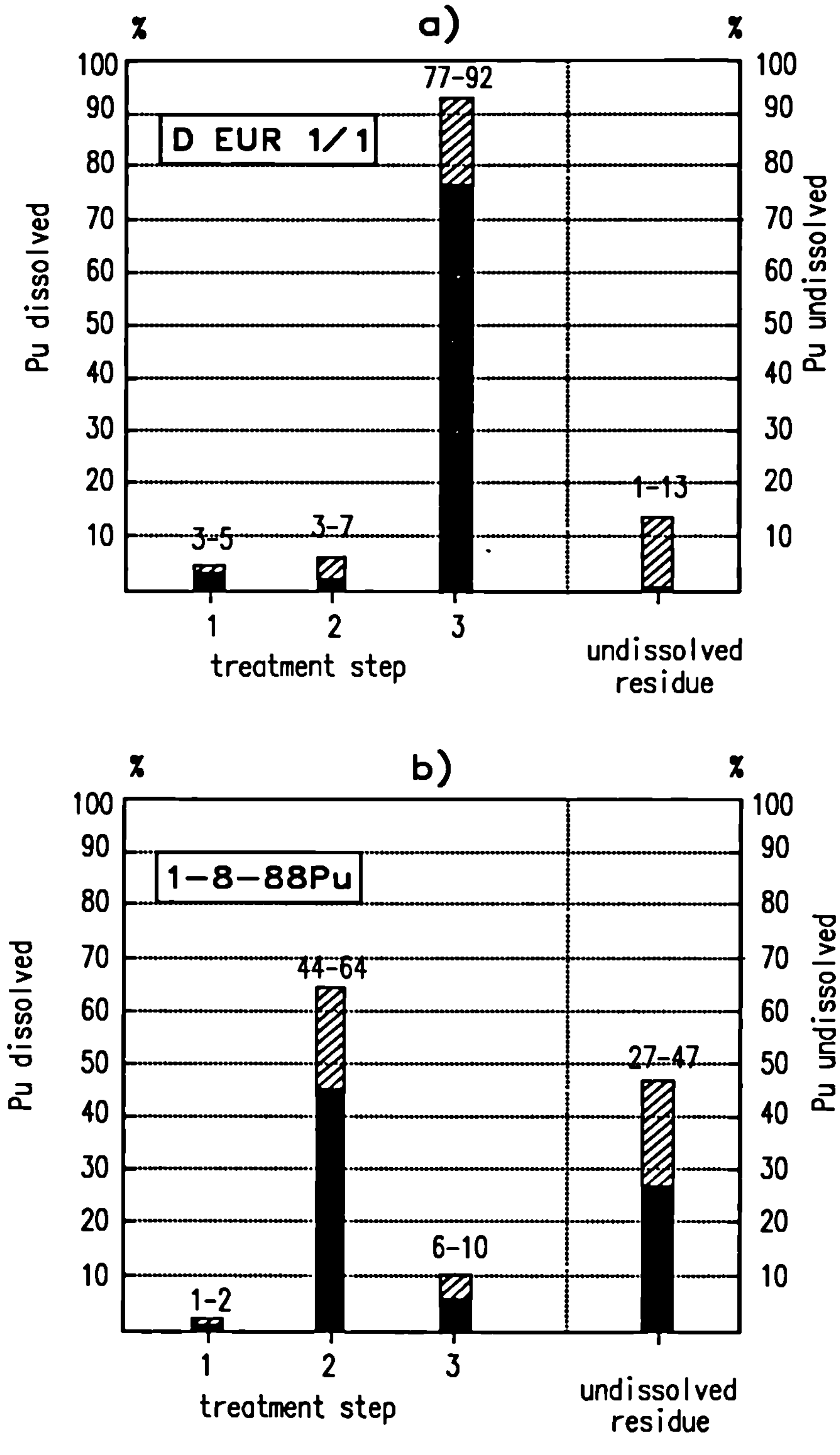


Figure 1: Pu -recovery from the ashes D EUR 1/1 (a) and 1-8-88Pu (b)
Step 1: Pretreatment with HNO_3
Step 2: Digestion with H_2SO_4
Step 3: Dissolution of $Pu(SO_4)_2$

Thermal denitration of reprocessing concentrate

Contractor : CEA, CEN-Cadarache, France
Contract n° FI.1.W.0141
Duration of contract : January 1988 - December 1989
Period covered : January 1989 - December 1989
Project leader : C. BRUGNOT

A. OBJECTIVES AND SCOPE

To reduce radioactive discharges in environment at the Marcoule reprocessing plant, the treatment of low and medium level liquid wastes by evaporation will take the place of chemical precipitation process. Due to the high sodium nitrate concentration of liquid wastes, the bituminization of concentrate will give rise to large volumes of waste forms for disposal in geological formation.

For safety objectives and to reduce the volume of wasteforms, it is important to destroy the nitrates ; different processes have been examined (electrodialysis, biological denitration, chemical denitration, calcination) but the fluidized bed calcination was chosen.

This project presents six main points :

- Analysis of the litterature data to show what advantages and drawbacks are for each denitration process which is quoted before.
- Conception and realization of a fluidized bed calcinator.
- Determination of the working conditions by studying in discontinuous working the influence of different parameters.
- Tests in continuous working.
- Evaluation of results and study of a conditioning way for the products obtained by calcination.
- Elaboration of a plan for an industrial plant able to come up to the expectations of the Marcoule reprocessing plant.

B. WORK PROGRAMME

2.2. Definition of the aims of the treatment ; modification involved by evaporation for the treatment of low and medium-level wastes will be studied.
2.3. Analysis of different denitration processes to explain the choice which was made with fluidized bed calcination.
2.4. Conception and realization of a fluidized bed calcinator the working of which will be explained. The treatment of gaseous wastes will be also described.
2.5. Determination of working conditions by studying the influence of different parameters.

3.1. Bed-temperature between 500-1000°C
3.2. Nature and concentration of the additive used to prevent agglomeration of the particules
3.3. Nature, concentration and granulometry of material used in the fluidized-bed
3.4. Flow and concentration of the solution to denitrate
3.5. Flow of the fluidizing gas
3.6. Place and type of the atomiser (nozzle)
3.7. Reaction time
All these experiments will be carried out with inactive products, in discontinuous working.

2.6. Experiments in continuous working
2.7. Evaluation of the results ; the packaging way of concentrates will be studied.
2.8. Elaboration of an industrial plan by extrapolating the characteristics of the pilot scale denitrator to an industrial scale.

C. PROGRESS OF WORK AND OBTAINED RESULTS
State of advancement

To destroy the nitrates in the concentrate obtained by evaporation of low and medium - level wastes, different processes have been examined : electrodialysis, biological denitration, chemical denitration, calcination. Taking into account the very high sodium nitrate content, electrodialysis and biological denitration were discarded. Experiments carried out at Cadarache led us to prefer calcination to chemical denitration by formic acid and phosphoric acid.

A calciner was designed and built, at the pilot scale, to carry out experiments of denitration of concentrates. To position the injection apparatus, we began by experiments on a transparent scale-model. Thanks to the results obtained at 150°C, we could choose the most appropriated injection apparatus and conclude that positionning the nozzle vertically, inside the fluidized-bed, was the best solution. To work on the pilot at higher temperatures, we have defined a cooling system for the brace in order that the liquid doesn't vaporize before being atomized in the layer of particles. We have begun experiments on the pilot, at about 500°C, to verify the working conditions determined just before.

In parallel with this experimental study, we have begun a modelisation study of the particle growth in the fluidized-bed. The results obtained for the discontinuous working of the process are rather encouraging, but they must be compared with the experimental ones

Progress and results

In a first time, different denitration processes have been examined. After electrodialysis and biological denitration have been discarded, ceramisation tests have been carried out on the products obtained by chemical denitration and have given bad results. On the other hand, the same tests carried out on the products of calcination have led to more attractive results. So the fluidized bed calcination process was chosen, according with the good results obtained by different industrial plants at Idaho. So the calcinator was built. It must work in the following way : liquid wastes with a high sodium nitrate concentration will be mixed with aluminium nitrate and injected in a sand fluidized-bed, the granulometry of which will be well defined. Aluminium nitrate must prevent agglomeration of the bed particles heated between 500 and 800°C. A silicate must be obtained, which will be converted into nepheline ($Na\ Al\ Si\ O_4$) by a later treatment.

The calcinator is presented in figure 1.

At the top of the reactor, we find a cyclone at the exit of which a gas analyser is placed ; this analyser will enable to follow the evolution of the denitration reaction by measuring NO and NO_2.

One of the most important problems to solve with this calcinator concerned the type and the position of the injection apparatus. Experiments have been carried out on a transparent scale-model. The first results obtained with non-heated particles have been then confirmed by those obtained on heated particles (at about 130°C). The injection apparatus will be a pneumatic atomizer working with pressurized liquid (Figure 2) ; the nozzle will be positionned vertically, inside the layer.

To work on the pilot, at higher temperatures, we had to define a cooling system for the injection apparatus. Indeed, in a layer of particles at about 500°C, the brace and the nozzle would get very hot and the liquid would be very quickly vaporized. So, after different estimates, we have decided to choose a cooling system with air circulating in two concentric tubes (Figure 3).

This injection apparatus has been installed on the pilot.

After the first experiments carried out on the pilot with a bed temperature of 500°C, we could verify that the injection system is working properly, with a constant liquid flowrate (2 l/h). But we have problems with the cooling system : we can only reach a rather low air flowrate (< 4,5 m^3/h). So we must verify that this flowrate will be sufficient to prevent the injected liquid from vaporizing.

Nevertheless, these first experiments have been encouraging . We have begun a modelising study of the particle growth in the fluidized-bed. The injected solution will cover the particles, the diameter of which will increase.So there will be a permanent evolution of the fluidized-layer characteristics, that it will be necessary to foresee, to control the good working of the process. If we success in finding the best mathematical model, it will be easier and faster to determine the most appropriate working conditions.

Since we don't know the kinetics of the formation of nepheline (the product which must be obtained), we have used kinetics of particle growth. This mathematical model is based on a linear expression of the growth as a function of the diameter (Figure 4). The first results obtained in discontinuous working are rather encouraging because they correspond to the expected physical phenomenons. But, before completing them by studying the continuous working of the process, we will have to compare these results with the experimental results.

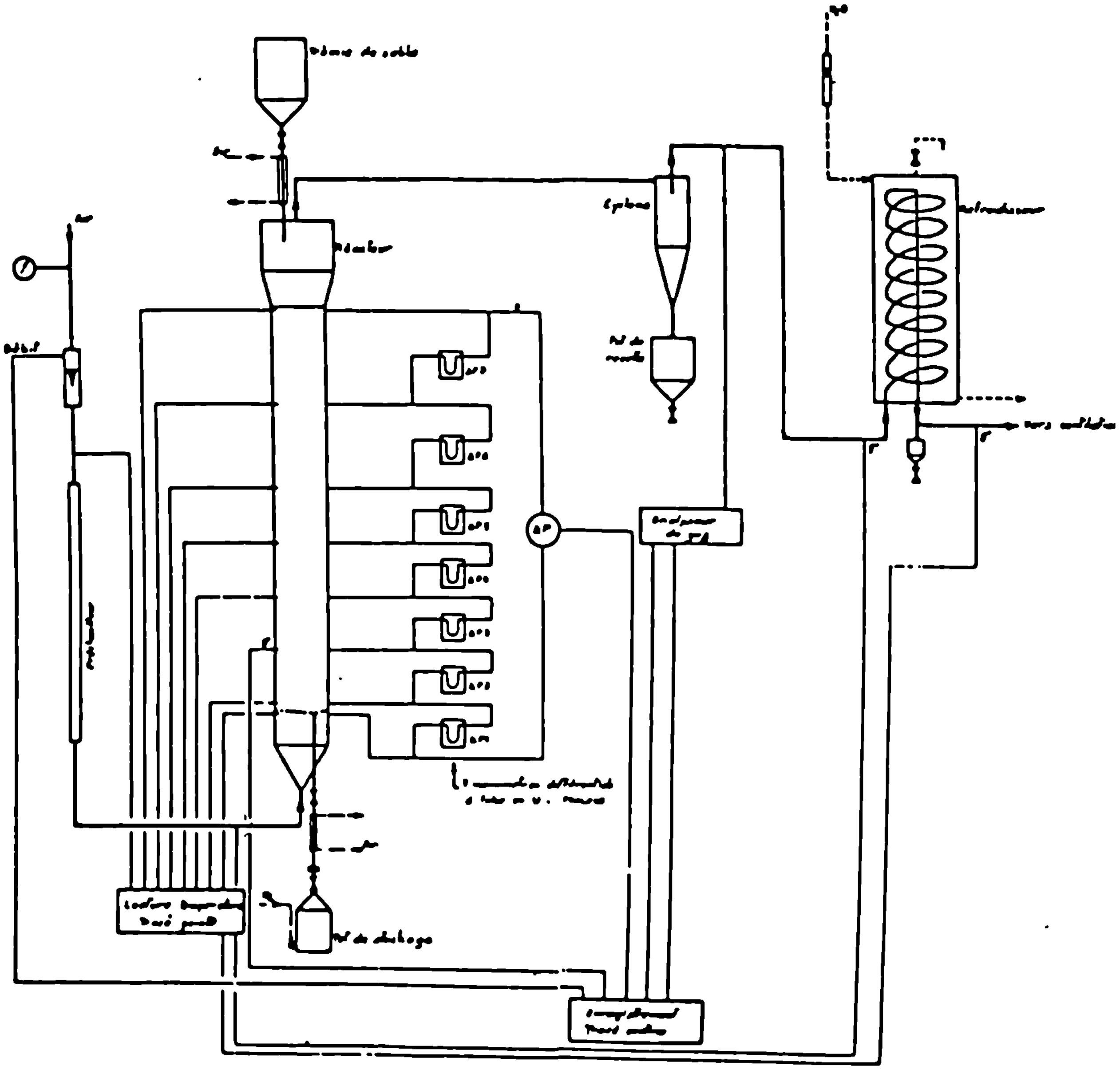


Figure 1 : Schema of a calcinator

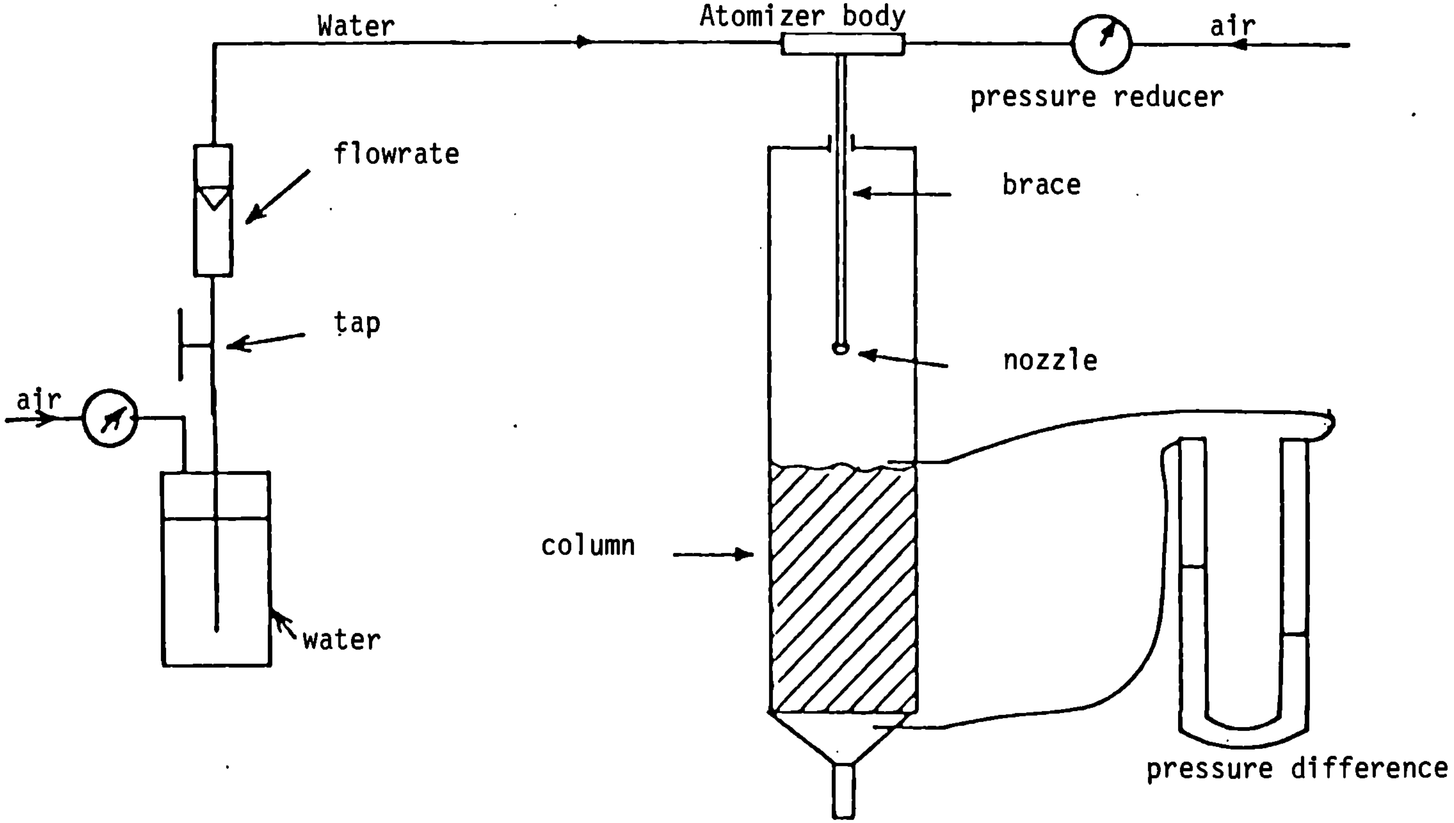


Figure 2 – Injection system in the calcinator

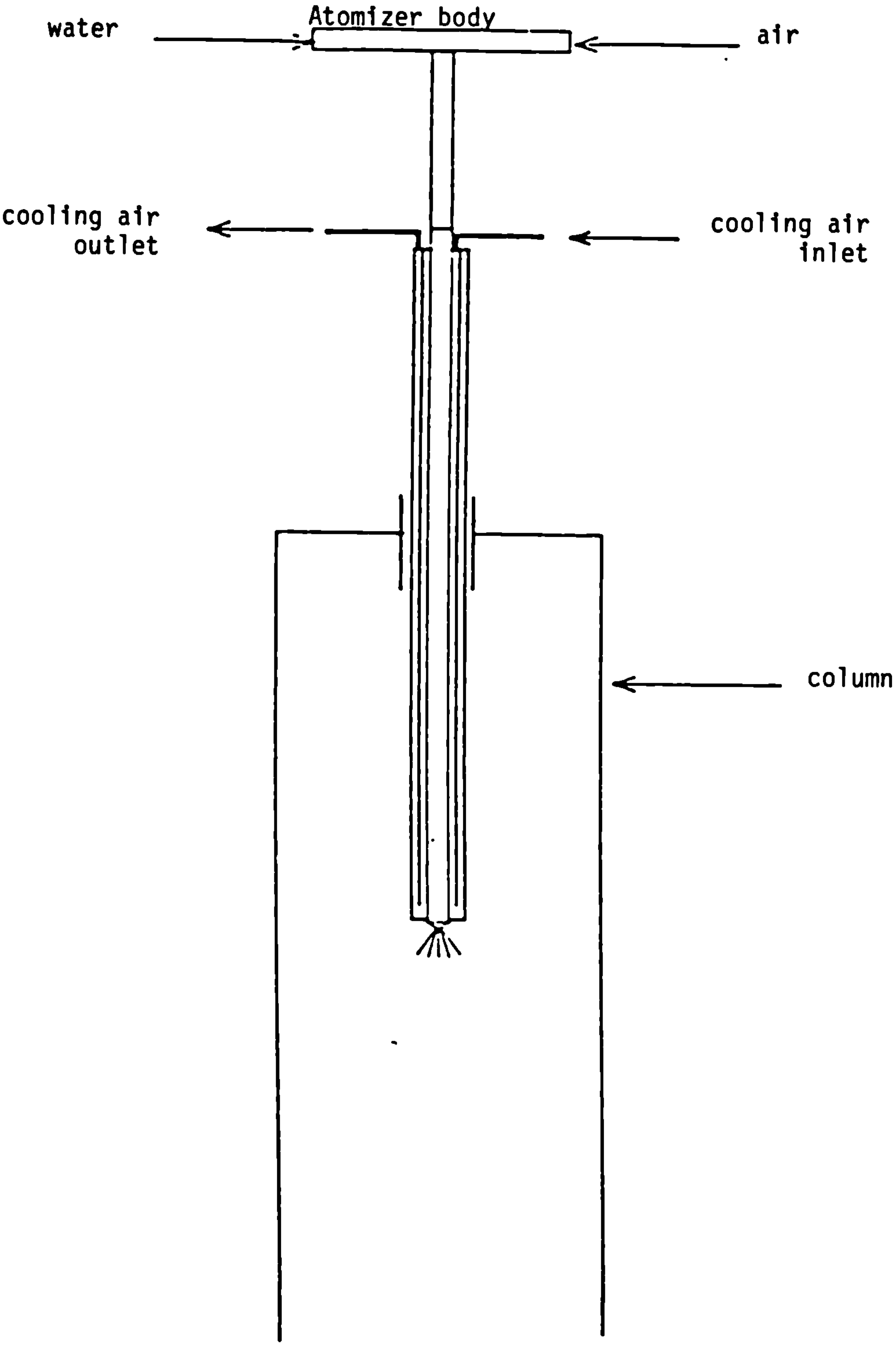
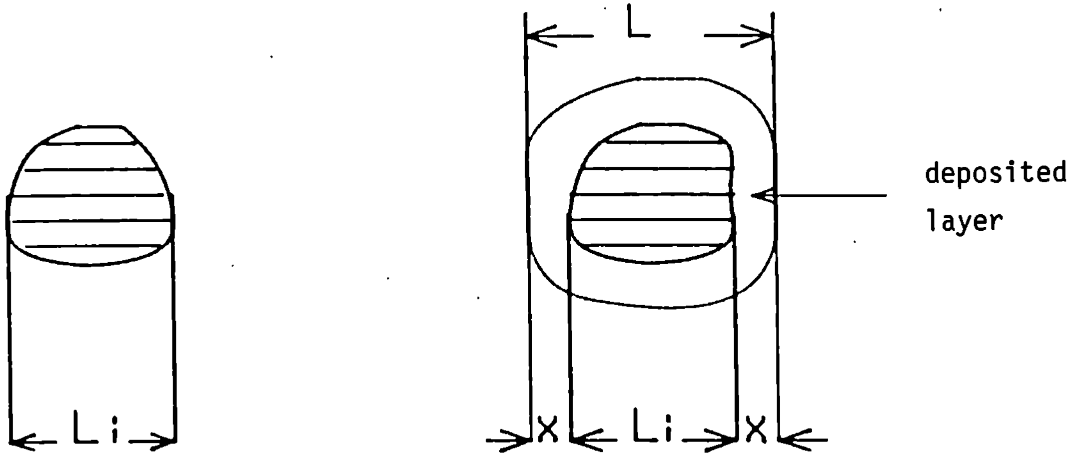


Figure 3 - Cooling system on the injection apparatus



particle at first

particle during deposition

$$\frac{dL}{dt} = 2\,\frac{dX}{dt} = K\,(A + B\,L)$$

Figure 4 – Particle growth in the fluidized-bed

TASK N. 2

2.C. OPTIMIZATION OF WASTE MANAGEMENT AT SOURCE

NO WORK HAS BEEN CARRIED OUT DURING 1989

TASK No 3

EVALUATION OF CONDITIONED WASTE AND QUALIFICATION OF ENGINEERED BARRIERS

3.1. MEDIUM ACTIVE WASTE FORM CHARACTERISATION

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

Contractor: The University of Aberdeen
Contract No.: F1.1W.0025 UK (H)
Duration of contract: 1 May 1986 - 31 March 1990
Period covered: 1 January 1989 - 31 December 1989
Project leader: Professor F.P. Glasser

A. OBJECTIVES AND SCOPE

Cements are a favoured material for immobilizing many low and medium level radioactive wastes; repository construction will also employ large quantities of cement. Therefore, the prediction of eventual dose rates to the public will require a sound understanding of cement per se and its interactions with included radioactive wastes, blending agents (such as blast furnace slag and fly ash), steel reinforcements and groundwaters. Cements, particularly when blended with blast furnace slag and fly ash, evolve over time, with changes in phase assemblage and consequently microstructure and aqueous chemistry. The aim of the present project is to achieve a greater understanding of these processes, and to develop a model for cements aged beyond laboratory timescales, ie. > ca.30 years. The work is cooperative, with studies on the effect of radiation on cements being conducted at UKAEA Harwell (Materials Development Division).

B. WORK PROGRAMME

2.1 Basic Property Measurements. Characterisation of the solid and aqueous phases of Portland cement system and developing a solubility model.

2.2 Modified Cement Systems. Determination and characterisation of the products of hydration of blended cements, especially those containing glassy slags, and the impact of these additives on solubility models.

2.3.1 Cement - Waste Stream Interactions. Determination and characterisation of cement properties in the presence of wastes, especially reference waste forms, containing sulphate, nitrate and borate.

2.3.2 Interaction Between Cement and Constructional Materials. Characterisation of the reaction between cement and steel, mainly by critical anlysis of the literature.

2.4.1 Radiation Stability and Radiation Effects. The impact of radiation effects at realistic dose rates will be determined through measurement of such factors as pH, Eh, sorptive capacity and phase stability.

2.4.2 Thermal Effects The effect of moderately elevated temperatures (up to 70° C) on the stability and solubility of hydrate phases will be assessed.

2.4.3 Pressure Effects. A scoping study will be made of the effect of pressure on cement systems at pressures up to the equivalent of 500m depth.

2.5 Selected Aspects of Cement- Near Field Interactions. The role of corrosive groundwaters and of brines will be assessed.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Further progress has been made on the solubility modelling of cements with the emphasis on validating the present model, and determining solubilities of relevant hydrate phases. A slag cement hydration study has been completed, with significant new knowledge gained on phase development and microstructure evolution in these important materials.

The study of cement- waste stream interactions has continued; with work on specific nuclide behaviour in cements, in particular I and U. The work on radioiodine in cements is now largely complete. In addition, cements loaded with simulates of waste streams RMA.01 and RMA.08 have undergone investigation, thus far over a 6 month period. The interaction of cement with steel has been the subject of a comprehensive literature review, with supporting experimental work.

Recent studies on the effect of radiation on cements has taken the form of comparative examination of micro -structural and -chemical characteristics. Thermal and pressure effects on the solubility of cement phases has progressed; work has focused on the important $Ca(OH)_2$ phase.

Investigation of groundwater effects on the durability of cements has concentrated on the dissolved CO_2 component, and is now being extended to include dissolved organics and brines.

Progress and Results

2.1 Basic Property Measurements. The emphasis of model development for cement blends has shifted to validating the current model, described in [1,2,3]. Relevant cement hydrate phases (see Table I) have been prepared, and undergone prolonged purification, by periodic filtration and characterisation of aqueous and solid phases (by xrd; x-ray diffraction and aem; analytical electron microscopy), followed by redispersion. This produces large datasets on the solubility properties of each phase, allowing the form of solubility to be determined, and where congruent, solubility products calculated with some confidence. Thus, C_3AH_6 and AF_t are both congruently soluble; their solubility products have been calculated and added to the MINEQL computer database. As in C-S-H, many of the other Si-containing phases appear to dissolve incongruently, with Si being the least soluble component. Compatibility experiments employing combinations of the purified phases are underway, to test the phase relations of the current model.

An outline conceptual model is given in Figure I. The (normative) model allows prediction of the equilibrium phase assemblage in a cement blend in the pre-processor stage. Presently available computer speciation codes, modified to be more relevant to cement systems, then calculate pore water compositions. When combined with other relevant models, this will allow more accurate prediction of the cement-dominated near field term in radiological risk assessments.

2.2 Modified Cement Systems. Work has concentrated on slag cements, with two papers accepted for publication [4,5]. The investigations have shown why these materials have such low permeability. In high slag (30-70%) blends, the slag grains quickly (ca.1- 7d.) become coated with a dense gel. This coating acts as a diffusion membrane; water diffusing inwards, allowing continuing hydration of the slag, while mobile ions diffuse outward, into the water-rich cement paste. Figure II shows the effect on the microstructure of the resulting paste. Mass balance calculations support the view that a net transfer of solid substance occurs across slag grain boundaries, on ageing. The result is a gradual decrease in porosity of the paste matrix. However, the overall porosity of the system is little affected; pores develop in the regions formerly occupied by slag grains. Thus the paste- the continuous phase- is densified while the slag grains become more porous (see Figure II).

It is predicted that the permeability of slag cement pastes will typically continue to decrease for some decades. At present, we do not know how to optimize slag cement formulations to obtain target permeabilities. But now that the mechanism has been elucidated, such predictions can be envisaged.

2.3.1 Cement- Waste Stream Interactions. The interaction of sulphate waste stream RMA.01 (225g/l Na_2SO_4) and nitrate waste stream RMA.08 (300g/l $NaNO_3$), with ordinary Portland cement (OPC) has been studied for samples aged to 6 months, relative to control samples. Little difference in gross mineralogy relative to the controls was observed (by xrd and thermal analysis). Some enrichment of Na levels in the C-S-H might be expected; this is yet to be confirmed, by aem analysis. Analysis of the pore fluid showed that most of the Na_2SO_4 and $NaNO_3$ remained in solution, but SO_4 levels were depleted relative to Na. The SO_4 uptake on to the solid phase may be due to sorption on C-S-H; again this awaits confirmation by aem.

The study of U behaviour in cements continues. Uranium (VI)- loaded C-S-H gels were prepared by (i) double decomposition, and (ii) direct reaction, with target Ca/Si and U/Ca ratios in the range 0.9 to 1.8 and 0.001 and 0.5, respectively. XRD on the gels prepared by (i) showed the presence of uranophane, whereas those prepared by (ii) showed only C-S-H after 390 days ageing. However, both sample suites gave rise to similar solubilities. With low Ca/Si ratio gels (0.9 to 1.4) U solubility is ca. 0.01 mol/l. At higher Ca/Si ratio, U solubility is slightly greater, at ca. 0.2 mol/l. The solubility- limiting processes are being investigated further.

Work on I in cements is published in [6]. Among the main findings are: (i) in the absence of strong radiation, I^- is the most likely speciation of I; (ii) in the short-term, OPC is an efficient scavenger for I^- with >99% removed from a ca.10^{-7} M solution; (iii) BFS removes 85% from solution, but this is likely to increase with more prolonged ageing; (iv) sorption studies have shown most of the immobilization occurs in AF_m and high Ca/Si ratio C-S-H. Modelling (see 2.1) indicates that a 30 to 40% slag blend should give rise to the optimum phase assemblage for I^- (chemical)immobilisation. The use of Ag as a selective precipitant has been reviewed, and found to be of limited value, due to redox and radiolytic instability of AgI.

2.3.2 Interaction Between Cement and Constructional Materials. Extensive analyses of the mechanisms of passivation and corrosion of steel reinforcements in concrete have been carried out. The reaction products formed during reinforcement corrosion have also been chracterised, by sem and aem. This work is reported in [7,8].

In the absence of chlorides, a passivating layer of spinel-type phases, ie. Fe_3O_4-γFe_2O_3, forms. In concretes with low w/c ratio, little excess $Ca(OH)_2$ forms at the steel- cement interface, contrary to wide opinion. As normal corrosion proceeds, the spinel- structured layer thickens at a mean rate of 1- 2 μm/yr. However, even very low levels of chloride (ca.0.01 wt % of cement) give rise to a concentration of Cl at the corrosion product/concrete interface, and alteration of the existing passivating layer, favouring formation of akageneite (β-FeOOH) and goethite (α-FeOOH). The severely degrading effect of chloride on the layer, as noted by others, has been confirmed.

A model incorporating the changing chemical and transport characteristics of the system as a function of chloride ion concentration is being developed.

2.4.1 Radiation Stability and Radiation Effects. A microstructural study has been made of 3:1 and 9:1 blast furnace slag/ OPC grouts which have been irradiated at 10^4 Gy/hr to a total dose of 87 MGy. Control samples maintained for 2 years at 50°C have also been examined. Little change attributable to irradiation had occured in the microstructure, apart from an AF_t type phase present only in the irradiated blends which may indicate enhanced oxidation of reduced S species to SO_4 under irradiation. The major hydration product, C-S-H gel, remained unchanged in both composition (see Table II) and morphology, and all other observed microstructural features were as would be expected in such blends at 20°C.

2.4.2, 2.4.3 Thermal and Pressure Effects. Pressure and temperature effects on the solubility of the important cement phase $Ca(OH)_2$ have been investigated, using a purpose built apparatus. The temperature range studied to date is 25 to 59°C, with a pressure range of 1 to 650 bars. The temperature range will be extended to 80 or 85°C, to cover P-T conditions envisaged in UK repositories. Sufficient time has to be allowed for equilibration of $Ca(OH)_2$ solubility, typically 10 to 30 days.

With increasing temperature solubility decreases (well documented). At a given temperature, increasing pressure increases $Ca(OH)_2$ solubility, especially at higher temperatures, as shown in Figure III. At 59°C, a 50% increase in solubility is observed between 1 and 650 bars. The corresponding value for the lower temperatures is only 7%. The causal interpretation of these observations is being investigated.

2.5 Selected Aspects of Cement- Near Field Interactions. The differing durability of cements in contact with groundwaters, revealed the need to establish criteria by which the effect of destructive agents on concrete could be predicted. A preliminary assessment revealed that dissolved CO_2 presented the most significant hazard.

A full review of the physical chemistry of the $CaCO_3$- CO_2- H_2O system was carried out. The speciation of solutions containing known amounts of 'aggressive CO_2' was computed using MINEQL, and these solutions equilibrated with $Ca(OH)_2$ and C-S-H (initial models for cement). The amount of Ca dissolved relative to pure water is plotted versus pH in Figure IV, as a contour map of leachability (aggressivity). It is suggested that repository lifetimes will be proportional to the reciprocal of the aggressivity factor. As equilibrium is reached $CaCO_3$ is precipitated. Using Fick's law, a basic model was developed to show the whereabouts and extent of layer coverage. These data will be used to modify the aggressivity map.

The effect of other components on the leachability of CO_2 containing groundwaters is being studied. NaCl has only been found to be significant for concentrations above 0.5 M. Attention is also being focussed on humic substances, and how best to represent these complex molecules for inclusion in the MINEQL database, for modelling their effect.

References see List of Publications.

Table I. Cement hydrate phases being studied in the modelling program

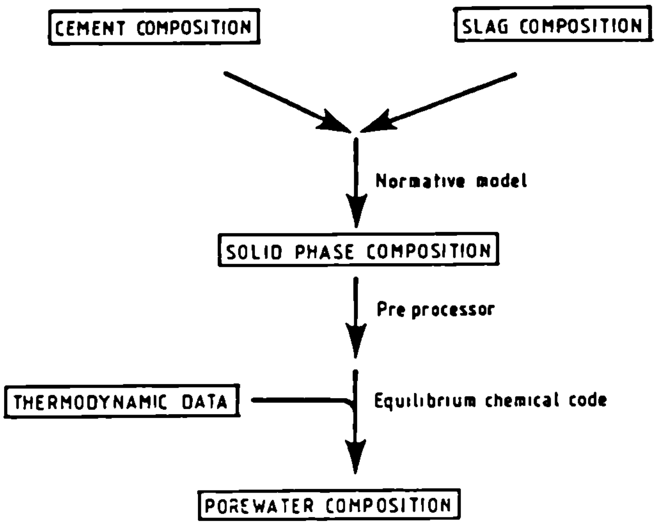
Formula[1]	Name
C_3AH_6	hydrogarnet
C_3ASH_4	ditto
C_4AH_{13}	
$C_6A\bar{S}H_{26}$	AF_t, ettringite
$C_4A\bar{S}H_{12}$	AF_m, monosulphate
C_2ASH_8	gehlenite hydrate
CSH	Calcium Silicate Hydro-gel (three ratios studied: 0.9, 1.3 and 1.7)
$C_5S_6H_5$	Tobermorite
M_6AH_{13}	hydrotacite
M_4AH_{10}	hydrotalcite
AH	Aluminium hydroxide (several polymorphs).

Notes. 1. Cement nomenclature is used; C= CaO, S= SiO_2, A= Al_2O_3, $\bar{S}$= SO_3, H= H_2O and M= MgO.

Table II. Atom ratios for C-S-H gels, determined by Electron microprobe analysis, in BFS/OPC 3:1 irradiated and control samples.

	irradiated 3:1 (n = 2267)	control 3:1 (n = 2313)
Ca/Si	1.357 ± 0.097	1.370 ± 0.104
Al/Ca	0.153 ± 0.075	0.157 ± 0.066
Mg/Ca	0.192 ± 0.175	0.208 ± 0.171
S/Ca	0.040 ± 0.026	0.044 ± 0.034
K/Ca	0.021 ± 0.004	0.016 ± 0.003
Mn/Ca	0.020 ± 0.011	0.020 ± 0.010
Ti/Ca	0.017 ± 0.010	0.016 ± 0.009

Fig.I. OUTLINE CONCEPTUAL MODEL



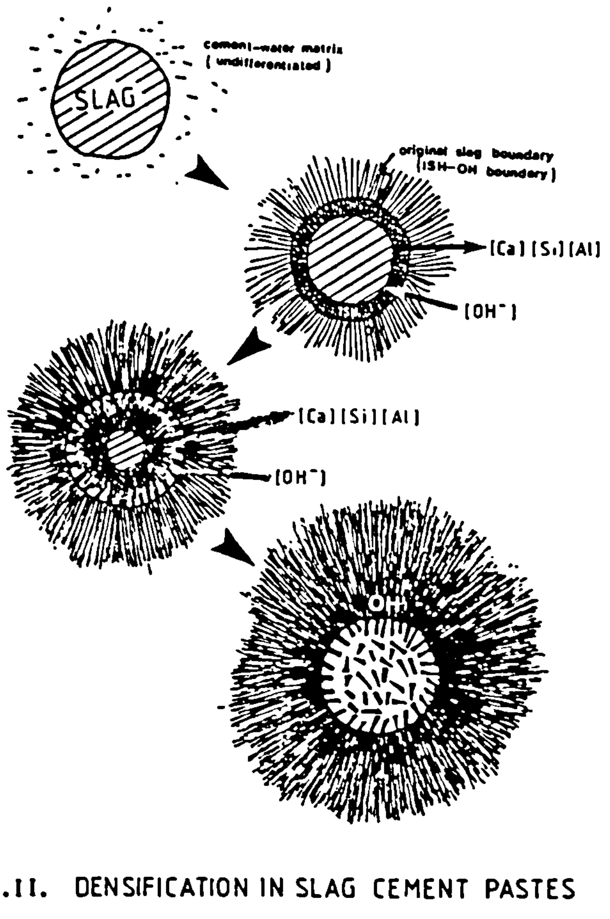


Fig.II. DENSIFICATION IN SLAG CEMENT PASTES

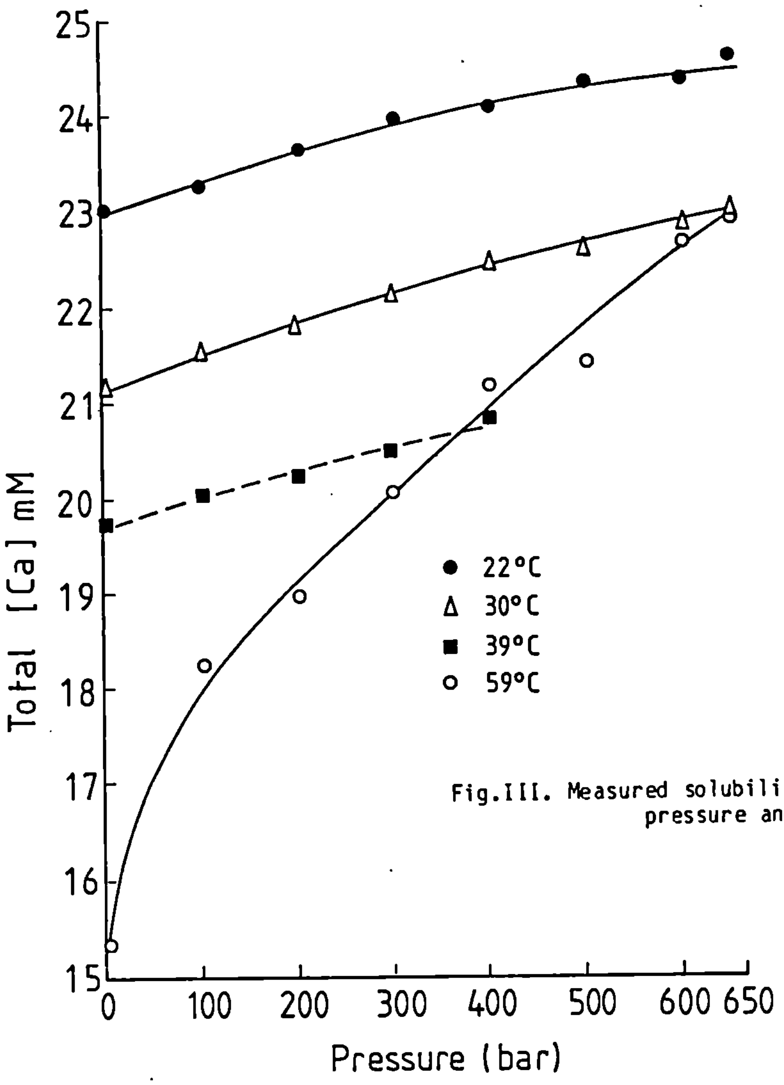
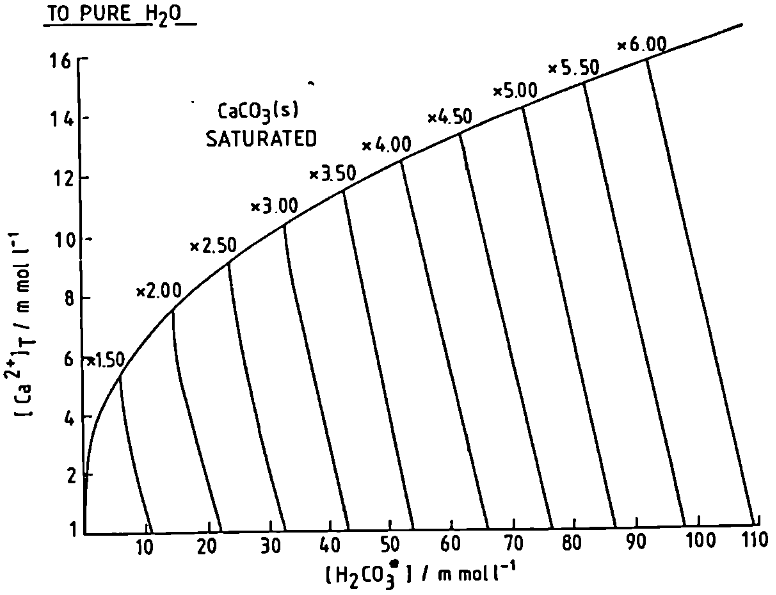


Fig.III. Measured solubility of $Ca(OH)_2$ as a function of pressure and temperature.

Fig.IV. Ca^{2+} LEACHING ABILITY OF CO_2-CONTAINING GROUNDWATERS RELATIVE TO PURE H_2O



List of Publications

/1/ D.E.Macphee, M.Atkins and F.P.Glasser, Phase Development and Pore Solution Chemistry in Ageing Blast Furnace Slag-Portland Cement Blends', in 'Scientific Basis for Nuclear Waste Management', MRS Proceedings, vol.127, p.475- 480, (1989).

/2/ M.Atkins, D.E.Macphee and F.P.Glasser, 'Chemical Modelling in Blended Cement Systems', in 'Fly Ash, Silica Fume, Slag and Natural Pozzalans in Concrete', Proc. 3rd. Int. Conf., Trondheim, vol.1, p.73- 96, (1989).

/3/ M.Atkins, J.Cowie, F.P.Glasser, T.Jappy, A.Kindness and C.Pointer, 'Assessment of the Performance of Cement-Based Composite Material for Radioactive Waste Immobilization', to be published in Proceedings of MRS Fall Meeting (1989) on 'Scientific Basis for Nuclear Waste Management'.

/4/ Q.L.Feng, E.E.Lachowski and F.P.Glasser, 'Densification and Migration of Ions in Blast Furnace Slag-Portland Cement Pastes', Proc. MRS Meeting, vol.136, p.263- 272, (1989).

/5/ Q.L.Feng and F.P.Glasser, 'Microstructure, Mass Transport and Densification of Slag Cement Pastes', to be published in Proceedings of MRS Fall Meeting (1989).

/6/ M.Atkins and F.P.Glasser, 'Encapsulation of Radioiodine in Cementitious Waste Forms', to be published in Proceedings of MRS Fall Meeting (1989) on 'Scientific Basis for Nuclear Waste Management'.

/7/ K.K.Sagoe-Crentsil and F.P.Glasser, 'Steel in Concrete'(in two parts), Mag. Concr. Res., vol 41, p.205- 212 and 213- 220, (1989).

D.E.Macphee, K.Luke, F.P.Glasser and E.E.Lachowski, 'Solubility and Ageing of Calcium Silicate Hydrates in Alkaline Solutions at $25^{\circ}C$', Jour. Amer. Ceram. Soc., vol.72, p.646- 654, (1989).

Study of Leaching Mechanisms of Ions Incorporated in Cement or Polymer

Contractor: Greek AEC, "Demokritos" Center, Greece
Contract No.: FI1W/0026/00, FI1W/0174/GR(TT) (Extension)
Duration of Contracts: May 1986 - December 1989
Period covered: 1 Jan. - 31 Dec. 1989
Project Leaders: S.G. Amarantos, J.H. Petropoulos

A. OBJECTIVES AND SCOPE

The present experimental study aims at further elucidation of some important aspects related to the leaching kinetics of Cs and Sr ions by water from solid matrices simulating cemented low-to-medium level radioactive wastes, as well as study of simpler model systems, such as a soluble or insoluble salt embedded in a well defined polymer matrix (e.g. cellulose acetate or an epoxy resin). The development of realistic theoretical models of the kinetics of ion release is also envisaged.

This work is expected to provide fundamental information necessary for the sound evaluation of the long-term elution kinetics of important ions from real waste products.

B. WORK PROGRAMME

B.1 Cement

B.1.1 Leaching kinetics of Cs in relation to the distribution of the ion in the specimen at various stages of the leaching process.
B.1.2 Examination of the effect of temperature on leaching rate by means of parallel experiments at different temperatures.
B.1.3 Effect of changing the thickness of the sample on the elution curve.
B.1.4 Examination of the possibility of setting up a theoretical model for the representation of the elution kinetic curve of Cs.
B.1.5 Effect of atmospheric CO_2 on the elution of Sr, in relation to the Sr content of the sample.
B.1.6 Characterization of the state of water and embedded ions in the cement matrix (porosimetry, differential scanning calorimetry-DSC, reversible sorption behaviour).
B.1.7 Development of a more advanced model for the elution process.

B.2 Polymer

B.2.1 Further experimental investigation of the cellulose acetate-salt system (effect of salt solubility, salt content, salt particle size or polymer water content).
B.2.2 Development of a more sophisticated theoretical model to describe the elution kinetics of soluble salts in particular.
B.2.3 Characterization of sorption and diffusion properties of cellulose acetate matrices (where possible).
B.2.4 Further investigation of the salt solubility effect in the case of elution of simple salts from epoxy resin matrices.
B.2.5 Simulation of real polymer-salt systems by the theoretical elution model previously developed.

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

The study of leaching kinetics and distribution profiles of Cs from cement specimens containing large and small amounts of embedded ion were continued and previous conclusions were confirmed. The same holds true for leaching tests on Sr-containing cement samples. Significant information regarding the mechanism of the elution process and the presence of concurrent processes, notably erosion of the cement matrix, was obtained by differential scanning calorimetry of hydrated, and mercury porosimetry of dried, cement samples. Measurement of sorption of Cs from aqueous solutions was carried out and showed that even the highest Cs loads used in leaching tests do not exceed the reversible sorption limit, thus confirming the applicability of Fick's, rather than Higuchi's, equation. Further measurements of NaCl elution from cellulose acetate matrices were carried out and complemented by determination of the sorption and diffusion coefficients of the salt-depleted matrices. Elution tests on epoxy resin specimens loaded with various amounts of NaCl or $SrSO_4$ were continued and some new specimens loaded with NaCl were prepared and subjected to leaching. Model calculations were carried out to test the predictions of the theoretical model previously developed regarding the elution behavior of polymer specimens loaded with realistic amounts of embedded salt.

Progress and Results

1. Studies with cemented specimens

B.1.1-B.1.5 Elution kinetics of cemented Cs and Sr

Leaching experiments with cylindrical cement specimens (height ~4 cm, diameter ~4 cm) containing either ~ 3.4% by wt inactive Cs_2SO_4 (Series A) or Cs-137 (370 kBq/sample), $CsNO_3$ (0.017% wt) and 8% by wt of $NaNO_3$ (Series D) in stagnant water at 30°C were continued /1,2,3/. The fractional amount of Cs^+ eluted was ~ 54% in 1050 days for series A and 25% in 850 days for series D (Cs-137). The plots of series A (fractional amounts vs $\sqrt{t}$) remained essentially linear in accordance with Fick's law (for values of the diffusion coefficient see reference /2/). In series D the corresponding plots had a discernible tendency to turn upwards (acceleration of elution). Rough estimates indicate approximate doubling of the value of the diffusion coefficient found originally, although this value is still about half that found for series A specimens. (The enhanced elution is attributed to pore enlargement due to the simultaneous elution of $NaNO_3$ which is present in considerable quantities in these specimens). Experimental concentration profiles on non eluted Cs along the diffusion axis, at ~ 50 % or ~ 25 % of Cs eluted (series A and D specimens correspondingly) were obtained as before. These new profiles can also be described by Fick's law (making allowance as in previous reports /2,3/ for some immobilized Cs in series A specimens). The Sr-containing specimens (height ~ 4 cm, diameter ~ 4 cm) contained 740 kBq/specimen of Sr-90 and 8% wt. of $NaNO_3$ (Series E,F) or 740 kBq/specimen of Sr-90, 0.15% of $Sr(NO_3)_2$ and 8% wt of $NaNO_3$ (Series G,H) and were subjected to leaching under "full" (Series E,G) or "minimum" (Series F,H) exposure to atmospheric CO_2. After 645 days the fractional amount of Sr-90 eluted was 0.4-0.6% for series E,G and 1.5-2.5% for series F,H in agreement with previous results. Also higher elution rates in the presence of additional amounts of Sr (Series G,H) were observed as before.

B.1.6 Characterization of the state of water and embedded ions in the cement matrix

(i) Results of DSC (Differential Scanning Calorimetry)

Further investigations by low temperature DSC of some series of cemented specimens were carried out. Values of the total water content w (estimated by drying the sample for 2 hours at 105°C) and of the "equivalent fraction of imbibed bulk water" f_{WB} are presented below ($f_{WB}=W_{fB}/W$, where W_{fB} is the equivalent amount of bulk imbibed water estimated from the total amount of heat absorbed by the hydrated sample, divided by the enthalpy of fusion of bulk water ΔH_{fB} and W is the water contained in the sample). In Figure 1, measured melting endotherm area of cement samples fully or partially hydrated (by exposure to different relative humidities) is plotted vs w. It is shown that $\Delta H_f \longrightarrow 0$ below w ~10 g H_2O/100 g of dry sample and ΔH_f remains below ΔH_{fB} over a substantial range of higher w extending up to w ~20 g/100g in many cases. Hence the actual fractions of freezable water are substantially higher than the values of f_{WB} quoted in Table I. However, the values of f_{WB} are useful in a relative sense. Both w and f_{WB} in Table I are substantially higher in the outer layers than in the interior of the leached cement specimen, indicating pore enlargement due to concurrent erosion of the cement matrix by leachant; and are higher at higher leaching temperatures, indicating the presence of larger pores at 70°C at both locations.

(ii) Porosimetry results

Mercury porosimetry was carried out on different cement specimens from the various specimen series subjected to leaching. In Table II total pore volume down to a radius of 1.8 nm and the fraction of pore volume contained in pores down to various pore radii are presented for the same specimens as in Table I. The results confirm the conclusions drawn from DSC. In particular, samples taken near the surface of the specimens show increased porosity coupled with the appearance of pores of large size. Also samples taken from specimens leached at 70°C exhibit higher porosity and increased number of wider pores than those leached at 30°C.

(iii) Sorption of Cs by cement

The sorprion of Cs ions by the cement used in this work was studied by equilibrating samples of cement granules with aqueous Cs_2SO_4 solutions in the range 10^{-3} to 1 mol Cs/liter. The cement granules (in the range 0.18-1.0 mm) were obtained from blank specimens subjected to leaching with distilled water for 900 days at 30°C. Typical results are shown in Figure 2. A linear log-log plot of unit slope is obtained, yielding a constant partition coefficient $K_D=C_c/C_\ell = 0.22$. This indicates that even the highest loads of Cs used in the elution tests do not exceed the reversible sorption limit corresponding to a saturated aqueous solution, thus confirming the applicability of Fick's, rather than Higuchi's, equation to the elution process /4/.

B.1.7 Advanced model for the elution process

Analysis of the distribution profiles of Cs in the cement specimen during the elution process shows that they can be fitted reasonably well by Fick's law in series D (low Cs content). In specimens containing large amounts of Cs, however, one must make allowance for the fact that part of the embedded Cs is immobilized in the cement matrix. Elution of the more readily leachable portion can then still be described reasonably well on the basis of Fick's law. There is little, if any, concurrent loss of "immobilized" Cs, thus obviating the need for a more elaborate model. Complications which can arise because of the concurrent erosion of the cement matrix are not easily quantifiable at the present time.

2. Studies with polymer-salt system

B.2.1, B.2.3 Cellulose acetate-NaCl system

Further leaching tests were carried out using membranes containing 11.1 or 20.5% (by wt) NaCl of particle size ≤ 5 µm. No significant difference from the previous elution curves was observed. In addition measurements of the sorption (partition) coefficient K_p and the diffusion coefficient D of NaCl in the salt-free membrane, as well as the relevant salt-depleted membranes, were carried out. Both K_p and D tended to increase with the original salt content of the membrane.

B.2.4 Epoxy resin-$SrSO_4$ or NaCl system

New specimens (disks of thickness 0.16 cm and diameter 5 cm) containing 12% or 25% by volume NaCl were prepared and subjected to leaching with stagnant distilled water. The elution curves are linear on a $\sqrt{t}$ scale (Figure 3). Leaching tests on specimens prepared previously (thickness $\sim$ 0.7 cm, diameter 5 cm) which were loaded with either NaCl or $SrSO_4$ (12%, 25% or 40% by vol.) were continued. Their elution behavior showed no new features; but a clear tendency of the specimens containing large amounts of NaCl to be detached from their holders was noted.

B.2.7 Simulation of real polymer-salt system by the elution model

Model calculations corresponding to relatively large salt loads (well above what can be dissolved by the imbibed water)have shown reasonable correspondence to Higuchi-type kinetics /4/.

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/2/ BRODERSEN, K. and NILSSON, K., Editors, Characterization of radioactive waste forms, Progress Report 1987, EUR 12077 EN, vol. 1, pp. 9-18 (1989).

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TABLE I: STATE OF WATER IN CEMENT BY DSC

Specimens		Total imbibed water content (g/100 g dried specimen) w	% Equivalent fraction of imbibed bulk water f_{WB}
<u>B1</u> (Blank, leached for 900 days, 30°C)	(a)	27.3	31.1
	(b)	20.9	21.0
<u>B3</u> (Blank, leached for 250 days, 70°C)	(a)	29.9	50.2
	(b)	22.2	41.4
		22.2	41.9

(a) Sample taken near the exposed to eluant surface of specimen

(b) Sample taken far from the exposed to eluant surface of specimen

TABLE II: POROSIMETRY MEASUREMENTS IN CEMENT

Specimens		Pore Volume $cm^3/100$ g (dry specimen)	Pore fractional volume (%) pertaining to pores of radius exceeding:			
			125 nm	31.2 nm	7.5 nm	2.5 nm
B1	(a)	11.5	4.2	20.1	45.8	91.2
	(b)	9.1	1.4	4.2	44.7	89.9
B3	(a)	18.5	16.3	33.7	64.1	94.2
	(b)	12.9	2.3	6.4	49.6	92.2
		12.3	1.4	4.3	50.1	92.2

B1, B3, (a), (b) as in Table I.

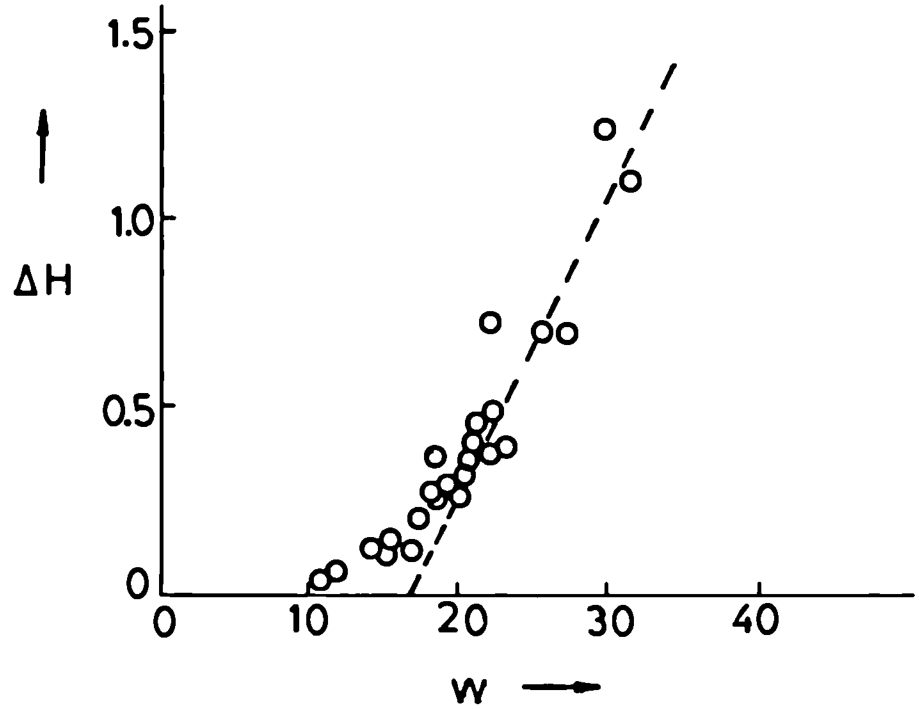

Fig. 1: Plot of normalized melting endotherm area ΔH (in kcal/100 g of dry cement) vs water content w (in g H_2O/100 g dry cement) of cement samples. The slope of the plot represents the enthalpy of fusion ΔH_f at given w. The broken line corresponds to the enthalpy of fusion of bulk water (ΔH_{fB}=79.7 cal/g).

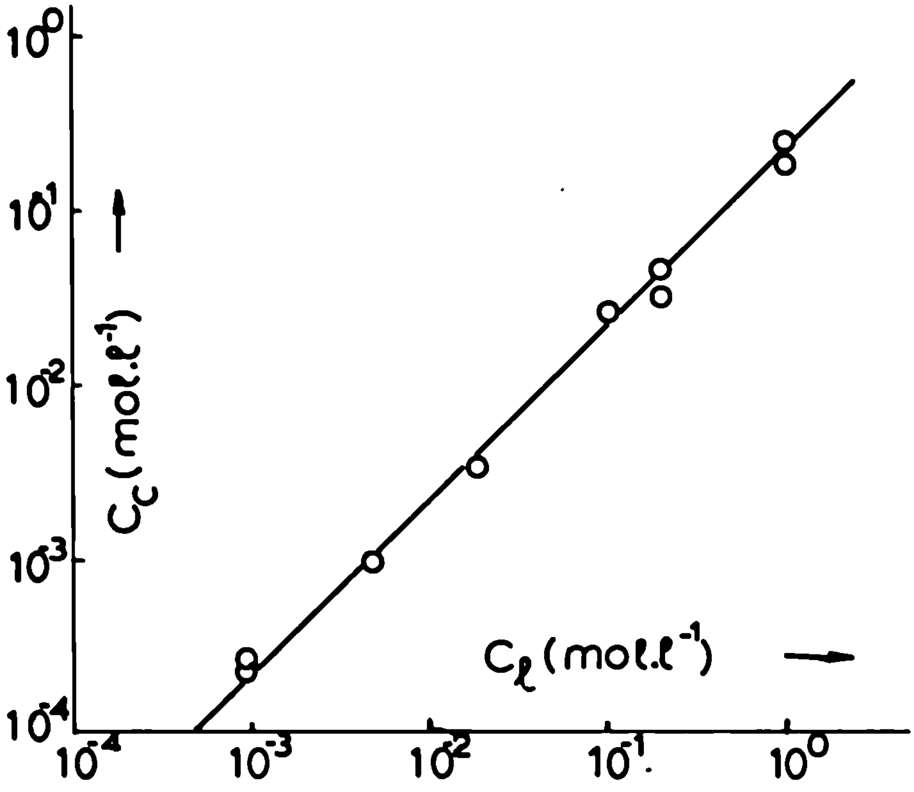

Fig. 2: Sorption of Cs by cement at room temperature from aqueous solutions of Cs_2SO_4 (C_c is given per unit volume of the cement sample).

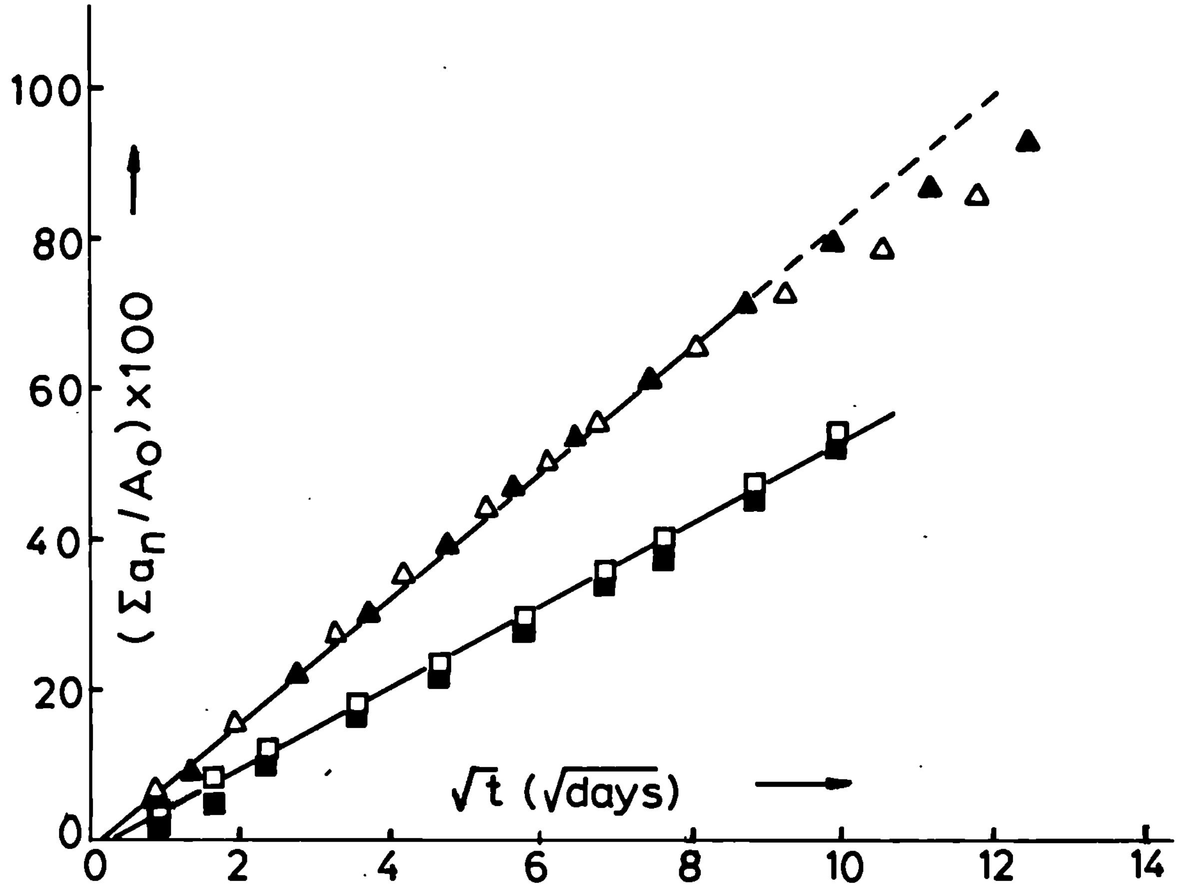

Fig. 3: Fractional amounts of NaCl eluted at 30°C from duplicate specimens (≈1.6 mm thick) of salt-loaded epoxy resin. Salt content (% vol.): 12 (□,■) or 25 (Δ,▲).

THE INFLUENCE OF ORGANIC COMPLEXING AGENTS ON 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	: Free University of Berlin
Contract No.	: FI1W-0091
Duration of contract	: July 1986 - July 1990
Project leader	: G. W. Marx
Group leader	: Ch. Keiling

A. Objektives and scope

Within the frame of the contract FI1W-0091 sponsored by the Commission of the European Communities solubilities of AgI, $AgIO_3$, $CsNO_3$, $Na_2U_2O_7$, NpO_2OH, $Pu(OH)_4$ and $Am(OH)_3$ should be determined under the influence of the complexing organics dibutylphosphate (DBP), tributylphosphate (TBP), ethylenediamminetetraacetic acid (EDTA), citrate and oxalate. The systems under investigation had to consist of various saturated salt solutions, the physical data of which were fixed by contacting the solidifying matrices cement and bitumen under practical conditions. The leachates had to be investigated with respect to sorption and migration, in order to characterize the transport behaviour of these elements in the near field of a waste repository.

Furthermore leachabilities of these radionuclides from the solidifying matrices cement and bitumen should be determined.

Finally sorption isotherms had to be calculated from data obtained from sorption experiments on the actinides U, Np, Pu and Am adsorbed by materials from the near field of a waste repository.

B. Work Programme

B.1 Solubility studies of the source term

B.1.1 Determination of solubilities of silver iodide, silver iodate, cesium nitrate, sodium diuranate, neptunium(V), plutonium(IV) and americium(III) hydroxides in concentrated salt solutions at equilibrium under the influence 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 present in cement and determination of their leachabilities

B.1.6 Solidification of elements with complexing organics in cement and determination of their leachabilities

B.2 Sorption and migration in the nearfield

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 use of salt columns

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

B.3 Calculation of sorption isotherms for materials from the near field of a waste repository

C. Progress of work and obtained results

State of advancement

Solubilities of AgI, $AgIO_3$, $CsNO_3$, $Na_2U_2O_7$, NpO_2OH, $Pu(OH)_4$ and $Am(OH)_3$ or $Eu(OH)_3$ respectively were determined from given salt solutions. Migration and batch experiments were carried out on these elements, in order to determine distribution coefficients in accordance with the scientific programme outlined before.

Sophisticated analytical methods were developed for investigating leachates from real waste /1/. The leachates from real waste forms were studied with respect to concentrations of activity vs leaching time.

After adding complexing organics the elements iodine, cesium, uranium, neptunium and americium were solidified with cement, in order to study the leaching behaviour of cement samples under the influence of saturated NaCl solution and Q brine.

In 1989 the main interest was focussed on sorption isotherms of europium, neptunium and uranium for materials from the near field of a waste repository located in a salt dome. The sorbent materials were Portland 35 F-cement, corrosion products of stainless steel and rock salt. Before starting the experiments the solutions used as solvent systems were saturated with the various complexing organics.

Progress and results obtained within the time period January-December 1989

B.1 Solubility studies of the source term

B.1.1 Determination of solubilities at equilibrium

In order to obtain data from experiments on solubilities of trivalent actinides $Am(OH)_3$ and its analogue $Eu(OH)_3$ were used as representatives. Especially for systems of low pH europium was taken instead of ^{241}Am because sufficient amounts of ^{241}Am were not available for these experiments.

The results obtained are listed in table 1 and figures 1-4.

In the four different systems under investigation the solubility of trivalent cations is the highest in case of EDTA being present. It is the lowest in solutions saturated with cement and DBP or TBP.

B.1.2 Ultrafiltration experiments

The results from ultrafiltration experiments on trivalent cations are listed in table 2.

In NaCl/cement solutions the americium concentration decreases after separating with filters the pore sizes of which are smaller 450 nm. In less alcaline systems the decrease of Am- or Eu-concentration is not so drastical.

B.2 Sorption and migration in the near field

B.2.1 Migration behaviour of trivalent cations

Column experiments were carried out with an apparatus, consisting of a peristaltic pump for transporting solutions, a chromatographic column and an automatic sample device /2/.

The activities were added in form of a pulse of approximately 2 cm^3 of the radioactive solution, the transport velocity was app. 1.5 $cm^3 \cdot h^{-1}$. NaCl GR was the fillament of the columns.

The results from the column experiments carried out with americium and europium are listed in table 3. They show a small recovery in the strong alcaline NaCl/cement solutions, its maximum being 30 % with respect to the added amount of americium for the solution containing oxalate.

For the more acidic systems of the NaCl/bitumen solutions the recoveries will be greater than 80 %, if EDTA and citrate are present. In presence of butylphosphoric esters trivalent cations are quantitatively kept back.

In Q brines more than 60 % of the added activity are recovered after the run.

B.2.3 Determination of the sorption behaviour by use of batch-type experiments

Sorption behaviour of trivalent cations

In order to study the sorption behaviour of trivalent elements on solid NaCl GR batch experiments were carried out in an air thermostate at 298 K. The results from the sorption experiments are listed in table 4.

The data obtained show R_s values to be in between 0.2 - 30 $cm^3 \cdot g^{-1}$. For three solvent systems the highest values are found when oxalate is present.

B.3 Determination of sorption isotherms for uranium and europium on materials from the near field of a waste repository in salt formations under the influence of complexing organics

For investigating the sorption behaviour of the elements mentioned above and the systems of the near field of a waste repository located in a salt dome sorption isotherms were calculated from data obtained at 298 K. The amount of material sorbed on these solids can be determined from the isotherms for a wide range of starting concentrations. These experiments were also made under the influence of complexing organics. The sorbing materials were Portland 35 F-cement, corrosion products of stainless steel and rock salt.

The data obtained were calculated by use of Freundlich's isotherm /3,4/

$$C_s = K_F \cdot C_g^N$$

C_s : amount of sorbate per mass unit of sorbent [$mol \cdot g^{-1}$]
C_g : concentration of sorbate at equilibrium [$mol \cdot dm^{-3}$]
K_F, N : constants

The values of lg K_F and N of Freundlich's equation are listed for uranium, neptunium and europium in tables 5-7. Some more systems are still to be investigated. From these results it can be seen that using corrosion products of stainless steel lg K_F values are the highest. Rock salt on the other hand has the smallest sorption capacity.

Work performed in the framework of the 1985–1989 programme of the European Atomic Energy Community: "Management and storage of radioactive waste"
Task 3 : Testing and evaluation of conditioned waste and engineered barriers
Item 1 : Characterization of low and medium level waste forms

Literature

1 2. Annual Report, "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", Contract No. FI1W-0091, Jan. 1988

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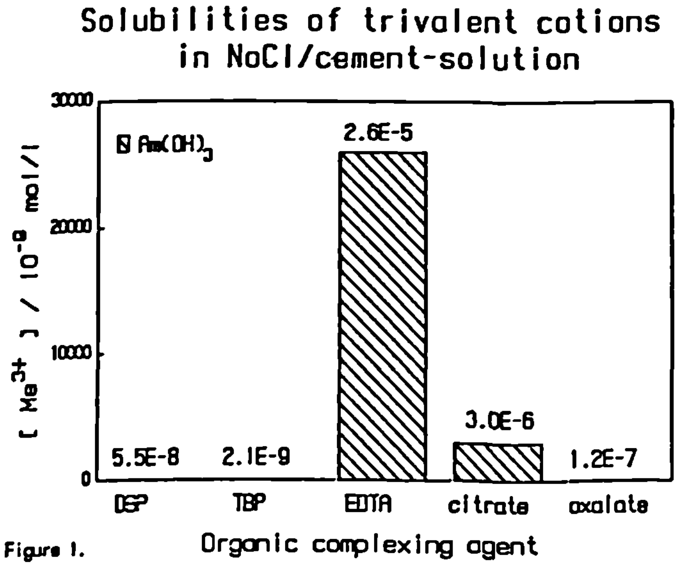

Figure 1.

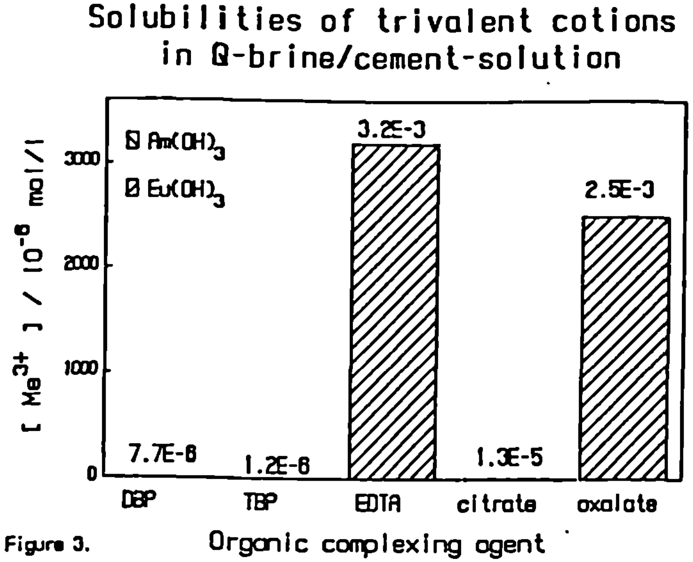

Figure 3.

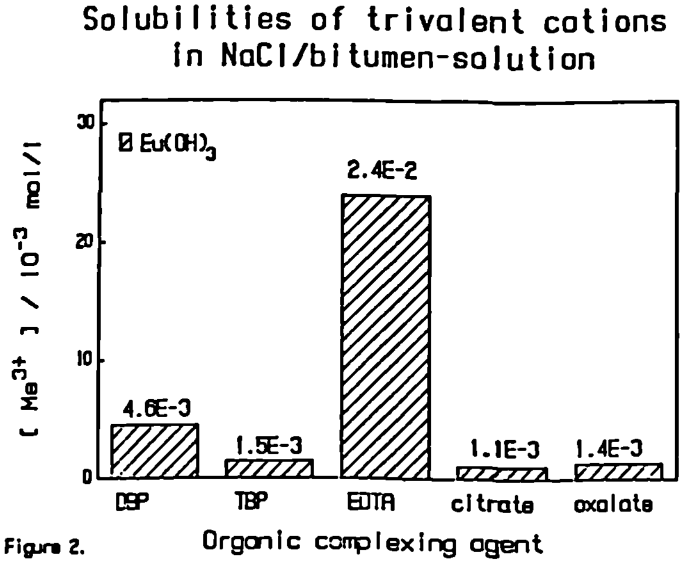

Figure 2.

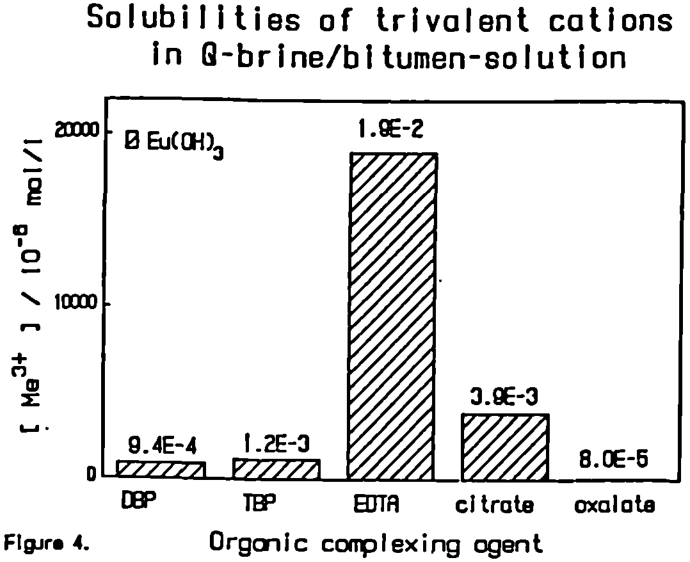

Figure 4.

Table I. Solubility of trivalent cations in various saturated salt solutions containing organic complexing agents

solution	compound	org. ligand	$[Me^{3+}]$ / mol·dm^{-3}
NaCl/Cement	$Am(OH)_3$	DBP	$5.5 \cdot 10^{-8}$
	$Am(OH)_3$	TBP	$2.1 \cdot 10^{-9}$
	$Am(OH)_3$	EDTA	$2.6 \cdot 10^{-5}$
	$Am(OH)_3$	Citrate	$3.0 \cdot 10^{-6}$
	$Am(OH)_3$	Oxalate	$1.2 \cdot 10^{-7}$
NaCl/Bitumen	$Eu(OH)_3$	DBP	$4.6 \cdot 10^{-3}$
	$Eu(OH)_3$	TBP	$1.5 \cdot 10^{-3}$
	$Eu(OH)_3$	EDTA	$2.4 \cdot 10^{-2}$
	$Eu(OH)_3$	Citrate	$1.1 \cdot 10^{-3}$
	$Eu(OH)_3$	Oxalate	$1.4 \cdot 10^{-3}$
Q-Brine/Cement	$Am(OH)_3$	DBP	$7.7 \cdot 10^{-6}$
	$Am(OH)_3$	TBP	$1.2 \cdot 10^{-6}$
	$Eu(OH)_3$	EDTA	$3.2 \cdot 10^{-3}$
	$Am(OH)_3$	Citrate	$1.3 \cdot 10^{-5}$
	$Eu(OH)_3$	Oxalate	$2.5 \cdot 10^{-3}$
Q-Brine/Bitumen	$Eu(OH)_3$	DBP	$9.4 \cdot 10^{-4}$
	$Eu(OH)_3$	TBP	$1.2 \cdot 10^{-3}$
	$Eu(OH)_3$	EDTA	$1.9 \cdot 10^{-2}$
	$Eu(OH)_3$	Citrate	$3.9 \cdot 10^{-3}$
	$Eu(OH)_3$	Oxalate	$8.0 \cdot 10^{-5}$

Table II. Results from ultrafiltration experiments with solutions containing trivalent cations

system		compound	pore size / nm					
			450	200	100	50	10	2
NaCl/Cement/	DBP	$Am(OH)_3$	100	83.9	80.8	80.3	76.0	69.9
	TBP	$Am(OH)_3$	100	8.9	4.9	4.9	3.2	2.1
	EDTA	$Am(OH)_3$	100	86.1	86.0	84.4	84.1	82.4
	Citrate	$Am(OH)_3$	100	69.3	4.2	4.0	3.1	2.6
	Oxalate	$Am(OH)_3$	100	6.5	3.9	2.6	1.6	0.2
NaCl/Bitumen/	DBP	$Eu(OH)_3$	100	90.7	88.1	83.4	78.1	68.9
	TBP	$Eu(OH)_3$	100	100.0	100.0	100.0	100.0	95.5
	EDTA	$Eu(OH)_3$	100	100.0	98.9	98.9	92.4	90.1
	Citrate	$Eu(OH)_3$	100	100.0	100.0	100.0	96.7	95.3
	Oxalate	$Eu(OH)_3$	100	93.8	81.3	73.4	73.4	62.5
Q-Brine/Cement/	DBP	$Am(OH)_3$	100	96.3	92.1	88.5	86.0	85.5
	TBP	$Am(OH)_3$	100	95.8	92.1	91.9	86.3	81.7
	EDTA	$Eu(OH)_3$	100	80.0	79.6	78.9	78.9	78.6
	Citrate	$Am(OH)_3$	100	92.6	87.9	84.4	79.7	67.3
	Oxalate	$Eu(OH)_3$	100	88.8	85.9	82.0	79.9	79.8
Q-Brine/Bitumen/	DBP	$Eu(OH)_3$	100	98.5	95.3	87.1	82.7	75.1
	TBP	$Eu(OH)_3$	100	92.1	91.1	81.8	77.8	76.7
	EDTA	$Eu(OH)_3$	100	100.0	100.0	95.5	92.3	83.4
	Citrate	$Eu(OH)_3$	100	98.9	98.8	96.0	84.3	71.3
	Oxalate	$Eu(OH)_3$	100	100.0	100.0	100.0	99.6	93.9

Table III. Results from the migration experiments on trivalent cations. (The column packings consisted of NaCl)

mass added / mol.	system	compound	porosity / % Vol/Vol	recovery / %	K_D / $cm^3\cdot g^{-1}$
$6.5\cdot10^{-11}$	NaCl/Cement/DBP	$Am(OH)_3$	39	19.5	
$8.2\cdot10^{-13}$	NaCl/Cement/TBP	$Am(OH)_3$	38	9.5	0.1
$2.3\cdot10^{-8}$	NaCl/Cement/EDTA	$Am(OH)_3$	37	15.3	
$2.9\cdot10^{-9}$	NaCl/Cement/Citrate	$Am(OH)_3$	36	4.4	
$1.7\cdot10^{-10}$	NaCl/Cement/Oxalate	$Am(OH)_3$	39	31.5	
$2.2\cdot10^{-6}$	NaCl/Bitumen/DBP	$Eu(OH)_3$	36	0.0	
$1.4\cdot10^{-3}$	NaCl/Bitumen/TBP	$Eu(OH)_3$	36	0.0	
$2.3\cdot10^{-5}$	NaCl/Bitumen/EDTA	$Eu(OH)_3$	37	86.3	0.0
$3.2\cdot10^{-7}$	NaCl/Bitumen/Citrate	$Eu(OH)_3$	38	79.7	0.0
$7.6\cdot10^{-9}$	Q-Brine/Cem./DBP	$Am(OH)_3$	39	95.5	
$1.0\cdot10^{-8}$	Q-Brine/Cem./TBP	$Am(OH)_3$	37	94.7	
$1.6\cdot10^{-6}$	Q-Brine/Cem./EDTA	$Eu(OH)_3$	36	62.7	0.0
$1.1\cdot10^{-8}$	Q-Brine/Cem./Citrate	$Am(OH)_3$	38	81.8	
$1.4\cdot10^{-6}$	Q-Brine/Cem./Oxalate	$Eu(OH)_3$	38	21.6	0.04
$8.7\cdot10^{-7}$	Q-Brine/Bit./DBP	$Eu(OH)_3$	37	76.9	0.0
$1.1\cdot10^{-6}$	Q-Brine/Bit./TBP	$Eu(OH)_3$	36	82.1	0.0
$1.2\cdot10^{-8}$	Q-Brine/Bit./EDTA	$Eu(OH)_3$	36	67.9	
$3.9\cdot10^{-6}$	Q-Brine/Bit./Citrate	$Eu(OH)_3$	34	98.3	
$7.5\cdot10^{-8}$	Q-Brine/Bit./Oxalate	$Eu(OH)_3$	34	79.8	

Table IV. Sorption of trivalent cations on solid NaCl under the influence of complexing organics

solution	org. ligand	compound	volume / cm^3	mass of NaCl / g	Rs /$cm^3\cdot g^{-1}$
NaCl/Cement	DBP	$Am(OH)_3$	5	2.0040	5.0
	TBP	$Am(OH)_3$	5	2.0012	21.5
	EDTA	$Am(OH)_3$	5	2.0008	0.27
	Citrate	$Am(OH)_3$	5	1.9907	0.58
	Oxalate	$Am(OH)_3$	5	2.0083	29.3
NaCl/Bitumen	DBP	$Eu(OH)_3$	5	2.0040	0.19
	TBP	$Eu(OH)_3$	5	2.0012	13.7
	EDTA	$Eu(OH)_3$	5	2.0008	0.41
	Citrate	$Eu(OH)_3$	5	1.9907	0.40
	Oxalate	$Eu(OH)_3$	5	2.0083	0.77
Q-Brine/Cement	DBP	$Am(OH)_3$	5	2.0031	0.41
	TBP	$Am(OH)_3$	5	2.0029	0.29
	EDTA	$Eu(OH)_3$	5	1.9987	1.8
	Citrate	$Am(OH)_3$	5	2.0000	6.16
	Oxalate	$Eu(OH)_3$	5	2.0010	13.7
Q-Brine/Bitumen	DBP	$Eu(OH)_3$	5	2.0001	0.16
	TBP	$Eu(OH)_3$	5	2.0219	0.59
	EDTA	$Eu(OH)_3$	5	1.9998	0.35
	Citrate	$Eu(OH)_3$	5	2.0100	0.25
	Oxalate	$Eu(OH)_3$	5	2.0006	15.0

Table V. Values for lg K_F and N obtained from Freundlich isotherms for sorption of uranium at 298 K

solution	org.ligand	solid	lg K_F	N
NaCl/cement	EDTA	rock salt	-3.26±0.15	1.07±0.06
NaCl/cement	EDTA	$Fe(OH)_3$	0.63±0.05	1.05±0.02
NaCl/cement	EDTA	cement	0.09±0.07	1.07±0.03
NaCl/cement	citrate	rock salt	-2.82±0.14	1.04±0.04
NaCl/cement	citrate	$Fe(OH)_3$	0.36±0.08	1.05±0.02
NaCl/cement	citrate	cement	-0.84±0.05	1.01±0.02
NaCl/bitumen	EDTA	rock salt	-2.43±0.66	1.09±0.30
NaCl/bitumen	citrate	rock salt	-0.73±0.23	1.85±0.19
NaCl/bitumen	citrate	$Fe(OH)_3$	-2.96±0.24	0.62±0.06
NaCl/bitumen	oxalate	rock salt	-3.30±0.13	0.92±0.04
NaCl/bitumen	oxalate	$Fe(OH)_3$	0.52±0.07	1.00±0.02
Q-brine/bitumen	EDTA	rock salt	-4.23±0.48	0.92±0.15
Q-brine/bitumen	EDTA	$Fe(OH)_3$	-2.41±0.22	0.96±0.08
Q-brine/bitumen	EDTA	cement	0.16±0.45	1.20±0.18
Q-brine/bitumen	citrate	rock salt	-3.65±0.24	0.88±0.08
Q-brine/bitumen	citrate	$Fe(OH)_3$	-0.99±0.12	0.96±0.04
Q-brine/bitumen	citrate	cement	-1.52±0.26	0.96±0.09
Q-brine/bitumen	oxalate	rock salt	-2.72±0.14	0.99±0.04
Q-brine/bitumen	oxalate	$Fe(OH)_3$	-0.55±0.07	0.95±0.02
Q-brine/bitumen	oxalate	cement	-1.60±0.08	0.91±0.02

Table VI. Values for lg K_F and N obtained from Freundlich isotherms for sorption of neptunium at 298 K

solution	org.ligand	solid	lg K_F	N
NaCl/bitumen	EDTA	rock salt	-4.94±0.16	0.49±0.06
NaCl/bitumen	EDTA	$Fe(OH)_3$	-0.29±0.40	1.07±0.13
NaCl/bitumen	citrate	rock salt	-3.36±0.16	1.00±0.10
NaCl/bitumen	citrate	$Fe(OH)_3$	1.63±0.81	1.44±0.55

Table VII. Values for lg K_F and N obtained from Freundlich isotherms for sorption of trivalent europium at 298 K

solution	org.ligand	solid	lg K_F	N
NaCl/cement	EDTA	rock salt	-4.08±0.51	0.99±0.20
NaCl/cement	EDTA	$Fe(OH)_3$	-2.37±0.18	0.59±0.07
NaCl/cement	citrate	rock salt	-2.88±0.17	0.92±0.05
NaCl/cement	citrate	cement	-3.12±0.18	0.74±0.07
NaCl/bitumen	EDTA	rock salt	-4.51±0.50	0.86±0.18
NaCl/bitumen	EDTA	$Fe(OH)_3$	-2.10±0.16	0.64±0.05
NaCl/bitumen	citrate	rock salt	-5.36±0.49	0.53±0.15
NaCl/bitumen	citrate	$Fe(OH)_3$	-2.16±0.13	0.64±0.05
Q-brine/bitumen	EDTA	rock salt	-3.35±0.18	0.93±0.05
Q-brine/bitumen	EDTA	cement	-3.28±0.56	0.65±0.16
Q-brine/bitumen	EDTA	$Fe(OH)_3$	-2.32±0.32	0.70±0.08
Q-brine/bitumen	citrate	rock salt	-3.39±0.27	0.96±0.09
Q-brine/bitumen	citrate	cement	-0.78±0.16	1.00±0.05
Q-brine/bitumen	citrate	$Fe(OH)_3$	-1.87±0.19	0.73±0.05
Q-brine/bitumen	oxalate	rock salt	-3.19±0.27	0.84±0.08
Q-brine/bitumen	oxalate	cement	-0.64±0.15	0.90±0.04
Q-brine/bitumen	oxalate	$Fe(OH)_3$	-0.59±0.16	0.82±0.04

INVESTIGATION OF LLW AND MLW CEMENT PRODUCTS FROM REPROCESSING

Contractor:	Kernforschungszentrum Karlsruhe GmbH Institut für Nukleare Ensorgungstechnik
Contract Nr.:	FI 1W-0092-D(B)
Duration of contract:	July 1, 1986 - December 31, 1989
Period covered:	January 1, 1989 - 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 varify the numerous results from experiments on simulated samples.

B. Work program

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

B.2. Investigations with simulated samples. Determination of the kinetic of the release of Pu, Am and Np in salt brines. Determination of effective Diffusioncoefficients for the release from laboratory samples. Determination of the equilibrium concentrations for Pu, Am and Np in the system waste form/salt brine.

C. Progress of work and results

State of advancement

In the period under review, studies were continued to determine the equilibrium concentrations for actinides in the cement waste form/brine system. For Pu, Am and Np the equilibrium concentrations in salt brines in contact with cementitious waste forms in the presence of complexing agents have been measured. In addition some experiments were performed determining the chemical stability of EDTA, NTA and citric acid under the conditions of the waste pretreatment (evaporation). Parallel first thermodynamic calculations were performed to illustrate the stability of the Am/EDTA complex as function of pH. The kinetic of actinide release from cemented waste forms in brines was also investigated and the leach tests with inactive and active full scale samples (200 l) in Q-brine at 40°C were continued.

Progress and results

EDTA, NTA and citric acid are chemically stable under the conditions of low level waste evaporation (T = 100°C, pH = 11,5). Under the conditions of medium level waste evaporation (T = 115°C, about 1 Mol/l HNO_3) citric acid is chemically stable whereas EDTA and NTA were degraded, especially in the presence of Fe^{3+} ions (average residence time 7 h). The degradation of NTA is slower than the degradation of EDTA.

For Pu, Am and Np doped samples the equilibrium concentrations in Q-brine and NaCl solution were determined in the presence of EDTA, NTA, Citric acid, Oxalic acid, Tartaric acid and TBP /1/. The procedure used was as follows: For each test, 30 ml NaCl solution or Q-brine were added to a sample of 2 g crushed cementitious waste form and 0.1 g of complexing agent. This ratio is much larger than expected in real waste forms, but was chosen to permit reasonable measurements. Actual species contain only about 3.E-4 g of complexant per gram. The radionuclides were added as a nitric acid solution to the suspension. Their total amount (9.1E-5 g Pu, 1.1E-6g Am, 1.7E-5 g Np) was selected so as to correspond to the content of the respective radionuclide in actual waste forms. After a storage time sufficient to attain equilibrium, samples were drawn from the brine, filtered in an Amicon system (1.8 nm) and the concentration of radionuclides determined by liquid scintillation counting and/or gamma counting techniques.Table I shows the results obtained in Q-Brine. The data in Table I indicate that the concentration of Pu is increased slightly if EDTA, NTA or TBP are added; there is no effect at all in case of Np. The concentration of Am is increased by a factor of 10 to 100 if EDTA, NTA, oxalic acid or tartaric acid are added. The influence of TBP is smaller and citric acid shows practically no effect. Yet, the concentration eventually attained is at most one tenth of that calculated if the total Am were in solution, despite the large excess of complexant. The results in saturated NaCl solution are listed in Table II. On contact with cement, the pH of the brine rises to 12 and there is no increase of the equilibrium concentration of Pu, Am and Np beyond the solubility limit caused by any complexant (last row of Table II). In another series of experiments, sodium hydroxide was used instead of cement (calcium hydroxide) to adjust to 12 the pH of a NaCl solution containing actinides and complexants. The data listed in Table 2 show that some of the complexes are still stable in the alkaline environment in the absence of Ca ions. This demonstrates that the actinide concentration in brine is not solely pH-dependent but there is a competition of calcium and actinide ions for the complexing agent. This is in agreement with computations performed for the system Am/Ca/EDTA and Am/Na/EDTA using the codes MIEQL and EQ3/6. The results obtained are represented in Figs. 1 and 2. According to Fig. 1, the Am/EDTA complex is decomposed above pH 11 and hydrolysis prevails. If calcium ions compete with the Am for the EDTA (Fig. 2), the limit of stability region of the Am complex is lowered to pH 8.

In addition to the determination of the equilibrium concentrations experiments were performed to investigate the kinetic of the radionuclide release. Pu doped cylindrical samples were leached in Q-brine and NaCl solution and the leachant was renewed daily. From the time dependence of the Pu release the diffusion coefficient was calculated. The obtained value for Q-brine amounts to D = 1. E-16 m^2/s. Due to the comparable low Pu concentration in NaCl solution and the low specific activity of Pu-239, the error for the Pu measurements in NaCl solution is too high and therefore no diffusion coefficient calculation was possible. For the same reason no experiments were performed for U and Np.

The full scale leach experiments with inactive and active samples were continued. Fig.3 shows the Cs release. The increase of the Cs release for the inactive samples after a period of about 2 years is due to the corrosion (Ca/Mg exchange) of the samples. For the real samples up to now, only Cs-134 and Cs-137 was detected in Q-brine. The value for the gross alpha-activity was always in the range of the detection limit.

References

/1/ P. Vejmelka, G. Rudolph, R. Köster
Source term evaluation for actinide elements in the system cemented waste form/salt brine - influence of organic complexants
"Migration 89", International Conference on Geochemistry and Migration of Actinides and FP, Monterey, USA, 6-10 Nov. 1989

Table I: Equilibrium concentrations of actinides in solution in the system cementitious waste form/ Q-brine (pH = 6,5)

Specimen	Pu	Am (mol/l)	Np
no complexant	7.E-8	5.E-10	3.E-8
EDTA	3.E-7	2.E-8	3.E-8
NTA	3.E-7	2.E-8	3.E-8
TBP	2.E-7	4.E-9	3.E-8
citric acid	3.E-8	1.E-9	3.E-8
oxalic acid	5.E-8	1.E-8	-
tartaric adid	4.E-8	2.E-8	-

Table II: Equilibrium concentrations of actinides in NaCl solution (0.1 g complexant, 30 ml solution, pH = 12)

Specimen	Pu	Am (mol/l)	Np
EDTA	1.2E-7	1. E-7	3.1E-6
NTA	1.2E-8	-	3. E-6
citric acid	7.E-10	-	6.6E-8
tartaric acid	3.4E-6	1.6E-7	-
oxalic acid	4. E-10	1.6E-7	-
with cement	4.E-10	2.E-10	<1. E-8

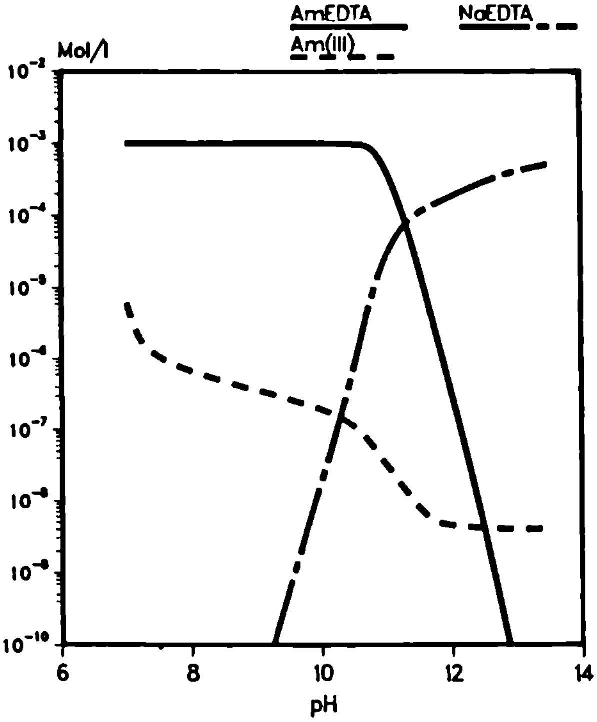

Figure 1. Calculated americium concentration as a function of pH with EDTA (0.001 mol/l) and Na (0.04 mol/l) added

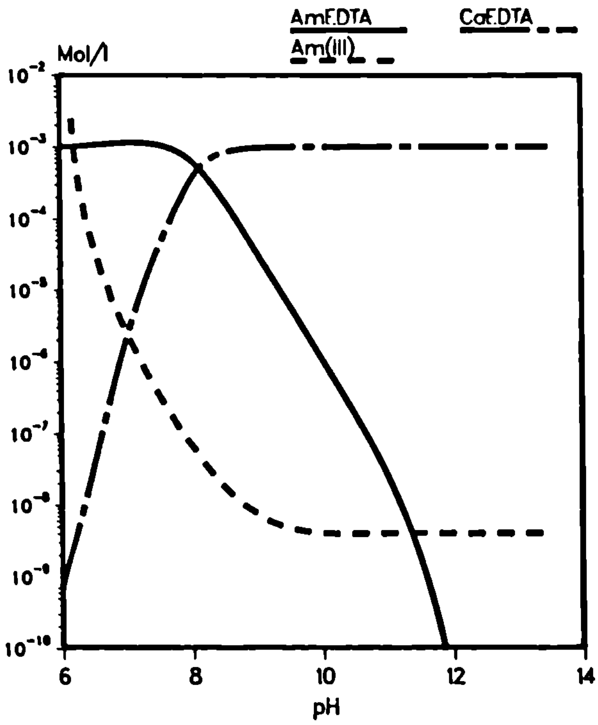

Figure 2. Calculated americium concentration as a function of pH with EDTA (0.001 mol/l) and Ca (0.01 mol/l) added

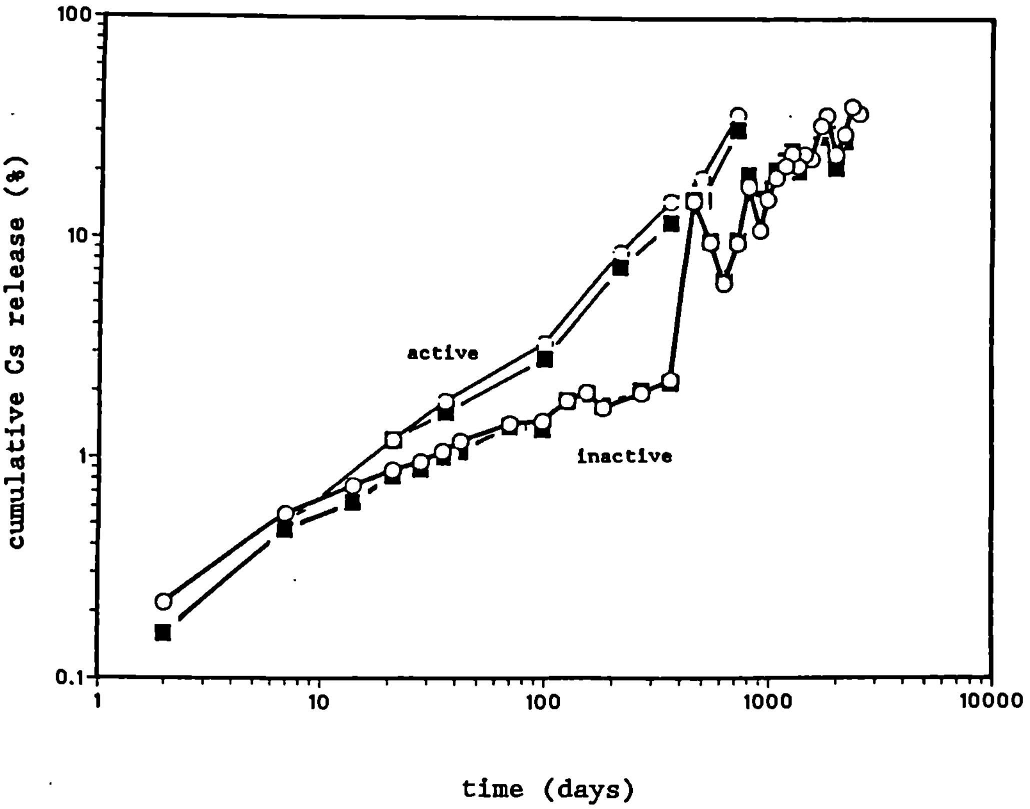

Figure 3. Cs release from inactive and active full scale cemented waste forms (200 l) in Q brine at 40°C (S/V = 0.096 cm^{-1})

Physico-chemical characterization of bitumized Eurochemic medium level waste

Contractor : S.C.K./C.E.N. Mol, Belgium
contract N° : FI1W/0094
Duration of Contract : 1/08/1986-31/12/1989
Period covered : 1/01/1989-31/12/1989
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 625, 220, 70 and 25 m^{-1}, to conclude about the swelling behaviour of full size blocks (10 m^{-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

All tests concerning part B.1 were completed in 1988 and the results reported in the report of that year.

During 1989 all remaining corrosion tests from part B.2 were finished : this includes tests on active Eurobitum samples at ambient and at repository like pressure in two clay related media, and also additional tests on inactive simulates at ambient pressure in the same media. For the tests at ambient pressure (both active and inactive tests) all results from chemical and radiochemical analyses are available, while for the tests at repository like pressure some results are still awaited.

The measurements of the physico-chemical properties on real Eurobitum stored for 6.5 years are underway, and will be finished early 1990.

Corrosion of inactive samples in clay related media

To link the data from the inactive tests of part B.1 with the active tests at ambient pressure of part B.2, inactive tests have been performed on samples of small (0.75 ml) and intermediate size (500 ml) in the media, used in B.2, being oxidizing interstitial claywater (OSIC) and a mixture containing 500 g Boom clay per liter OSIC (CCOSICM). The tests were analysed in terms of dimensional changes for the bitumen, and cation (Na, Ca, Fe, Zr, Mn, U) and anion (NO_3, SO_4, F) analysis of the solution. The main conclusions are :

- The substitution of distilled water (DW) by OSIC lowers the swelling with a factor 2 to 3, but the influence of the sample size upon (relative) swelling persists (10 times higher swelling for the 0,75 ml samples than for the 500 ml samples).
- The change of the leachate does not result in large differences in the leaching behaviour of the simulates, and therefore the main conclusions from part B.1 are confirmed : incongruent leaching of the waste constituents with on one side the diffusion controlled losses for $NaNO_3$ ($D_e = 1.7*10^{-13}$ $m^2.sec^{-1}$) and $CaSO_4$ ($D_e = 1.0*10^{-15}$ $m^2.sec^{-1}$) and on the other side the much lower (and probably solubility controlled) losses for U, Fe, Zr, Mn. The main difference between the results in DW and OSIC is the much slower release of $CaSO_4$ in OSIC (D_e 10 * lower than in DW), probably due to the high initial sulphate concentration of the OSIC.
- Addition of clay to the OSIC might slightly increase the swelling of the 0.75 ml samples (after 1 year 13 % in CCOSICM against 9 % in OSIC), the losses for most waste components (especially Ca and Mn) do increase. Also in the preponderant leaching mechanisms some differences occur : the characteristics of a diffusion controlled mechanism were not observed for $CaSO_4$, while for Mn the losses might show here a diffusion controlled mechanism.

Effect of pressure on the corrosion and swelling behaviour

Active Eurobitum samples of about 0.85 ml each were exposed to corrosion in OSIC and CCOSICM at ambient pressure or repository like pressure (4.0 MPa). For the tests in CCOSICM, a separation of the clay from the leachate is performed after the tests by means of high speed centrifugation ; the liquid fraction is thereafter ultrafiltered (10^5 MW cut-off) before analysis. The same analyses as for the inactive tests are performed, but with additional radiochemical analysis (of Cs-137, Co-60, Sr-90 and the total amount of alpha-emitters) on the liquid fraction, the clay and the rinsing water (of the test cup and of the ultrafilter) in case of CCOSICM, and on the leachate and the rinsing water (of the test cup only) in case of OSIC.

The main conclusions are :

- The swelling measured on the active samples is always an order of magnitute higher than for the inactive simulates, primarily due to the larger hardness of the simulates ; in comparison with this, the effect of all other changes (leachate, pressure) upon swelling is marginal. The raising of the pressure results for the longer durations (180 days and more) in a decrease of the swelling with a factor 2 in CCOSICM, while in OSIC the decrease is hardly significant. Addition of clay to OSIC might increase the swelling at ambient pressure (140 % in OSIC against 190 % in CCOSICM after 1 year), but at repository like pressure the swelling in both media is almost equal (105 % in OSIC and 95 % in CCOSICM after 1 year).
- As the results from chemical and radiochemical analyses for the tests under repository like pressure are only partially available, no conclusions about the influence of the pressure on the leaching behaviour can be put forward yet. A comparison between the leaching behaviour of the active samples at atmospheric pressure and the inactive samples in the same leaching media can however be made : contrary to the huge differences in swelling behaviour, only minor differences occur concerning the leaching behaviour for both materials in OSIC : the active samples show higher losses for F and Mn and a less pronounced diffusion like mechanism for $NaNO_3$. The addition of clay does not increase the losses (for $NaNO_3$ and U they even decrease) from the active material ; the differences between the leaching results for both materials in CCOSICM are therefore larger, and in favour of the active material.
- The tests at atmospheric pressure in OSIC indicate that the retention capacity of Eurobitum for the radionuclides is very inhomogeneous : the alpha-emitters and Cs-137 are leached for a small fraction only (resp. < 0.1 % and < 0.02 % of the inventory), being constant with time while Co-60 and Sr-90 are further leached till 180 days (losses of 0.4 % and 15 % resp.), whereafter the losses stay constant. The addition of clay seems to have a positive effect on the retention of Sr-90 and Co-60 : till 90 days the releases are almost equal to those in OSIC, but as they stay constant afterwards, the releases for the longer durations are reduced with a factor 2. The Cs-137 release does not seem to be influenced by the addition of clay, while the releases of the alpha-emitters are raised (and probably not constant with time) : after 1 year 0.5 % of the inventory has been leached (and a further increase with longer durations can not be excluded).

List of publications and lectures

(1) Physico-chemical characterization of bituminized Eurochemic medium-level waste. Annual report 1988 (R2757). Presented at the CEC progress meeting for task 3, sections 1 + 5 (Ispra, April 1989).

(2) Physico-chemical characterization of bituminized Eurochemic medium-level waste. Semestrial progress report January-June 1989, presented at the CEC progress meeting for task 3, sections 1 + 5 (Madrid, September 1989).

(3) P. Van Iseghem et al., Characterization and compatibility of low- and intermediate level waste forms, presented at the IAEA Third Research Coordination Meeting on Evaluation of Low and Intermediate Level Radioactive Solidified Waste Forms and Packages, (Harwell, November 1989).

FULL SCALE LEACHING TESTS, LYSIMETER TESTS, SCALE EFFECT

Contractor : CEA CEN CADARACHE - FRANCE
Contract N° : FI 1W/0095 Task 1/5
Duration of contract : From August 86 to December 89
Period covered : January 89 - December 89
Project leader : A. SAAS
Executant of task 1 : J.C. NOMINE - CEN SACLAY

A) OBJECTIVE AND SCOPES

The task 3 deals with the following areas of applied research : full scale leaching tests, laboratory lysimeter tests and the study of the scale effect in the leachability of radioactive blocks.

B) WORK PROGRAM

B1) Knowledge of the transfer of radionuclides by leaching of full scale packages coming from the producer's facilities.

B2) Laboratory lysimetric tests.

B3) Study of the scale effect for a cement 137 Cs waste system. Possibilities of extrapolation from laboratory samples to full size active packages.

C) PROGRESS OF WORK AND OBTAINED RESULTS

During the period January. December 1989 new and substential results on the above mentionned objectives have been obtained, specially in the fields of leaching tests carried out on full size active package lysimeter tests, and scale effect studies.

1. FULL SCALE LEACHING TESTS

Full scale leaching tests, using a static method with or without leachant renewal have been performed.

1.1. Cement $\beta\gamma$ concentrate block from KfK (200 l)

This test has been stopped after a duration of 1450 days. The major radionuclides leached where ^{137}Cs and ^{90}Sr. The block which is now completely broken under the leachant effect will be reconditionned for transportation to the KfK producer facility.

1.2. Cement cladding Hulls representative samples (2 l)

Two blocks have been leached, the foremost at 20°C, the later at 70°C in order to appreciate the temperature effect on the leachability of the main radionuclides embedded. It has been observed that the leachability of ^{137}Cs is multiplied by a factor 7 between 20 and 70°C. For ^{60}Co, ^{125}Sb and the traces of α emitters no significant results have been seen.

1.3. Epoxy. Ion exchange resins packages (200 l)

The leachability of ^{137}Cs and ^{60}Co which were the most important radionuclides encapsulated has been measured ; very low fraction of them have been leached, demonstrating the quality of the confinement.

2. LYSIMETER TESTS

Lysimeters apparatus are now operational. After several tests with inactive samples surrounded by simulated host engineered barriers, it has been decided to carry out active tests.

In a first step they have been conducting using the following protocol :

- standard leaching test as a reference,
- lysimeter tests with cement part doped with Cesium 137 :
- "inactive" host barriers as surrounding materials (glass balls, silica sand).

The comparison of the first results between lysimeter and traditional leaching tests are surprising ; to day, no really significant differences have been observed ; no explanation is yet avalaible. Tests are continuing.

3. SCALE EFFECT

A complete study of the scale effect in the area of the leachability of radioactive wastes embedded in cement has been achieved.

The final report will be published. These study has been carried out on a cement. Cesium 137 system using samples of differents sizes (200, 20, 2 and 0,2 l). In conclusion, for this system only extrapolation between laboratories samples and full size parts is possible.

BITUMEN AND POLYMER CHARACTERIZATION

Contractor : CEA CEN CADARACHE - FRANCE
Contract N° : FI 1W/0095 Task 2/5
Duration of contract : From August 86 to December 89
Period covered : January 89 - December 89
Project leader : A. SAAS
Executant of task 2 : MM. C. COURTOIS -
H. VIDAL - DE TASSIGNY
Mme N. LANGOMAZINO

A) OBJECTIVES AND SCOPES

This part of contract includes three main items.

1. BIODEGRADATION STUDIES - Mme N. LANGOMAZINO - CEN CADARACHE

The scope of these studies is the assessment of hydrocarbons biodegradation.

The quantitative evaluation of the biodegradation is measured by the CO_2 production.

The influence of the content of salts in the embedded waste is also studied.

2. LEACHING STUDIES - C. COURTOIS - H. VIDAL - CEN CADARACHE

The scope of these leaching studies is the collection of data from :

- leaching test of real reprocessing sludges embedded in blown bitumen,
- leaching test of real ion exchangers (P.W.R. Origin) embedded in thermosetting resins (epoxide matrix).

3. DIFFUSION COEFFICIENT STUDIES - M. DE TASSIGNY SPR CEN.G

Characterization test of ageing of embedded radioactive wastes in polymers is looking for among several spectroscopic methods adapted to the analysis of different polymeric matrices.

Comparison between old and reference samples are studied mainly with epoxide materials.

B) WORK PROGRAM

B1) Biodegradation studies Mme N. LANGOMAZINO.

B1.1) Screening of microorganisms able to degrade hydrocarbons.
B1.2) Qualitative evaluation of biodegradation of bitumen MR 90/40.
B1.3) Quantitative evaluation of biodegradation of bitumen MR 90/40 and waste forms by measure of CO_2.
B1.4) Chemical evolution of bitumen after attack of microorganisms.
B1.5) Influence of waste forms salts on the rate of biodegradation and microbial metabolism.

B2) Leaching studies - C. COURTOIS - H. VIDAL.

B2.1) Manufacturing of the samples (bitumen and polymer).
B2.2) Initial analysis (bitumen and polymer).
B2.3) Work survey.
B2.4) Data collection and conclusion.

B3) Diffusion coefficient studies - M. DE TASSIGNY.

B3.1) Bibliography.
Bibliography state of the research in the field of ageing has been done for spectroscopic methods.

B3.2) Study of the chemical state of degradation
UV and IR spectrum in polymers give usefull informations of a state of degradation in the structure of the polymeric matrix. Degradation profiles have been obtained by analysis of samples coming from old wastes ageed in climatic conditions at the open air.

B3.3) Study of morphologic degradation.
Optical microscopic methods on thin layers cutted in samples will give information on thermomechanic ageing of the matrix.

B3.4) Test of degradation.
Correlation between these different kinds of analysis may give a test for defining a state of ageing.

C) PROGRESS OF WORK AND OBTAINED RESULTS

1. BIODEGRADATION STUDIES - Mme N. LANGOMAZINO

This part of programme (B1) is finished for one year. No progress and no new results are available during 1989.

We are writting the final report.

2. LEACHING STUDES -C. COURTOIS - H. VIDAL

2.1. Wastes embedded in bitumen (B2.3)

Wastes are chemical precipitation sludges issued from reprocessing plant of La Hague and embedded in blown bitumen type 90/40.

Leaching tests are conducted on cylindrical samples (Ø 50 mm, h 50 mm) manufactured in hot cell.

The leaching surface is the upper part of the cylinder as for AIEA standard test.

Radionuclides inclued in the matrix are ^{60}Co, ^{106}Ru, ^{134} and ^{137}Cs, ^{238}Pu and ^{241}Am. Release of these nuclides is followed.

Leach test are done in static manner during over a year.

State of advancement

Results after 540 days are available and have been given last April : the standardized cumulative leached ratio are close to 10^{-5} for ^{238}Pu and ^{90}Sr and one order of magnitude below for ^{137}Cs.

2.2. Wastes embedded in polymers (B2.3)

These studies are set on ion exchangers embedded in an epoxide thermosetting resin.

Leaching tests are conducted on cylindric samples (Ø 80 mm, h 80 mm) manufactured in hot laboratory.

Leaching surface is the entire surface of the sample : no mould is necessary to maintain its integrity.

Main radionuclides included in the matrix are ^{58} and ^{60}Co, ^{134} and ^{137}Cs and are being looked after.

Leach test are done in static manner during over a year.

State of advancement

Results after 548 days (1,5 years) are available and balance is beeing set up : the standardized cumulative leached ratio are close to 10^{-3} for ^{60}Co and 10^{-2} for ^{137}Cs.

Leach test is definitively stopped.

Final report for both bitumen and epoxy studies is under way.

3. DIFFUSION COEFFICIENT STUDIES

During 1989 the determination of concentration profile of cesium inside epoxy resins was achieved by two methods :

- Secondary Ion Mass Spectrometry (SIMS) which gives a local determination of mass,
- Neutron Activation Analysis which gives a total rate of element in samples (layers of polymer for instance). This was a reference method for determination of mass of cesium.

Profiles of concentration inside epoxy samples were obtained for cesium after immersion in aqueous of cesium chloride. Results were given after several diffusion times.

An estimation of diffusion coefficient was calculated from the concentration profiles. Correlation between the two methods was rather good.

SPECIATION OF THE TRANSURANIUM ELEMENTS STEMMING FROM LOW AND INTERMEDIATE ACTIVITY LEVEL WASTES

Contractor : CEA CEN CADARACHE - FRANCE
Contract N° : FI 1 W/095 Task 3/5
Duration of contract : From August 86 to December 89
Period covered : January 89 - December 89
Project leader : A. SAAS
Executants of task 3 : D. STAMMOSE, P. MEIER
CEN Fontenay aux Roses

A) OBJECTIVE AND SCOPE

The behaviour of radionucleides in the biosphere depends on their chemical form. The alpha emitters which can be present in solution, on several forms (complexes, precipitates, colloids...) need a particular attention. The aim of this program is to improve speciation methods soon in the laboratory and to set up new procedures giving more precise information (nature, size, charge) on the different species present in the leachates.

B) WORK PROGRAM

B1) Study of the conditions of formation of radiocolloids of plutonium at trace level and first essays of characterisation of these colloids.

B2) Study of two speciation procedures allowing the discrimination, in solution, between the valences V and VI of plutonium.

C) PROGRESS OF WORK AND OBTAINED RESULTS

State of avancement

(B1) Experiments on the formation of radiocolloids of plutonium versus time have been conducted in $NaClO_4$ medium at pH 2 and pH 8, and for a plutonium concentration of 10^{-6} M. Ultrafiltration and ultracentrifugation experiments have been used to isolate and characterize the insoluble species. Some measurements using Photon Correlation Spectroscopy have been made on resulting solutions.

(B2) According to literature data, two new procedures allowing the speciation in solution of the valences V and VI of plutonium have been tested. The first one, using the high retention of Pu VI onto silica (Pu V remaining in solution) has been set up and is now usable in our speciation studies. In the second one, the solid phase (calcite) was reported as a selective adsorbent of Pu V (Pu VI remaining in solution). First experiments have pointed out the importance of parameters : pH, contact time, mass of solide.. . This study is continued.

Progress and results

(B1) Colloids of plutonium

In acidic conditions (pH-2), evidence for radiocolloids formation occurs after 3 weeks while for a higher pH (pH-8.5), insoluble species are decelable after 3 days of settling time. At this pH value, for contact time higher than 2 weeks, the distribution of plutonium between the insoluble and soluble fractions seems constant. Some Photon

Correlation Spectroscopy (PCS) experiments conducted on solutions 3 weeks old (pH 8.5) permit an estimation of the size of the Pu-colloid to 400 nm. The ultracentrifugation measurements on the same solutions give a density valueclose to those of water. The radiocolloids formed in these conditions (pH 8.5, 3 weeks of ageing) seem highly hydrated.

The addition of calcium to the solution at two concentrations (above and below the solubility of calcium in this medium) does not induce a significative modification in the formation of Pu-colloids (similar kinetic and size).

(B2) Speciation of Pu V/Pu VI

Choppin [1] has reported a procedure using silica to separate Pu V from Pu VI. This method has been first tested on Np V because of its stability in solution. The results obtained for Np V and Pu V are quite similar : the quantity of radioelement sorbed on silica is less than 5 % of the total concentration. In the opposite, the sorption of Pu VI reaches 95 % of the total concentration.

This procedure allows the separation of Pu V from Pu VI at pH 8 if the solution does not contain others Pu valency like Pu III for which a strong retention is predicted by analogy with Am III [3].

The other speciation method proposed by the same authors, using the calcite as support, seems in view of the first results not usable for a good speciation between the two oxydation degrees. First experiments have pointed out the sorption of Pu VI together with Pu V onto calcite. Moreover, solubility of calcite is pH dependent and kinetic of the Pu sorption is slow. Complementary experiments need to improve this method.

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EMBEDDED WASTES AND LEACHATES ANALYSIS

Contractor : CEA - CEN CADARACHE - FRANCE
Contract n° : FI 1W/0095 Task 4/5
Duration of contract : from August 86 - to December 89
Period covered : January 89 - December 89
Project leader : A. SAAS
Executant of task 4/5 : A. RAYMOND - D. REVY - 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 final objective of the program is to provide an acceptable set of methods for the characterization of each type of embedded waste.

B - Work programme

B1. Full destruction of embedded thermosetting resins.

B2. Measurement of pure beta emitters (^{63} + ^{59}Ni ; ^{55}Fe, ^{99}Tc)

B3. Mineralization of bitumen matrices and solubilisation of sludges used to coprecipitate nuclides.

B4. Solubilization of cement matrices.

B5. Method for concentration and measurement of alpha-emitters at low level in leachates.

B6. Isolation of gamma-emitters at low concentration (such as ^{94}Nb).

C - PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In 1989, we completed this program by the development of procedures for measuring alpha-emitting radionuclides at low concentration in leachates. This corresponds to the task B.5 of the work program.

Progress and results

Detection yield

Detection yields of our four detectors were measured as a function of the source-detector distances by means of a 10.3 Bq - ^{243}Am source electroplated on 19 mm (O.D) stainless steel disk. Results are in table 1.

Detector	A	B	C	D
Detector/source distance (mm)				
1	59 %	67 %	60 %	61 %
4	35 %	42 %	37 %	38 %
7	25 %	28 %	25 %	26 %
21	6.9 %	7.9 %	7.2 %	7.3 %

Table 1 - Detection yield (2π) of 4 different Si(Li) detectors as a function of the source/detection distance.

Background level

A major parameter for determining limits of detection, the background levels of our 4 detectors were mesured with 24 hours counting times. The results are in table 2.

Window / Detector	3-7 MeV	5.05-5.25 MeV (Pu-239)	5.25-5.40 MeV (U-232/ Am-243)	5.40-5.60 MeV (Pu-238/ Am-241)	5.60-5.90 MeV (Pu-236/ Cm-244)	≥ 6 MeV
A	51	2	5	2	11	10
B	105	6	17	23	11	21
C	55	2	12	10	5	15
D	41	2	3	4	4	10

Table 2 - Background levels (impulses/24 H) of four different Si(Li) detectors.

Theorical limits of detection

The data display in table 1 and 2 were used to calculate theorical limits of detection (table 3) by mean of the equation .

$$m_D = \frac{4}{t.R} [1 + \sqrt{1 + 2 Bt}] . 1000$$

where mD is the minimum activity, in mBq, detectable with 97,5 % probability

t is the counting time (54000 s)

R is the measurement yield for 4π geometry with a detector/source distance of 1 mm.

B is the counting rate of the background in cps.

Radio-nuclides / Detector	Total α	Pu-239/ 240	U-232/ Am-243	Pu-238/ Am-241	Pu-236/ Cm-244
A	2.28	0.72	0.92	0.72	1.20
B	2.76	0.87	1.26	1.43	1.07
C	2.31	0.71	1.23	1.15	0.91
D	2.00	0.70	0.77	0.84	0.84

Table 3 - Theorical limits of detection in mBq for 4 different Si(Li) detectors.

Pratical limits of detection

Taking into account that several different determinations must be performed on the same leachate sample, aliquotes limited to 100 ml, are usually only available for α analyses.

The electrodeposition yields being around 80 % and the chemical separation yields between 50 and 90 %, all this leads to pratical detection limits for each seperate peak between 18 Bq/m^3 (PU-239/240) and 36 Bq/m^3 (PU-238/Am-241).

Optimization and characterization of cement products incorporating ashes from radwaste inceneration.

Contractor: E.N.E.A. Italy
Contract No. : FI1W-0171-I (A)
Duration of contract: January 1988 - December 1989
Period covered: January 1988 - December 1989
Project leader: G. Ricci

A. OBJECTIVE AND SCOPE

The incineration is presently considered a very good way to obtain strong volume reductions of intermediate and low activity solid radwastes obtaining at the same time a product apparently easy to be conditioned. In some cases nevertheless the ash solidification can give in the practice some problems: this was ascertained, for example, during the cementation of the ashes coming from the incineration of the Caorso radwastes at Studsvik (Sweden). It was observed there in fact a mortar swelling during the cement setting phase and moreover an ammonia evolution was noticed. Because of this strong swelling produced in the case mentioned before the mortar went out of the drums and the solidified product was very porous. Similar problems are reported to have been met in other nuclear plants /1/.

So this research contract aims to investigate about the reasons of these phenomena by means of a physico-chemical characterization of the mentioned ashes with the objective to define the best waste/cement mixtures with respect to the mechanical and leaching resistance properties.

B. WORK PROGRAMME

2.2 Ash selection and supplying.
2.3 Ash characterization by:
- AA metal analysis
- nitric, organic and ammoniacal nitrogen content
- gamma spectroscopy radiochemical analysis
- tap density
- ash particle size.

2.4 Ash cementation at 1/2, 1/3, 1/4 ash/cement ratio.
2.5 Samples characterization by mechanical strength, setting time, thermal evolution.Depending on the first results obtained the program will be continued accordingly, if the case operating some ash pretreatment. Best composition selection.
2.6 Best composition characterization by the ISO 6961-82 long term leach test.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In the last year of activity concerning this contract the contractual planned actions have been finished.

An investigation about the swelling phenomenon performed on the ashes Nust1 and Nust2 showed that during the ash cementation an Hydrogen evolution happens in the mortar due to the reaction of metals like Aluminum present in the ashes and easely oxidable in alkaline media.

To avoid the swelling phenomenon and the Hydrogen evolution an ash pretreatment has been proposed, based on the preliminary alkalinization of the ashes by 0.01 N NaOH solution.

The ISO 6961-82 long term leach test performed at 40°C in deionized water on the Nust1 and Nust2 cemented ashes with and without pretreatment gives results, concerning Cs and Co, similar to those reported in the literature for cemented radwastes.

Progress and results

Investigation on the swelling phenomenon and pretreatment proposal.

The cementation of the Nust 1 and Nust 2 ash types has shown that the swelling concerns both ashes in a similar extent. The volume increase due to the swelling amounts to about 6% and occurs in the first hours after the mortar preparation. In order to understand the origin of the swelling phenomenon a chromatographic analysis has been carried out on the gases collected during the cemented ashes setting. The analysis has shown the presence in them of remarkable H_2 amounts, at a concentration of about 10^{-5} moles H_2/gr.ash. Moreover the microscopic analysis of the ash has shown the presence of small metallic pieces in both ash types . In order to understand the origin of the H_2 evolution from the mortar, some experiments have been carried out by cementation of metallic powders composed of Aluminum, Iron and Zinc. An important H_2 gas evolution during the cementation was detected only in the case of Aluminum metal powder, and at an Aluminum concentration of 50 ppm the same swelling effect as in the case of the Nust 1 and Nust 2 cementation was observed.

Some experiments have been therefore carried out in order to avoid the swelling phenomena by a suitable pretreatment. In this way it was possible to establish that the swelling effects could be avoided if the ashes are contacted, for more than 24 hours, before the cementation, with a 0.01 M NaOH solution at the same ratio as the water-cement. This solution will therefore replace the water needed by the cementation process. Some samples obtained by the cementation of the Nust 2 ash after the above-mentioned pretreatment have shown the characteristics given in Table I.

Apart the setting time, which is slightly longer, the other product characteristics demonstrate that no effects appear by using NaOH 0.01 N in the place of water, according to the proposed pretreatment.

Long term leach test

The long term leach test procedure applied for the leachability determination is the ISO 6961/82 Standard Method, performed at 40°C in distilled water /2/ with real radioactive cemented ashes.

The shape of the cemented ash samples was cylindrical, 5 cm both in diameter and height.

The leaching rate measurements regarded the Cs137 and Co60 nuclides, the only ones detectable.

The leach test has been performed on the following ash-cement mixtures:

Nust1 ash: ash/cement = 1/2 w/w
ash/cement = 1/2 w/w after ash pretreatment with NaOH 0.01 N
Nust2 ash: ash/cement = 1/4 w/w
ash/cement = 1/3 w/w
ash/cement = 1/2 w/w
ash/cement = 1/2 w/w after ash pretreatment with NaOH 0.01 N.

In the Figures 1, 2, and 3 the leach test resuls are given in terms of % leached fractions.

The obtained results, concerning Cs and Co, are similar to those reported in the literature for cemented radwastes /3/, /4/, /5/, /6/.

From the results shown in the Figure 1 and regarding the Nust2 ash unpretreated it seems that the Cs leached fraction increases remarkably when the ash-cement ratio exceed 1/3 w/w. Moreover the ash pretreatment by NaOH 0.01 N seems to be more effective for the Nust2 ash (Figure 2) than for the Nust1 ash (Figure 3) from the point of view of the leaching. In fact the ash pretreatment in the case of the Nust2 ash improve the leaching results for the ash-cement ratio 1/2 so that these are similar to those ones obtained in the case of the ash-cement ratio 1/3 of the unpretreated ash.

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TABLE I MECHANICAL STRENGTH, SETTING TIME AND EXOTHERMIC TEMPERATURE PEAK RESULTS OF THE NUST2 PRETREATED CEMENTED ASH, IN COMPARISON WITH THE SAME CEMENTED UNPRETREATED ASH CHARACTERISTICS.

		Nust2 unpretreated	Nust2 pretreated
Ash/Cement	w/w	1/2	1/2
Water/Cement	w/w	0.5	0.5
Size		cube 10 cm.	cube 10 cm.
Mechanical Strength after 28 days	kN/m^2	13000	14000
Exothermic Peack	°C	35	38
Setting Time	h	9	10

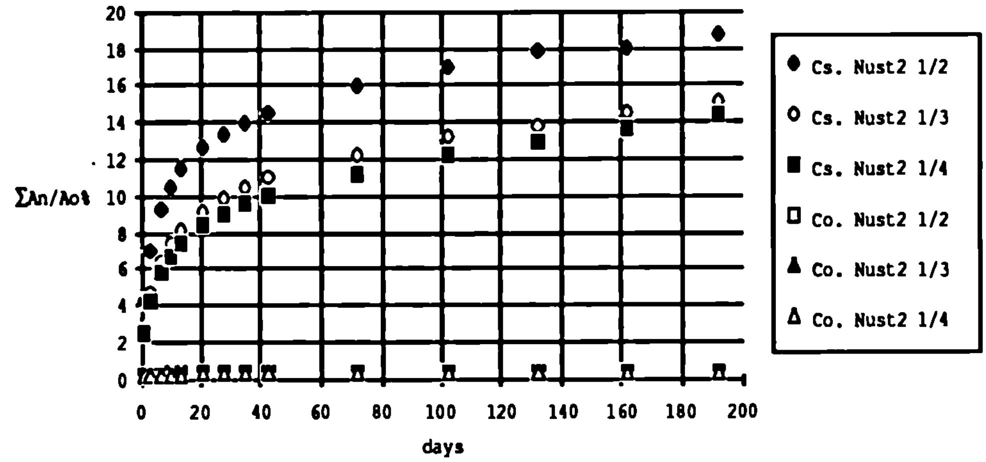


Figure 1 Cs137 and Co60 % leached fraction of Nust2 ash in cement at various ash-cement ratios.

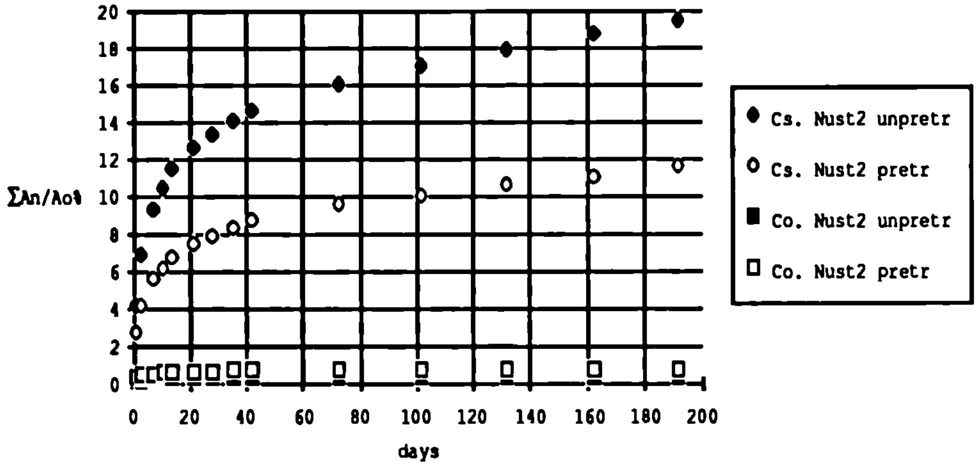


Figure 2 Cs137 and Co60 % leached fraction of Nust2 ash in cement at ash-cement ratio 1/2 with and without pretreatment.

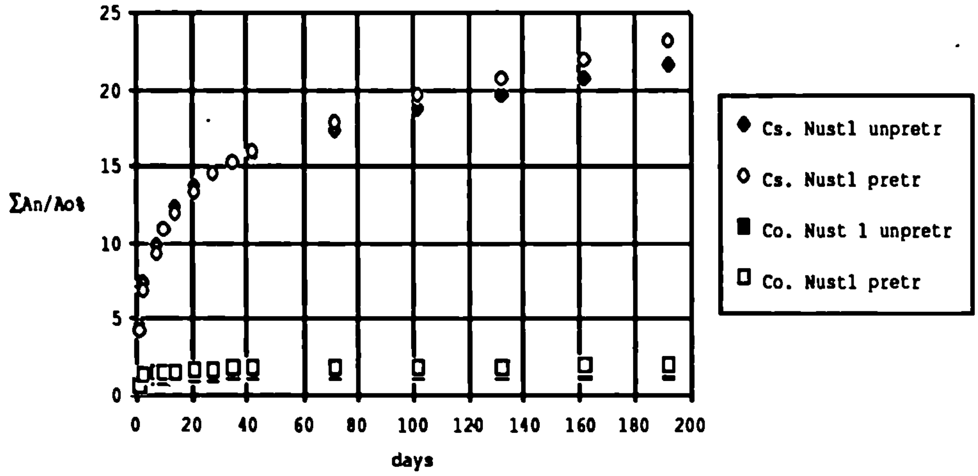


Figure 3 Cs137 and Co60 % leached fraction of Nust1 ash in cement at 1/2 ash-cement ratio.

EXPERIMENTAL STUDIES OF THE EDF REACTOR WASTES LEACHING (RMA4 and 5)

Contractor : CEA/CEN CADARACHE - FRANCE
Contract N° : FI 1W/0172
Duration of the contract : From August 1988 to June 1990
Covered period : January 1989 - December 1989
Project leader : A. SAAS
Executant : J. GIRARD - CEN CADARACHE

A) OBJECTIVES AND SCOPE

Qualification studies of IER. coating, with polymeric (PEC/SIE - Dow Method), were achieved by E.D.F. and CEA.

Very active IER conduct to difficult chemical problems. So, experimental studies about reactor wastes leaching with sample of IER coating with polymeric (and catalyser, promoter) are necessary to study parameters and quality of confinement. This experimental work is beginning since 1988. Five investigation directions, in research, will be study :

- optimization of sampling, "Ao" measure (initial activity),
- reproductiveness of leaching levels, with load and IER type,
- influence about leaching level of the load of the lixiviation liquid (type of storage),
- influence of coating about lixiviation level,
- influence of full-scale about parameters.

B) WORK PROGRAMME

All tests use active and inactive samples with high and low amount of ^{60}Co, ^{137}Cs, B, Li in impurities.

The static lixiviation timing is 15, 30, 60, 90 days.

B1) "Ao" making up of samples and Ao studies :
- disc thickness : 3, 5, 10, 20 mm,
- clip mass : 1, 10, 20 g

Destructive and non destructive method for analytical measures.

B2) Lixiviation studies in RFS water (4 x 2 measures with active samples)
Lixiviation speed (cm/d)

B3) Idem with inactive samples

B4) Active sample test procedure with :
- de-ionized water,
- RFS water pH8,
- RFS water pH4,
- RFS water with E.D.T.A.

(4 x 2 measures)

B5) Inactive sample test procedure with :
- IER type coating : anionic, only
- de-ionized water,
- RFS water pH13,
- RFS water 5°C,
- RFS water + boron.

B6) Inactive sample test with 2 different volumes of leaching (0,8 and 3 liters)

B7) Inactive sample test with different V/S values

B8) Inactive sample test with different sequences :
- 4 x 7 days, (shorter)
- 30 and 90 days, instead 15, 30, 60, 90 days.

B9) Inactive sample test with agitation of water at :
- 30 and 90 days.

B10) Coating studies with active samples
- RFS water and IER without coating,
- RFS water + ^{3}H and IER with coating,

- RFS water + ^{134}Cs and IER with coating,
- Active sample and, then, inactive sample in the same RFS water

B11) Coating studies with inactive samples
- RFS water and IER without coating,
- RFS water and carrot type sample,
- RFS water and greater coated sample (0,66 instead 0,60),
- Sample with B + Li and, then, sample without B + Li in the same RFS water.

B12) Effect of irradiation
- 2 samples loaded with B + Li and then leaching study.

B13) Full-scale effect
- RFS leaching on two industrial full-scale packages for one year.

C) PROGRESS OF WORK AND OBTAINED RESULTS

Samples

All samples for B1 to B13 are realized and under studies.

Inactive studies

All tests concerning inactive samples are finished, except :

- optimization of measures of initial concentration (B1), on study,

- irradiation of samples for leaching comparative tests (B12), on study.

All results are presented in annual report 1989 and resumed in table 1.

Active studies

Studies with samples

All tests concerning the actives samples are finished, except :

- optimization of measures of initial concentration (B1), on study ;

- three last tests of B10 (RFS water with ^3H or ^{134}Cs ; active and inactive samples in the same volume of RFS water) ;

- measure of leaching ratio for B and Li obtained on active samples, in regard of the same values for inactive samples.

All results are presented in the annual 1989 report and resumed in table 2.

Full-scale studies

On two full-scale samples, fabricated by EDF (Power Plant of ST ALBAN), the following operations are realized :

- measure of "Ao" by direct gamma spectrometry (results in table 3),

- beginning of leaching studies on november 89 ; the first results are presented in table 4.

TABLE 1

Inactive samples - Results

N°	Test type	Conclusions
B3	Low and high load in B, Li, (k ≃ 10)	With low loads, lixiviation parameters are lower : Reference speeds B = 76.10^{-5} $cm.d^{-1}$ Li= 66.10^{-5} $cm.d^{-1}$
B5	IER type (anionic, only)	No influence on lixiviation parameters
B5	Lixiviation water temperature (5°C and 20°C)	No influence
B5	Basic lixiviation water (with PORTLAND cement ; pH ≃ 13)	Lixiviation parameters are more important : boron : k = 6 ; Li : k = 4
B5	De-ionized lixiviation water	Lixiviation parameters are lower for B(k = 1/15), and for Li (no lixiviation)
B5	Lixiviation water with B (175.10^{-6} g/l)	Results dispersion
B6	Volume lower of lixiviation water (k = 1/4)	For Li, k = 0,7. For B, k = 1,1.
B7	V/S parameter (V/S, k = 1,2)	Lixiviation parameters are lower (k = 0,5 for B ; k = 0,7 for Li)
B8	Endurance sequences (4x7 days) (shorter) instead of 14, 14, 35, 28 days	No influence for B : but k = 1,4 for Li.
B8	Endurance sequences (greater : 28 and 63 days)	No influence

NB : k (multiplying factor) = ratio between caracteristics samples results and reference results

TABLE 1 (continued)

Inactive samples - Results

N°	Test type	Conclusions
B9	Lixiviation water agitation	B : no influence Li : $k \simeq 1,3$
B11	IER without coating	A clear influence for B : $k \simeq 3$ (Li : $k \simeq 0,8$)
B11	Test with a carotted sample	No influence
B11	Test about coated coefficient (0,66 instead 0,60)	B : $k = 1,25$ Li : $k = 0,9$
B11	Test with 2 samples, (one without B, Li ; one with B, Li)	For now, partial results and B : no influence Li : $k = 0,6$ (?)

TABLE 2

Active samples - Results

N°	Nature	Results
B2	Various load in B, Li, Cs, Co ("1" et "x10") in RFS lixiviation water	Reference speed : Cs 7 7.10^{-5} $cm.d^{-1}$ Co 3 3.10^{-5} $cm.d^{-1}$ For low charges : Co : $k = 0,8$ Cs : $k \simeq 1,0$
B4	De-ionized water	Co : $k = 7.10^{-3}$ Cs : $k = 6.10^{-3}$
B4	at pH13	Co : $k = 1,1$ Cs : $k = 1,2$
B4	at pH4	Co : $k = 1,5$ Cs : $k = 0,9$
B4	With E.D.T.A. (0,75 g/l)	Co : $k = 5$ Cs : $k = 1,6$
B10	IER (only)	Co : $k = 0,2$ Cs : $k = 0,2$

NB : k (multiplying factor) = ratio between caracteristics samples results and reference samples results

TABLE 3

Values of activities for the 2 full-scale samples
(in MBq at 10.05.89)

	L 28	L 29
^{54}Mn	3000 ± 360	2575 ± 295
^{58}Co	6885 ± 785	5910 ± 660
^{60}Co	14370 ± 1560	12200 ± 1310
^{110m}Ag	308 ± 54	243 ± 34
^{124}Sb	381 ± 45	269 ± 30

TABLE 4

First results of leaching test ("L28" sample)

- leaching ratio (%) (at 60 d)
- leaching speed (cm d^{-1})

parameters element	$\frac{\Sigma ai}{Ao}$ %	L.S. $cm.d^{-1}$
^{60}Co	0,002	$0,45.10^{-5}$
($^{60}Co^{*}$)	(1,86)	(40.10^{-5})

($^{60}Co^{*}$) : little sample reference values at 62 d with $Ao^{60Co} \simeq 0,7$ MBq

RADIATION EFFECTS ON MEDIUM ACTIVE WASTE FORMS

Contractor:	UKAEA, Harwell, U.K.
Contract No.:	FI.1W.0175 U.K.(H)
Duration of Contract:	January 1 1988 - December 31 1989
Period Covered:	January 1 1989 - December 31 1989
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 includes cemented inorganic waste forms; organic matrix waste forms; and cement waste forms with a substantial organic component. Irradiation of simulated waste forms is 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 include matrix materials as well as simulated waste forms. Real fully active waste forms (FAWF) will also be studied.

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

B. WORK PROGRAMME

B.1 Selection and procurement or manufacture of specimens of simulated waste forms and matrix materials.

B.2 Gamma-damage experiments on materials from B.1. Measure gas evolution and absorption. Provide specimens for B.4.

B.3 Alpha-damage experiments on materials from B.1. 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 Basic mechanisms. Develop theoretical models. Measure any additional necessary material properties of simulates and matrices.

B.6 Procure and characterise fully active wastes.

B.7 Manufacture fully active waste forms (FAWF).

B.8 Age FAWF through self-irradiation.

B.9 Measure gas release during B.8.

B.10 Measure physical properties of FAWF during ageing.

B.11 Conclusions and feedback to B.6.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Summary

Work has continued on measurements of dimensional changes, strength, and gas evolution on samples of several simulated waste forms under accelerated γ and α irradiation conditions. Samples of RMA5 (mixed ion exchanger materials in a modified vinyl ester polymer matrix) spiked with ^{137}Cs have been prepared and are undergoing leach testing. Samples of RAM11.1 (mixed PCM materials in cement) subjected to both internal α irradiation and external γ irradiation have continued to be monitored. Under some γ irradiation conditions RMA11.1 swells, no swelling has been observed in α irradiation experiments. Samples of fully active fuel hulls from reprocessing fast reactor fuel at Dounreay have been characterised and immobilised in a 3:1 BFS/OPC cement grout. The samples have now reached a self-radiation dose of 4 MGy and have remained in good physical condition with no measurable dimensional changes. The effects of γ irradiation on cement grouts based on BFS/OPC has continued. Gas pressure calculations indicate that pressure build up in isolated pores over a period of 12 hours or so could approach the tensile strength of the matrix but that a permeability lower than 10^{-21} m^2 would be needed to continue this pressure. γ irradiation of fully saturated samples indicates that cracking/spallation occurs at a high dose rate of 3 Gy s^{-1}.

Progress and results

1. Gas evolution/absorption during γ irradiation (B2)

Measurements of gas evolution in RMA11.1 during gamma irradiation at a dose rate of 0.09 Gy s^{-1} were continued during this period. Data has been obtained on:

(i) 10 cm diameter samples irradiated immersed in water in both air and argon atmospheres;
(ii) 15 cm diameter decanned samples irradiated in air and argon;
(iii) 5 cm diameter decanned sample in argon.

The G values for hydrogen evolution are similar in all decanned samples, independent of sample size or the atmosphere in which the sample was irradiated; the mean value for $G(H_2)$ in RMA11.1 is 0.078. In samples irradiated while immersed in water, water radiolysis dominates the evolution of hydrogen, the G value increasing to 0.19.

In all of the samples RMA11.1 which were irradiated in air, oxygen absorption was observed. Values of $G(O_2)$ are more difficult to estimate since in many cases all of the oxygen initially present had been absorbed by the end of the dose interval. Best estimates indicate that the G value may be dependent on sample size, the 15 cm diameter sample having a marked smaller G value (of the order of 0.08) than the 5 cm diameter sample (>1).

There is no completely unambiguous evidence for the emission of HCl, just some indications that it may be present at the limits of detectability in samples irradiated dry.

Irradiations are continuing at a dose rate of 0.3 Gy s^{-1} to a total dose of 12 MGy for samples of 3:1 and 9:1 BFS/OPC grouts. Up to a total dose of 9 MGy oxygen has continued to be adsorbed.

2. Gas evolution/absorption during α irradiation (B3)

Samples of coarsely shredded PCM (RMA11.1) containing plutonium-238 have now received a total α-dose of 6.5 MGy. The rate of hydrogen production has decreased from an early value of $G(H_2)$ = 0.3 to $G(H_2)$ = 0.23. When the samples are exposed to air oxygen absorption occurs. The only other gases observed are traces of carbon monoxide, methane and ethane.

3. Dimensional stability, etc. (B4)

In earlier work on the leaching of ^{137}Cs from polymer-based wasteforms (RMA5) containing wet wastes, enhanced leaching was observed in the early stages of leach tests in irradiated samples. It was proposed that this could arise as a result of water loss from the surfaces of the sample, forming a Cs rich layer close to the surface, rather than being a radiation effect. To test this hypothesis, a series of leach samples have been prepared with known levels of water loss, irradiated at two different dose rates for the same periods of time as control samples. The full results of these leach tests are not yet available, but preliminary indications are that there is a significant difference between the irradiated samples and control samples with a similar level of water loss.

Samples of RMA11.1 wasteform comprised of coarsely shredded PCM immobilised in PFA/OPC have remained in good physical condition with negligible weight loss and no significant dimensional change after an α dose of 6.5 MGy received in 1130 days. Samples of a similar composition but using finely divided organic waste materials have achieved α-radiation doses of 54 MGy and remain in good physical condition.

4. Additional measurement (B5)

Samples of RMA11.1 containing powdered organic PCM were analysed after receiving a total α-radiation dose of 54 MGy to determine the breakdown of the PVC present. The wasteform was leached with 4M nitric acid and it was found that the leachate contained chloride ion equivalent to 11% of the chlorine present as PVC in the starting material.

Previous studies have indicated that BFS/OPC grouts exhibit cracking and spalling during γ irradiation at high dose rates (3 Gy s^{-1}). This behaviour may have been caused by radiolysis gas, mainly hydrogen, becoming trapped in the closed pore network of the cement matrix. Gas pressure calculations have indicated that pressure build up in isolated pores over a period of 12 hours or so could approach the tensile strength of the matrix but that a permeability lower than 10^{-21} m^2 would be needed to contain this pressure. At this stage it is difficult to be conclusive about whether hydrogen pressurisation is the cause of failure. However, γ irradiation of a limited number of saturated 3:1 BFS/OPC grouts have shown a tendency to crack. Further irradiations are in progress.

5. Immobilisation of fast reactor fuel hulls in cement (B7, B8, B9, B10)

Samples of fuel hulls waste from reprocessing fuel subjected to high burn-up in the PFR at Dounreay have been immobilised in a 3:1 BFS/OPC cement grout. The samples have reached a self-radiation dose of 4M Gy and remain in good physical condition with no measurable dimension change. When the samples are held in a closed container initially filled with air there is a rapid absorption of oxygen. Hydrogen then continues to be evolved steadily to give a $G(H_2)$ = 0.02 for stainless steel hulls (from 8% burn-up fuel) and $G(H_2)$ = 0.002 for PE16 alloy hulls (16% burn-up fuel).

Publications

/1/ PHILLIPS, D.C., McHUGH, G., HITCHON, J.W., WILDING, C.R., SPINDLER, W.E., LYON, C.E., WINTER, J.A., LINDSELL, P.H.R., The effects of radiation on intermediate level wasteforms, 1987 Annual Report, AERE-R13019 (1988).

/2/ JOHNSON, D.I., WILDING, C.R., LYON, C.E., BURNAY, S.G., WINTER, J.A., PHILLIPS, D.C., SPINDLER, W.E., LINDSELL, P.H.R., Radiation effects on medium active wasteforms, Annual Report, AERE-R13398 (1988).

/3/ WILDING, C.R., PHILLIPS, D.C., LYON, C.E., The effects of radiation on intermediate level wasteforms, MRS Conference on Waste Management, Berlin, October 1988.

FIRE TESTING OF FULLY ACTIVE MEDIUM LEVEL WASTE FORMS

Contractor	: UKAEA, Harwell Laboratory, UK.
Contract No	: FI. 1W. 0176. UK(H)
Duration of contract	: July 1988 to March 1990
Period covered	: January-December 1989
Project Leader	: Dr RP Bush

A. OBJECTIVES AND SCOPE

The behaviour of medium level waste forms is being studied at temperatures that might be encountered in accidents involving fires. The information obtained will be useful in safety assessments in the transport and disposal of these packaged radioactive wastes.

There are two parts to the programme:

(a) an experimental part in which samples of waste form are heated to obtain data on the radionuclides released, the gases evolved and the physical effects on the waste form,

(b) a theoretical and interpretive part in which experimental data is used to describe the behaviour of the waste form in a fire. Information from a concurrent programme at Winfrith on heating full scale inactive drums will be included.

B. WORK PROGRAMME

2.2 Procurement of samples of fully active wastes for study.
2.3 Manufacture of small-scale samples of waste form to reference specifications for each waste.
2.4 Heating the samples of packaged waste form under conditions to simulate a fire accident during transport (in which case the full size drums would be in a transport flask) or in a repository.
2.5 Measurement of the radioactive material released from the heated packaged waste form as a function of temperature.
2.6 Measurement of the inactive materials produced when the waste form is heated, including solid particulates, steam and other condensable materials and gases.
2.7 Examination of the residues from heating the waste form.
2.8 Information derived from the experimental programme is to be assessed and used as an input to the development of a mathematical model.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The four waste streams selected for study have been subjected to heating to 300°C and 1000°C in furnace experiments. The programme of experiments has been completed. Analysis of the products released from the waste form during heating is nearing completion. These data are being subjected to interpretation and fitted to a theoretical model to predict the release of radioactive materials from drums containing immobilised radioactive wastes when they are subjected to heat. The programme has been extended in time by three months to be complete by March 31st 1990.

Progress and Results

2.3 Samples of each of the active waste forms were prepared according to the producer's specification. The four waste streams are listed below:

(a) Magnox sludge ex BNFL Sellafield was immobilised in a mixture of 3 parts Blast Furnace Slag (BFS) and 1 part Ordinary Portland Cement (OPC).

(b) Fuel hulls from reprocessing PFR fuel at Dounreay were immobilised in a 3:1 BFS/OPC cement.

(c) A mixture of shredded organic material typical of UK PCM was contaminated with aged plutonium dioxide powder and immobilised in a 3:1 PFA (Pulverised Fuel Ash)/OPC cement grout. The waste was contained within a mesh basket positioned centrally in the stainless steel can.

(d) A mixture of inorganic and organic ion exchangers was loaded with caesium-137, strontium-85 and cobalt-60 and then immobilised in a vinyl ester resin matrix.

2.4 HEATING OF WASTE FORMS

Samples of each waste form contained in a stainless steel can (12cm diameter) were heated by placing them in an oven at 300°C or 1000°C. The samples were generally held in the oven until dryout of the sample was achieved.

2.5 MEASUREMENT OF MATERIALS RELEASED FROM HEATED WASTE FORM SAMPLES

When cemented waste forms were heated in a vented container vapourisation of the contained water was observed. The condensate from this evaporation was initially alkaline and it is believed that some of the alkali and alkaline earth elements present in the cement pore water were carried forward with the steam. Wasteforms containing BFS were found to produce hydrogen sulphide and sulphur dioxide gases when heated above 300°C and solid sulphur was deposited in the collecting circuit.

(a) Magnox sludge in 3:1 BFS/OPC

At temperatures up to 300°C the steam produced was condensed to give an alkaline solution (pH 10-11). No solid phase was observed to be carried forward. The release of radioactive material was low with only the cobalt-60, strontium-90 and caesium-137 being detected. The highest release was 0.05% of the caesium-137 in 12 hours. When the waste form was heated to 1000°C sulphur was deposited in the off-gas collection system. The aqueous condensate was initially of pH 12 but this decreased rapidly to pH 1 as the sulphur species were produced. The levels of radioactivity released from the container were initially high, probably because bleed water present in the sample was boiled to release higher than normal levels of activity. The level of radioactivity in the condensate then fell to a minimum before increasing to higher values again a volatile caesium species were formed.

(b) Fuel hulls in BFS/OPC

At 300°C the only significant release was a steam which condensed to give an alkaline liquid (pH 11). The levels of radioactivity released were low with Ru-106, Cs-137, Sb-125, Te-125 being detected. The highest release was $2x10^{-5}$% of the caesium-137.

When the active waste form was heated to 1000°C no significant quantity of solid was seen to be released unlike the inactive SS hulls simulant where sulphur was collected. The aqueous condensate remained alkaline. This behaviour is believed to be due to reaction of sulphur with the PE16 alloy hulls. Releases of radioactive material were low and showed an increasing rate of release of caesium-137 with temperature. The total caesium-137 released was 0.14%.

(c) PCM in PFA/OPC

When the PCM waste form was heated to 300°C an aqueous condensate was obtained. The pH of the condensate rose from 3 to 9. Releases of radioactive materials were very low. Heating the waste form to 1000°C caused decomposition of the organic material as well as dehydration of the cement. Organic and aqueous condensate phases were obtained. The pH of the aqueous phase decreased from 11 to 1 due to production of hydrochloric acid from the PVC present. Releases of radioactive material were very low.

(d) Ion exchangers in vinyl ester

When the waste form was heated to 300°C an aqueous condensate was obtained together with a small amount of oil.

When the waste form was heated to 1000°C then the organic materials were decomposed to give tars, oils and gas. Despite this severe decomposition very little of the inventory of radioactive materials was released (10^{-4}% of the caesium-137).

2.8 THEORETICAL ASSESSMENT OF BEHAVIOUR OF WASTE FORMS ON HEATING

A theoretical model has been developed to calculate the temperature distribution through a drum of waste form subjected to heat. Early calculations gave inadequate correlation of calculated temperatures with those observed in the small scale heating experiments. Measurement of the thermal conductivity of waste forms as a function of temperature has provided better data for the thermal capacity of the waste forms and permitted good agreement between calculated and observed data.

The mechanisms of release of radioactivity from drums of immobilised waste subjected to heat are considered to be:

(i) ejection of solid particles of waste form by the steam produced

(ii) carry forward of a fraction of initially present as dissolved species in the pore water of the waste form

(iii) creation of a volatile species which is subsequently condensed when cooled.

The contribution of mechanism (i) is not believed to be significant info the small scale experiments or in the full size (inactive) experiments carried out at Winfrith. Mechanism (ii) may be responsible for most of the transport of radioactive material observed at up to 300°C. The formation volatile species increases with temperature and generally becomes more significant at waste form temperatures above 500°C.

When the data from all experiments are available, an empirical relationship will be fitted to the calculated temperature profiles to enable the prediction of the release of radioactive material from drums of waste forms subjected to external heating.

TITLE: **Investigations into the behaviour of highly compacted dry low level radioactive waste under repository conditions**

Contractor: Taylor Woodrow Construction Limited
Contract No: FI 1W.0178. UK(H)
Duration of Contract: April 1988 - December 1989
Period Covered: January 1989 to December 1989
Project Leader: Mr S N Field

A. OBJECTIVES AND SCOPE

The supercompaction process (in which a steel drum containing low level radioactive waste is subjected to axial pressures of up to 70 MPa) results in a significant saving in the volume of a repository necessary for disposal of such wastes. Whilst it is likely that some compacted waste forms are inert, for other materials the energy dissipated in the compaction process may result in time dependent swelling. Such expansion may, if restrained, induce stresses which could potentially disrupt containers, or the overall integrity of the repository. Many materials swell when wetted, and the elimination of voidage by the supercompaction process may significantly increase the extent of swelling-on-wetting. Supercompaction of the waste may limit the mobility of soluble material within the waste; biological and chemical degradation of waste and drum may also be altered by the supercompaction process.

The project is a scoping study to determine which if any of the above factors are of significance in the use of supercompacted waste forms in a repository. All work is being carried out on full scale 200 litre drums of simulated waste.

The work is being undertaken in collaboration with Hansa Projekt GmbH, British Nuclear Fuels, U.K.A.E.A., UK. Nirex and the N.I.I.

B. WORK PROGRAMME

B1 Waste characterisation - definitions of range and types of LLW that would be considered suitable for supercompaction.

B2 Simulant LLW Specification - identifying the types of material that could exhibit interesting behaviour, and preparing schedules of drum contents.

B3 Define test programme to monitor dimensional stability of compacted waste forms, force generation, mobility of soluble materials and generation of gas.

B4 Design, fabricate and commission test rigs.

B5 Procure simulant materials, prepare drums, tranship to Hansa Projekt GmbH, supercompact drums, and tranship back to UK.

B6 Undertake physical test programme on compacted drums.

B7 Complete final report.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Summary

All experimental work has now been completed with the exception of a small number of tests in which the monitoring of stresses developed by long term expansion is continuing. These on-going tests are outside the scope of the current CEC contract.

The experimental work has been successful and the original aims of the project have been largely met. A time-only extension was granted during 1989 by the CEC for this project. Contract completion is now on 31 December 1989 and preparation of the final report is well advanced.

During 1989 dimensional monitoring of the drums compacted in 1988 continued. Compacted drums were also observed under conditions of continued wet storage both with and without the restraining influence of the metal drum. Gases evolved during storage have been collected and analysed. A variety of measurements of the mechanical behaviour of the compacted drums has also been made, including stress/strain relationships during loading/recompaction, stress relaxation in loaded drums, and stress generation in drums loaded and subsequently restrained. Stress development on restrained drums subjected to water immersion was also measured.

Progress and Results

1) Dimensional Monitoring of Dry Compacted Drums (B6)

A set of nine datums were affixed to each drum immediately after compaction, although data for only three of these has been used for analysis (centre and two on diametrically opposite edges). Engineering calipers and a vernier were used to measure the thickness of each disc; the diameter of each disc was also monitored, but not found to change in the course of the programme.

Two main conclusions have been drawn from the data:

i) Swelling in dry conditions after supercompaction is of the order of 1mm only, and takes place within a few days of compaction.

ii) There is no significant swelling in the period between 1 month and 1 year after compaction.

It should however be noted that different drums of the same contents gave similar (but not identical) expansions.

2) Wet Storage of Unconstrained Drums (B6)

The immersion of such specimens was intended to provide general comments on the integrity of the compacted waste when not constrained by the presence of the compacted drum. The original depths of the compacted drums were 50-100mm; all expanded to depths of 170 to 240mm, an expansion factor of between 2 and 4.

Generally the waste remained intact, although the fibre board drums split due to the expansion of the contents. Signs of escaping methylene blue dye (from the centre of each disk) were seen. It can be concluded that compacted waste of several types (plastic, paper, mixed and vermiculite) all have significant potential for swelling-on-wetting.

3) Wet Specimens Stored Sealed

The object of this test was to investigate the effects of water saturation on the compacted discs. Specimens used contained vermiculite, paper, paper and plastic, and mixed soft and hard material. To ensure saturation took place within a reasonable period of time, a series of holes was drilled to pierce the unpunctured ends of the drums. The compacted drums were then vacuum saturated.

Figs. 1 and 2 show schematically the vacuum storage rig, and the permanent storage tanks (four in number, one for each compact disc).

The storage tanks were designed to catch any gas produced, and to measure any volume of water expelled from the specimen. As all rigs were stored in a temperature-controlled lab it is possible to dismiss temperature changes as a cause of fluid expulsion.

In all four specimens, water was expelled into the gas bag. This was removed incrementally once every four days. In summary:

i. Vermiculite steadily expelled 600ml over 10 days and then stopped.

ii. Paper and paper-and-plastic steadily expelled of the order of 1 litre over a two month period.

iii. Mixed soft-and-hard expelled nearly 2 litres over 3 weeks and then stopped.

Significant gas (of the order of 0.5 litres) was generated by W18 (mixed soft and hard). This has been analysed; the predominant component is hydrogen.

4) Stress Development Under Dry Conditions (B6)

The objective of this part of the programme was to enable a prediction to be made of the stress developed when a freshly-compacted waste drum is placed in an environment in which it is not free to expand, eg. grouted into a concrete box. Ideally the compacted waste (at various ages after compaction), would be placed between fixed platens, and the specimen expansion would then induce stresses. The shipping of suitable rigs to Hamburg, was not however possible under this contract, and to provide suitable data, additional work to that originally envisaged was undertaken.

The stress rig of Figs. 3 and 4 was used. It can apply up to 50 tonnes to a disc either by the nuts on the threaded bars, or by the flat jack. A variety of load regimes have been used, including the measurement of stress-strain curves, stress relaxation tests and stress development tests. The latter are novel and are described in more detail below.

Stress-strain tests indicate that stiffnesses are of the order of 10 MPa (for 3 MPa applied load). Stress relaxation takes an applied load down to between half and two thirds of its original value over about a week. Little relaxation occurs after this time.

The development of restrained stresses was measured by conditioning specimens at high loads for several days (thus allowing most of the potential creep to occur), releasing them, and trapping any subsequent expansion between fixed platens. The loads developed were typically of the order of 0.03 to 0.3 MPa, depending on the actual waste form.

5) Stress Development - Wet Conditions (B6)

For this work, specimens were allowed to become wet whilst restrained between fixed platens. The stresses developed are important to repository designers.

Tests on three waste types have been undertaken and the results are currently being evaluated as the final report is prepared. Preliminary conclusions are as follows:-

i. Stresses and expansions occur predominantly as the waste becomes wet (the original scheme of vacuum saturating specimens prior to wetting had to be modified as expansion was taking place too rapidly). A time delayed component of expansion does however exist.

ii. Maximum stresses developed were of the order of 0.5 to 1 MPa. These are transient and would be reduced in practice due to creep.

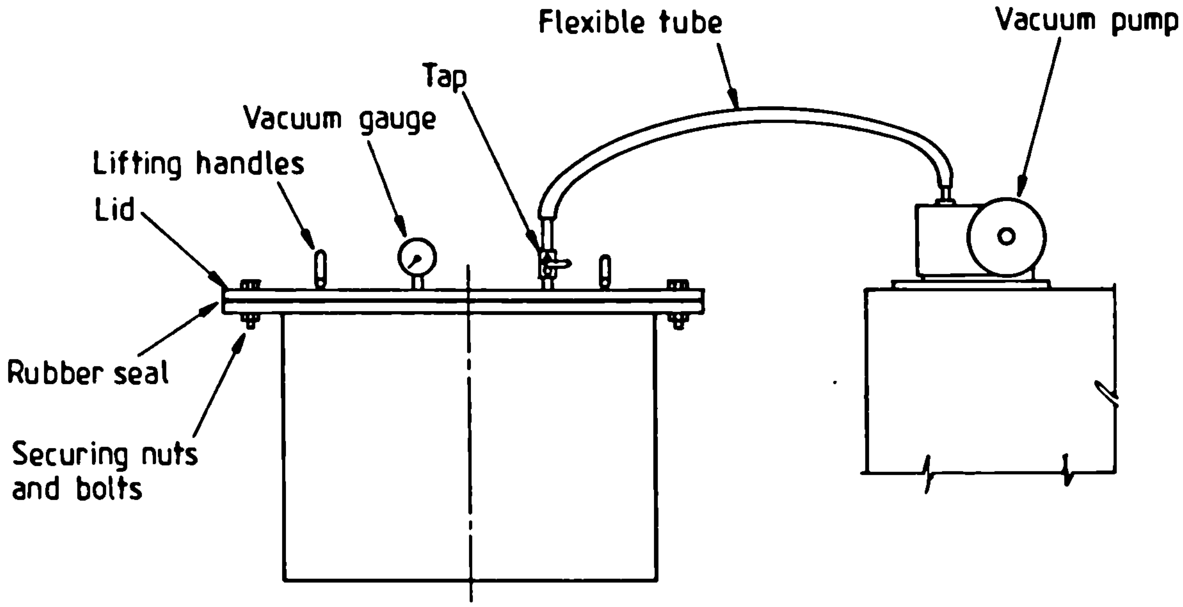


Figure 1. Vacuum Saturation Rig

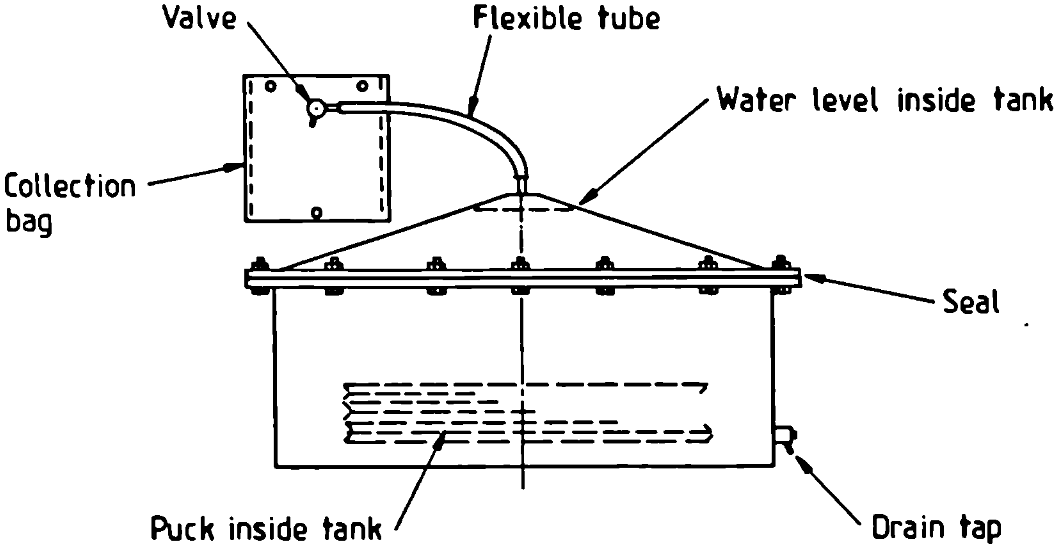


Figure 2. Permanent Storage Tanks - for Expansion, Leaching, Gas Collection. Pucks W15, W16, W17 and W18

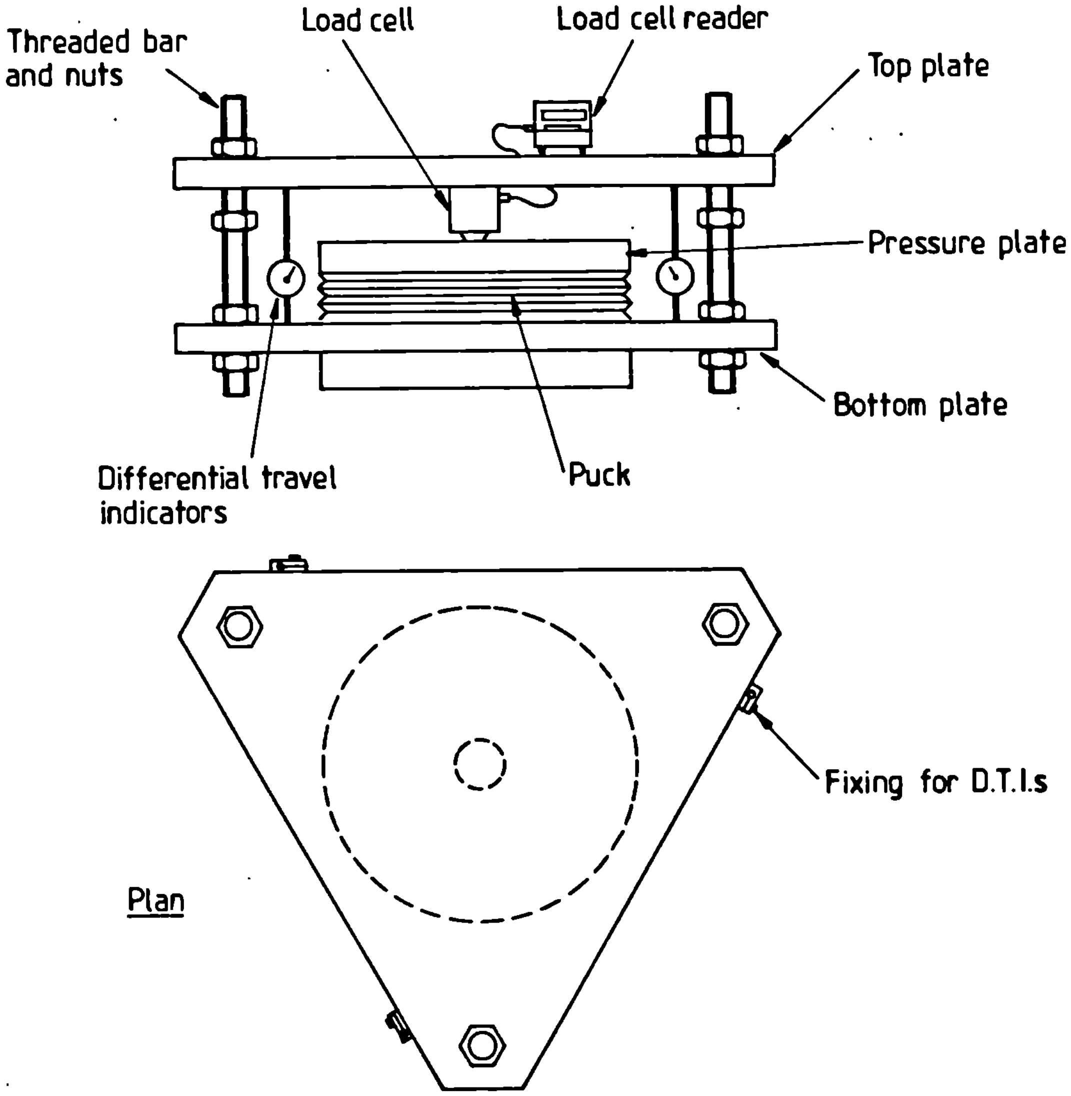


Figure 3. Stress Rig - Basic Set-up

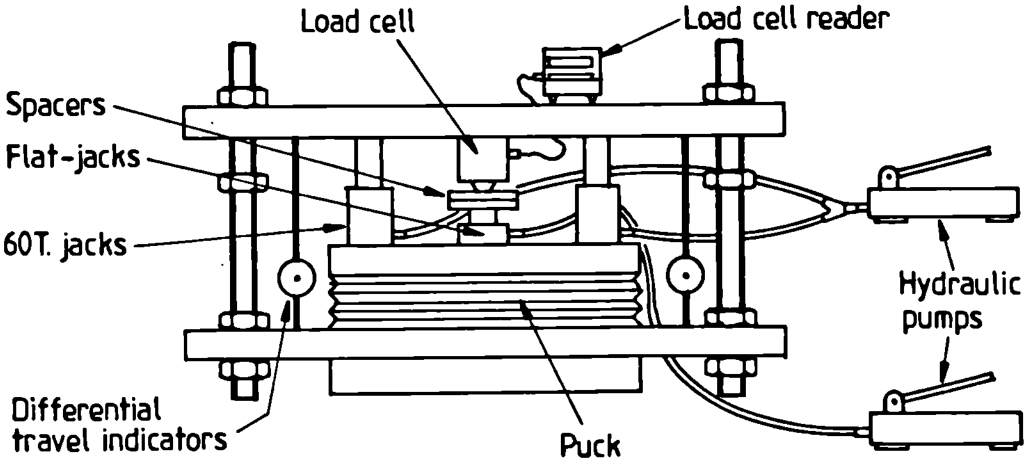


Figure 4. Stress Rig -as Set up for Puck W11

FIRE EXPOSURE TESTING OF ENCAPSULATED SIMULANT RADIOACTIVE WASTES

Contractor: UKAEA - AEE Winfrith, UK
Contract No: F1 1W 0198
Duration of Contract: July 1988 - December 1989
Period Covered: January 1989 - December 1989
Project Leaders: D J Holman, C J Griffiths, D A Wells

A. OBJECTIVES AND SCOPE

In order to establish criteria for the safe storage, transport and disposal of intermediate level wastes a knowledge of the response of waste packages to fire accident conditions is required.

IAEA Regulations exist for transport and a transport flask or overpack is provided to protect the package from the damaging effects of fire. There are, however, no such regulations in the UK or elsewhere in the CEC that deal specifically with situations such as may occur at a repository where unprotected waste packages could be exposed directly to fires.

This programme will provide data on the behaviour of typical waste packages in such fire accidents using full scale non-radioactive simulated packaged wasteforms. Information on the behaviour of a range of waste types will be provided.

The initial objective is to identify the test conditions for packages, which will allow interpolation of results rather than extrapolation, for fires in which drums of waste are directly exposed to a hydrocarbon pool fire, and those in which packages are in their transport overpacks leading to significantly lower heat fluxes. These conditions provide the experimental parameters for the execution of thermal tests to measure the performance of full scale packages.

A theoretical model already exists in rough form which predicts waste form temperature profiles and steam release rates from immobilised waste. The results from this programme of work will enable the modellers at Harwell to develop and validate this model and consequently predict both the gaseous and particulate transport and release mechanisms from the waste matrix which may be encountered in fire accident conditions.

This programme is being conducted in parallel and close liaison with small scale fully active studies at AERE Harwell under contract number FI 1W 0176.

B. WORK PROGRAMME

The packages tested are stainless steel drums of nominal 0.5 m^3 volume containing simulated immobilised waste. The drums have been fully instrumented with thermocouples and are vented, in a controlled manner, in order to study any released material. The wastes selected for study are:

- Shredded Combustible PCM in PFA/OPC (RMA 11.1).
- Oxide Fuel Element Hulls in BFS/OPC (RMA 6).
- Metal Hydroxide Sludge in BFS/OPC (RMA 8).
- Organic/Inorganic Ion Exchange Resin in Vinyl Esters (RMA 4).

The cement based products are allowed to cure, under ambient conditions, for at least 90 days, in order to achieve optimum product stability. The vinyl ester based products require no extended curing period.

The test programme can be split into two distinct categories:-

(a) Furnace Test - representing a Transport fire. In transport, drums are placed within an overpack that performs the function of a thermal barrier protecting the drums during a fire. These tests are performed at 300°C, the temperature calculated by the modellers to be the maximum average a drum would be subjected to, in an overpack, under transport fire accident conditions. The duration of the test is that time taken to raise the outer 10% of the specimen radius (ie 40 mm) to a temperature exceeding 100°C.

(b) Pool Fire Test - simulating the fire conditions which bare drums could be subjected to in storage. The specimens are mounted over a continuous feed pool of petrol. The duration of each fire test is a minimum of 2 hours at an average flame temperature of 800-1000°C.

One specimen of each of the packaged wastes was subjected to a pool fire test and one to heating in an electric furnace. Measurements were made during these tests in order to identify the activity release mechanisms, the activity release fraction and the consequence for subsequent package disposal.

C. PROGRAMME OF WORK AND OBTAINED RESULTS

A range of instrumentation designs were developed in order to accommodate the variation of waste types. For each specimen thermocouples were attached to the inner and outer surfaces of the drum after which the thermocouple space frame was fitted in the drum. The drums were then filled with waste and cement (or vinyl ester) and allowed to cure for the appropriate period.

During thermal tests on-line measurements of gaseous and particulate release from the specimen under test was required. An analysis circuit was designed and constructed in order to make these measurements. This was commissioned using the Furnace Test Facility and drums filled with water heated at 300°C.

The thermal tests were performed in two campaigns, the Pool Fire Tests following the Furnace Tests. Each test is summarised below.

FURNACE TESTS

Magnesium Hydroxide Sludge in BFS/OPC - Duration of test 25 hours. Condensate - clear and colourless with progressively greater sulphurous odour. No liquid collected in cold trap. Nitrogen only on gas chromatograph. No discolouration/damage/blinding of filter cartridges. Specimen undamaged.

Oxide Fuel Element Hulls in BFS/OPC - Duration of test 9 hours. Condensate - clear and colourless with progressively greater ammoniacal odour. No liquid collected in cold trap. Nitrogen only on gas chromatograph. No discolouration/damage blinding of filter cartridges. Specimen undamaged.

Shredded Combustible PCM in PFA/OPC - Duration of test 12.5 hours. Condensate - initially clear/pale yellow, becoming opaque and white in colour with oily droplets on the surface and a strong odour, similar to PVC. No liquid collected in cold trap. Nitrogen only on gas chromatograph. No damage, but, a small amount of discolouration and some blinding (ie pressure increase) of filter cartridges. Specimen undamaged.

Organic/Inorganic Exchange Resin in Vinyl Ester - Duration of test 13 hours. Condensate - initially clear and colourless with thin, brown oily layer on surface becoming opaque and white in colour, all with a strong odour, similar to styrene. Small amount of yellow liquid (< 5 ml) in cold trap. Nitrogen only on gas chromatograph. Apart from small black patches no discolouration/damage/blinding of filter cartridges. Specimen undamaged.

POOL FIRE TESTS

Magnesium Hydroxide Sludge in BFS/OPC

Condensate - clear and white/pale yellow in colour accompanied by a white gas with a progressively greater sulphurous odour (samples taken). Some fine black particles in condensate. No liquid in cold trap. Nitrogen only on gas chromatograph. Apart from small grey patches no discolouration/damage/blinding of filter cartridges. Specimen undamaged.

Oxide Fuel Element Hulls in BFS/OPC - Condensate - clear and colourless or pale yellow with a sulphurous odour. Some fine black particles in condensate. No liquid in cold trap. Nitrogen only on gas chromatograph (off gas samples taken for further analysis). Apart from small grey/black patches no discolouration/damage/blinding of filter cartridges. Specimen undamaged.

Shredded Combustible PCM in PFA/OPC - Condensate - initially slightly opaque with a white/pale green colour becoming more opaque and brown in colour with a progressively greater odour similar to PVC. Some black particles in condensate. White off-gas throughout test - pH ~ 1. Small amount of liquid (< 5 ml) in cold trap. Nitrogen only on gas chromatograph. Small amount of discolouration, but no damage/blinding of filter cartridges. During the first filtration bypass a small leak occurred in the specimen at the thermocouple loom outlet - no other specimen damage.

Organic/Inorganic Exchange Resin in Vinyl Ester - Condensate - all samples were a mixture of an aqueous emulsion and a less-dense black tar like liquid with a strong organic odour. High flowrate of material released from specimen required some venting to atmosphere to maintain the back pressure across the analysis circuit within the capacity of the lute (~ 0.2 Bar). Cold trap and gas chromatograph not used in this test. Filter cartridge covered in viscous black tar like liquid. Large quantities of wet (fine brown droplets) off gas (ph ~ 7). No specimen damage.

SUMMARY OF POST TEST ANALYSIS

Thermal Profile - Typical thermal profiles across specimen mid - height radii are shown in Figure 1 of a Furnace and Fire Test (Fuel Element Hulls) indicating smooth thermal gradients throughout the tests.

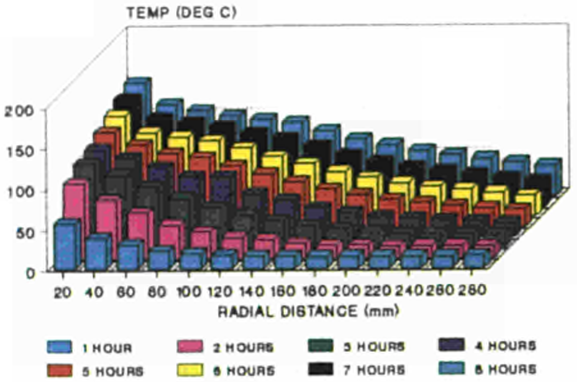
Material Release - Bulk of material release was steam - up to 50 w/o loss of the original water inventory (weight loss up to 103 kg). Figure 2 shows the steam release rate expressed as volume of condensed steam released plotted against time. Particulate release only from fire Test specimens (sizes ranging from < 1 µm to > 100 µm) - chemical analysis of these revealed decomposition of binder components rather than waste. Chemical analysis of condensates again revealed leaching of binder components into solution. Samples of released, non-condensable gases were analysed and found to principally consist of hydrogen and carbon dioxide from the reduction of steam and carbonates. The pH of condensates from the Furnance Test specimens remained alkali throughout the tests - associated with cement alkalinity. The Magnesium Hydroxide Sludge and PCM Combustible Fire Test specimen condensates became acidic with the release and dissolution of SO_2 and HCl from the matrix during the tests.

Specimen Examination - Coring and sectioning the specimens after the tests revealed little damage to the matrix (all specimens except the Magnesium Hydroxide Sludge Fire Test specimen remained monolithic). Some radial cracking was seen in the matrices, particularly close to the drum wall. These cracks provide steam paths to the edge of the specimen, with steam then able to travel along the matrix/drum interface and out of the top of the drum. Where monolithic cores were taken, strength tests revealed little reduction in strength from exposure to thermal test conditions.

The full scale packages of simulated encapsulated ILW's exposed to conditions representing transport and storage fires underwent minimal material release - the bulk of which was associated with the binder, not the waste. All of the specimens were retrievable at the end of each test - no loss of package integrity - for subsequent storage (or transport, if required).

This programme of work was completed, on schedule, by the end of December 1989.

FURNACE TEST



FIRE TEST

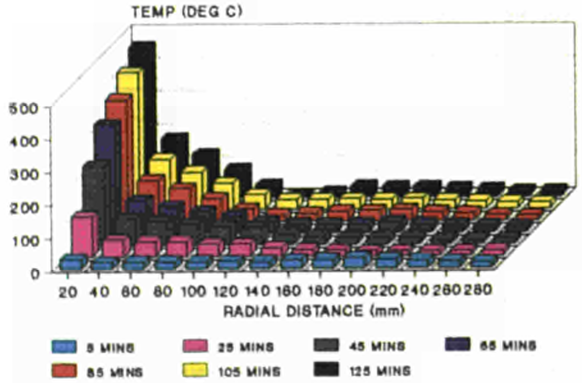
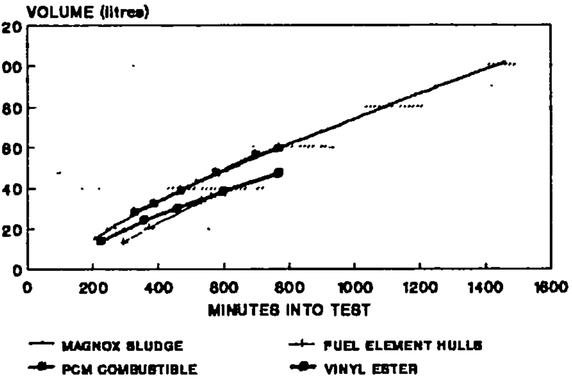


FIG.1 Thermal Profiles Of Fuel Element Hulls In BFS/OPC.

FURNACE TEST



FIRE TEST

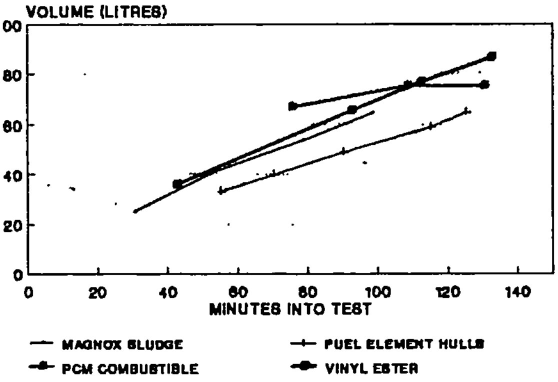


FIG.2 Steam Release From Thermal Test Specimens

3.2. HIGH ACTIVE AND ALPHA WASTE FORM CHARACTERISATION

LEACHING SENSITIVITY TO GEOLOGIC ENVIRONMENTAL PARAMETERS

Contractor: CEA, CEN-Valrhô, SDHA, F
Contract No: FI1W-0027
Duration of Contract: January 1987 - December 1989
Period Covered: January 1989 - December 1989
Project Leader: E. Vernaz

A. OBJECTIVES AND SCOPE

1 Round Robin Test (RSST)

Our objective in participating in this test is to investigate the behavior of SON 68 glass and the concentrations in solution under semi-integral conditions simulating a granite repository, and to compare our results with those of other laboratories – notably the evolution of SON 68 glass in the various media investigated.

2 Leaching of Actinide-Doped Glass Specimens: Eh and CO_2 Effects

We propose to investigate leaching of actinide-doped glasses, first in oxidative and reducing conditions, then with high CO_2 partial pressures.

The dissolution kinetics for the mobile elements during the first few days of leaching will provide an indication of whether the oxidation-reduction potential and CO_2 concentration affect matrix alterability.

The longer term evolution of the active and inactive element concentrations will allow the effects of these two parameters to be assessed with regard to glass corrosion product solubility limits and possible reprecipitation phenomena.

Finally, careful analysis of the actinides in the surface layers and in the leachates will qualify their specific behavior with regard to the matrix and their physicochemical form in the leachates under oxidative and reducing conditions and in the presence of CO_2.

B. WORK PROGRAM

B.1 Participation in the Repository System Simulation Test (granite option).

B.2 Definition of the operating procedure: different means of obtaining oxidative, reducing and carbonated conditions will be investigated and compared.

B.3 Leaching of inactive samples in semi-integral conditions in oxidative, reducing and carbonated media.

B.4 Leaching of glass samples doped with neptunium and plutonium in oxidative, reducing and carbonated media.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Inactive Experiments

The inactive experiments under semi-integral conditions raised problems in maintaining stable electrochemical conditions in the test medium. Additional experiments were conducted separately from the contractual program in order to develop a more suitable protocol for future tests.

Under the new protocol, oxygen fugacity is controlled in reducing media by means of a reducing buffer: the results were compared with those obtained in uncontrolled media and oxidative media (30% H_2O_2).

Active Experiments

The active experiments were initiated in 1989 with two types of glass (one doped with ^{237}Np, the other with ^{239}Pu) in three test media: oxidative, reducing and carbonated.

Results

- Inactive Experiments

The purpose of this test was to quantify the effect of controlled oxygen fugacity and of the type of autoclave on the behavior of R7T7 glass in an aqueous solution at 90°C. Tests were conducted under oxidative and reducing conditions with two types of autoclaves: a 316L stainless steel unit and a gold-lined unit to ensure chemical inertia.

Experimental Conditions

The same procedure was used for both types of autoclaves:

Temperature: 90°C
Pressure: atmospheric
Test media: reference medium: H_2O
oxidative medium: 30% H_2O_2
reducing media: Ca/CaO buffer
hematite/magnetite buffer
Duration: 14, 28 and 56 days
SA/V ratio: 0.5 cm^{-1}

Experimental Procedure

Reducing conditions were obtained by the use of buffers (a metal-oxide pair or an oxide mixture) to impose electrochemical properties on the test medium by controlling oxygen fugacity. The buffer mixture was placed in a 4 mm diameter platinum cylinder sealed at one end and simply crimped at the other end, which extended above the solution level. The electrochemical conditions were maintained constant as long as any redox reactants remained in the platinum tube.

Analysis of Results

The normalized mass losses are indicated in Table I. The values obtained in the stainless steel autoclaves were generally higher than those for the gold-lined units, and were in close agreement with the solution analysis results. The metal vessel probably attenuated the effect imposed on the medium. Glass corrosion in both series of experiments under oxidative conditions was higher than in the reference medium, which in turn was higher than in the reducing media.

- Active Experiments

The tests were conducted in two 50 cm^3 leaching cells: a conditioning vessel containing materials representative of a granitic environment (granite, sand and clay) and a leaching vessel containing 2 grams of inactive glass powder and 2 glass coupons doped with 0.85% neptunium or plutonium. The leaching conditions were as follows:

Temperature:	90°C
Oxidative medium:	2 bars O_2 above the solution
Reducing medium:	2 bars of (Ar + 5% H_2) mixture
Carbonated medium:	$NaHCO_3$ (0.5 $g \cdot l^{-1}$)
Duration:	14, 28, 56 and 91 days

The currently available mass loss values measured for the glass coupons are indicated in Table II.

The glass corrosion observed in both series of experiments was significantly different depending on the test media:

reducing < oxidative < carbonated.

The initial released activity distribution results for ^{237}Np-doped glass leached in a carbonated medium showed that the normalized mass loss and normalized neptunium mass loss values were comparable. The interstitial solution activity in the environmental materials was low compared with the activity measured in the leaching vessel solution; in both cases, the filtered and ultrafiltered solution activities were the same, showing that neptunium entered solution in soluble rather than colloidal form. The released activity was found principally in the clay with very little in the granite at the bottom of the vessel. This test shows the important role of clay in glass leaching: it increases bulk corrosion by adsorbing silica from solution, but this detrimental effect can also be partially offset in some cases by adsorption of radionuclides which limits their release into the geosphere.

Table I - Comparative Normalized Mass Losses ($g \cdot m^{-2}$) for R7T7 Glass in Oxidative and Reducing Media

Autoclave	Duration (days)	H_2O	H_2O_2	Hematite-Magnetite	Ca/CaO
Stainless Steel	14	2.48	3.05	2.35	2.69
	30	4.46	6.16	-	-
	34	-	-	3.34	3.60
	57	4.85	6.85	4.21	3.84
Gold-Lined	14	2.79	3.74	1.95	2.30
	29	-	-	2.60	3.20
	31	2.03	4.38	-	-
	57	2.88	4.79	2.37	4.09

Table II - pH of Leachate and interstitial Water, and Mass Losses for Radioactive Glass Specimens

Leaching of ^{237}Np-Doped Glass Specimens

Medium	Duration (days)	Leachate pH	Interst. pH	Specimen mass loss (mg)	
Carbonated	14	6.7	8.0	11.5	12.4
	28	6.2	7.3	19.4	23.2
	57	6.5	7.4	45.8	36.6
	91	-	-	-	-
Oxidative	14	8.2	7.4	3.3	2.6
	28	7.6	7.4	13.4	13.0
	56	-	-	-	-
	91	7.7	8.5	41.0	37.0
Reducing	14	-	-	-	-
	28	-	-	-	-
	56	8.9	8.1	4.6	3.9
	91	7.5	8.4	46.7	44.0

Leaching of ^{239}Pu-Doped Glass Specimens

Medium	Duration (days)	Leachate pH	Interst. pH	Specimen mass loss (mg)	
Carbonated	14	5.9	7	3.9	3.8
	28	7	8.3	15.1	13.1
	57	7.6	8	11.2	9.5
	91	6.7	-	24.1	23.6
Oxidative	14	8.1	7.5	5	4.6
	28	7.5	7	4.2	3.6
	56	8.5	-	5.3	4.9
	91	8.7	8.5	28.7	33.4
Reducing	14	8.6	6.7	3.1	2.7
	28	8.6	7.4	9.6	9.6
	56	8.3	7.7	2.9	3
	91	8.7	8.4	16.2	17.2

BASIC MECHANISMS OF AQUEOUS CORROSION OF WASTE GLASSES

Contractor:	CEA, CEN-Valrhô, SDHA, F
Contract No:	FI1W-0030
Duration of Contract:	August 1986 - November 1989
Period Covered:	January 1989 - December 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] our understanding of the basic corrosion mechanisms is essentially phenomenological and many important questions remain unanswered. This understanding is indispensable 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 behavior of technetium and the actinides.

B. WORK PROGRAM

B.1 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?)

B.2 Hydrothermal leaching and analysis of the crystalline phases formed between 50°C and 250°C.

B.3 Examination of the interface or ionization layer between the surface layers and the sound underlying glass.

B.4 Determination of the concentration profiles in the surface layers for the principal actinides.

B.5 Filtration study of the physicochemical form in which plutonium is found in the leachates.

B.6 Investigation of technetium behavior.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Most of the contractual experimental program was completed by the end of 1988. Additional "solubility" experiments at very high SA/V ratios (20000 m^{-1}) were conducted in 1989, together with an investigation of the physicochemical form of plutonium in the leachates after filtration, which had not been completed earlier.

Progress and Results

B.1 Solubility

- SA/V = 20 000 m^{-1}

Variations in the silicon and boron concentrations for this experiment are shown in Figure 1. The total silicon concentration in solution rose to 350 ppm after 28 days, then diminished. The dissolved silicon concentration (after 1.8 nm filtration) is indicated by the broken line in the figure: it remained virtually constant at 120 ± 10 ppm throughout the experiment. The boron concentration increased up to 112 days, showing that corrosion initially progressed despite apparent silicon saturation in solution. Beyond 112 days the concentration of boron and other mobile elements (Na, Li) in solution no longer increased, indicating that the residual corrosion rate was nil (less than 3×10^{-4} $g \cdot m^{-2} d^{-1}$). Thus no subsequent increase in corrosion was observed at any time due to precipitation of any phases, despite significant silica supersaturation.

- R7T7 Glass Silica Saturation Limit

Saturation of the silicon concentration appeared to be reached quickly in all the solubility experiments at SA/V ratios of 400 m^{-1}, 2000 m^{-1}, 8000 m^{-1} and 20000 m^{-1}. The slight increase in slope that can be observed for long durations is probably related to the formation of colloidal silica particles. This is confirmed by the 20000 m^{-1} experiment which showed that after ultrafiltration the silicon concentration was constant at about 120 ± 10 ppm. The sharp rise followed by a slow decline in the total silicon concentration is probably related to the formation, then floculation and decanting of silicated colloids, but not to precipitation of a new silicated phase, which would have resulted in significantly increased corrosion.

Although the dissolved silicon fraction was not measured for the three lowest SA/V ratios, it may be estimated from the following observation. At the three highest SA/V ratios, very high concentrations of relatively insoluble elements (Fe, Al, Zn, etc.) were measured in solution with values ranging from a few ppm to over 20 ppm, well above the corresponding hydroxide solubility limits. This suggests that these cations were adsorbed or contributed to the formation of silica colloids. Figure 2 shows a linear relation between the concentrations of these elements and the total silicon concentration. A good estimate of the dissolved silicon concentration is then obtained when no more colloids are present, i.e. when the Fe (or Zn) curve is extrapolated to zero (or < 0.1 ppm). The extrapolated value was in excellent agreement with the value measured after ultrafiltration at SA/V = 20000 m^{-1}. This gives the following glass silica saturation values:

Table I - Glass Silica Saturation Values

SA/V (m^{-1})	pH at 90°C	(M)easured or (E)xtrapolated C*	Calculated C* (log K_{sat} = −2.80)
400	8.35	52 ± 3 (M)	51
2000	8.66	60 ± 3 (E)	58
8000	9.04	81 ± 5 (E)	78
		116 ± 6 (E)	
20000	9.42	122 ± 15 (M)	127

The right-hand column represents the total dissolved silicon concentration calculated from an empirical equilibrium constant K_{sat} ($SiO_2 + 2H_2O \rightleftharpoons H_4SiO_4$) and allowing for hydrolysis of silicic acid with the following constants:

$$H_4SiO_4 \rightleftharpoons H_3SiO_4^- + H^+ \quad (\log K_1 = -9.17 \text{ at } 90°C)$$

$$H_3SiO_4^- \rightleftharpoons H_2SiO_4^{=} + 2H^+ \quad (\log K_2 = -10.70 \text{ at } 90°C)$$

A good fit with the test results is obtained with log K_{sat} = -2.80.

- Conclusion

A glass silica solubility limit was observed at 90°C for R7T7 glass. A constant residual corrosion rate was not observed, however. The final rate measured in the experiments cannot be considered as a characteristic glass property which can be used in long-term behavior models. As this rate dropped to less than 3×10^{-4} $g \cdot m^2 d^{-1}$ at the highest SA/V ratio, it may be assumed that there is no "residual affinity" but rather a "contextual" affinity which depends on the way saturation conditions occur and may be related to the formation of colloids.

B.5 Plutonium Filtration Studies

Although most of the plutonium remained trapped in the surface gel layer (the retention factor was about 100 times higher than for boron), a small fraction entered solution. This fraction initially remained in solution, suggesting that it was extracted in ionic form rather than as surface gel fragments. However, after a few days at 90°C or 100°C in oxidizing alkaline conditions (pH 8-10) the plutonium floculated and was either retained by a 0.45 µm filter or fixed on the container walls. The Pu content of the ultrafiltered solution was then extremely low: after 3 months at 90°C, for example, the ultrafiltered solution contained 1400 $Bq \cdot l^{-1}$ or about 0.3 ppb of plutonium in solution. This concentration could be controlled by the very low solubility of plutonium hydroxide $Pu(OH)_4$ in alkaline media.

REFERENCES

[1] E.Y. Vernaz, T. Advocat and J.L. Dussossoy. *Effect of the SA/V Ratio on the Long-Term Corrosion Kinetics of R7T7 Glass*. 4th International Symposium on Ceramics in Nuclear Waste Management. Indianapolis, April 23-27, 1989.

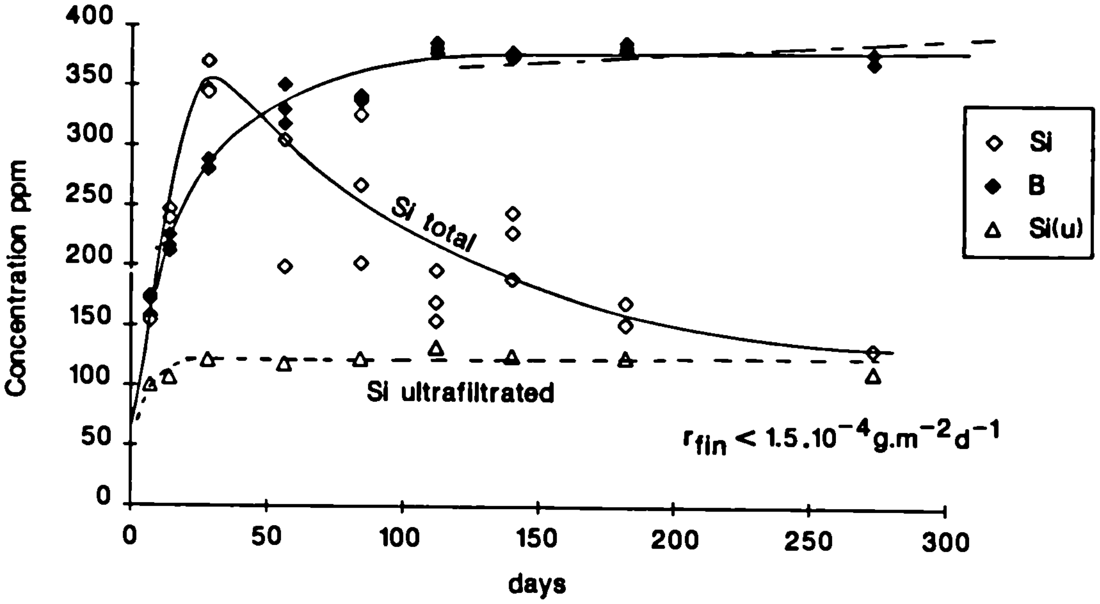


Figure 1 - Silicon and Boron Concentrations versus Time for SA/V = 20000 m^{-1}

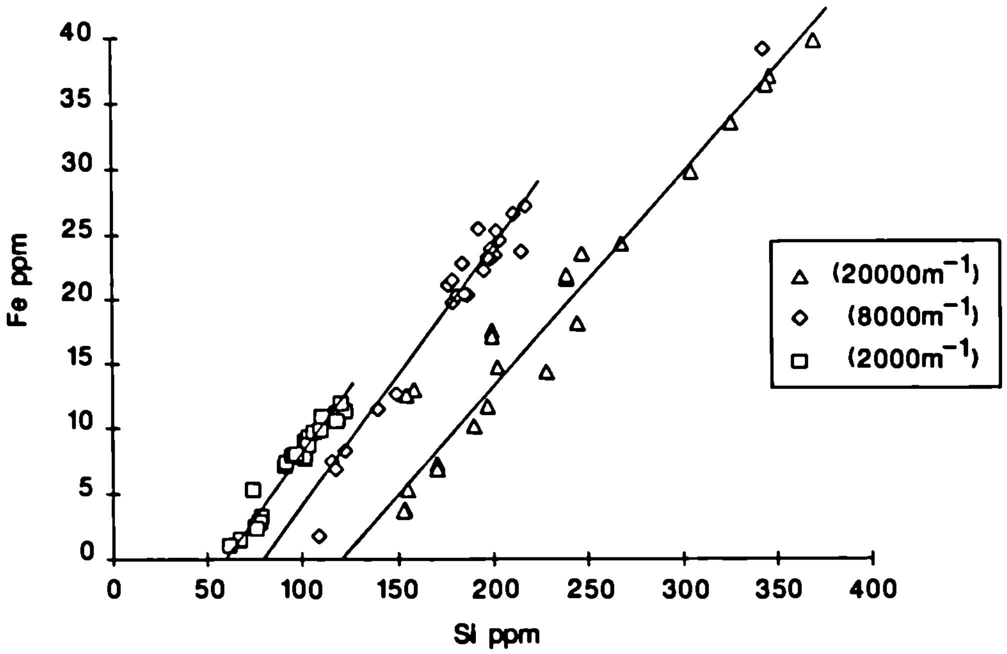


Figure 2 - Leachate Iron Concentration versus Silicon Content

RADIONUCLIDE RELEASE FROM SOLIDIFIED HIGH LEVEL WASTE

Contractor:	UKAEA. Chemistry Division, Harwell Laboratory, UK.
Contract No:	FI.1W.0097.UK(H)
Duration of Contract:	July 1986 - December 1989
Project Leader:	J.A.C Marples

A. OBJECTIVES AND SCOPE

The aim of the research is to ensure that vitrified waste forms in general and the UK's reference glass MW in particular are suitable for eventual disposal in either hard-rock or clay.

Studies are in progress of the leaching behaviour of MW and PFR 273 glasses which have been doped with selected radioisotopes. In particular, measurements have been made of the concentrations, under a range of conditions that could occur after disposal, of the radiologically important elements Tc, Np, Pu and Am. It is assumed that the release of these elements from the repository must be less than this concentration multiplied by the water flow-rate through the repository. Similar measurements have also been made on fully active waste glasses.

Studies are also in progress of the glasses radiation stability to ensure that this will not cause problems.

B. WORK PROGRAMME

B.1. Leaching behaviour of reference materials and solubility of selected radioisotopes.

B.2. Effect of radiation and radiolysis.

B.3. Effect of product quality on the release rate.

C. PROGRESS OF THE WORK AND RESULTS OBTAINED

Present position

Using doped glasses, previous work had shown that the concentrations of Tc, Np, Pu and Am in equilibrium with various possible components of a future repository for vitrified high-level waste were comparable to but usually somewhat greater than the 'limiting concentrations' of those elements. These are the concentrations which, if present in drinking water, would lead to an annual dose of lmSv to someone drinking 2 litres of that water per day. Subsequent experiments have shown that in most cases this was also true for several possible variations in the conditions. Only oxidising conditions (rather than reducing) which greatly increased the concentration of Tc, produced any significant change in the concentrations.

Similar experiments with fully active glass gave concentrations which were about a factor of 10 higher for Tc, Np and Am but a factor of over 1000 higher for plutonium.

The densities of Pu-238 doped MW and SON68 glasses are decreasing on exponentially saturating curves in a similar way to that shown by other similar glasses.

The extreme case of poor product quality glass occurs when the calcined waste fails to become incorporated in the frit. Equilibrium concentrations have been measured in the presence of unmelted frit and doped calcine and have been found not to be significantly different from similar experiments when they had been melted together to form a good quality glass.

The general progress of the work is as follows:
All three sections, B.1, B.2 and B.3 have progressed normally.

PROGRESS AND RESULTS

1. Leaching behaviour of reference materials and solubility of selected isotopes

One possible scenario for the disposal of the vitrified waste is as follows: the steel canisters in which the glass is cast will be surrounded by an overpack of thick cast iron or thin Ti alloy. The overpacked cylinders will be emplaced in galleries or boreholes deep underground and held in place with a backfill either of clay or of a Portland-cement concrete. In the period between a few hundred and many thousands of years, potentially the most hazardous radioactive elements in the vitrified high-level waste will be Am, Pu, Np and Tc.

The release of one of these elements from the repository cannot be greater than the product of the water flow through it, multiplied by the 'steady state concentration' of that element. i.e. the concentration in the presence of all the components of the repository and which will result from a combination of the solubility and sorption of that element.

Samples of glass containing a full inactive simulant of the high-level waste were doped with Tc-99, Np-237, Pu-238 and Am-241. After crushing (to speed up the approach to equilibrium) they were mixed with possible components of the repository and with water and sealed into capsules in an argon - 5% hydrogen filled glove-box to enable the reducing conditions, that will occur in a repository, to be established. The capsules were held in an oven at, normally, 60°C, for periods of up to a year before they were opened and the water overlying the solids sampled and analysed.

In previous capsule tests, Pu-238 has been used to dope the glass because it could be detected in solution at lower concentrations due to its 240 times greater activity than Pu-239/6% Pu-240. However this lead to the experiments being done with total Pu concentrations in the glass of $\sim 6x10^{-5}$ wt.%. The concentrations in solution were typically 10^{-13}-10^{-14}M /1/. however in the fully active glass experiments /1/, the Pu concentrations in solutions were 10^{-10}-10^{-11}M. It was suggested that this could be due to radiolysis but it was also noted that the Pu concentration in the glass was much higher - 0.03wt.%.

Capsule tests have now been set up with MW glass doped with a mixture of Pu-238 and Pu-239/240, with a total Pu concentration in the glass of 0.12wt.%. The capsules contained 1g glass, 5g Fe, 10g OPC(1)/PFA(10) and 20mℓ deionised water as before.

The measured concentrations after 1, 3 and 6 months are given in Table I, where they are compared with the concentrations found in the Pu-238 capsule experiments and the fully active glass experiments. Increasing the Pu concentration in the glass by a factor of 2000 has increased the concentration in the aqueous phase by about a factor of 40. The increased concentration found in the fully active glass experiment is now therefore thought to be due to the high Pu concentration in that glass.

It is possible that the repository will be established beneath the sea-bed or near the shore and thus that the composition of the water entering it may be close to that of sea-water. Accordingly some capsules were set up with the standard conditions except that sea-water was used instead of deionised water. The results are given in Table II. For Tc, the concentrations are about a factor of four higher in sea-water, despite the reducing conditions. For Np the concentrations are similar and for Am they are about 2-6 times higher. For Pu, they are between 5 and 50 times higher and seem to be increasing with time. Mass loss leach rates measured on coupons of glass included in the capsules were about 0.5µg.cm^{-2}.day^{-1}.

Additional experiments based on the EC Repository System Simulation Test /2/ have been carried out. These used OPC(1)/PFA(10) (Ordinary Portland Cement/Pulverised Fuel Ash) as the "backfill" rather than a sand-smectite mixture, with sea-water in one pair of tests and the "standard' Volvic granite water in another. Only the supernatant water from the specimen chamber was analysed, for Tc and the actinides only. The results are given in Table III. Reducing conditions were achieved in these experiments and the Tc results were much lower than in the original experiments where conditions were more oxidising /3/. Similarly, the actinide concentrations were also lower than in the original experiments, very considerably so in the case of neptunium. This is presumably also due partly to the reducing conditions but more particularly due to the higher pH arising from the presence of the OPC in the backfill. In these experiments, the equilibrium concentrations after filtering through a 25000 molecular weight cut-off membrane were less than the "limiting concentrations" for Tc and Np but higher by factors of about 8 and 5 for Pu and Am respectively.

The weight loss leach-rates, measured on coupons of glass included in the experiments were about a factor of five greater in the sea-water than in the granite water (8µg.cm^{-2}.day^{-1} compared to 1.5).

2. The effect of radiation and radiolysis

Glasses MW, SON68 and PFR116 have been doped with about 2.5wt.% Pu-238 to study the effect of α-decay damage on their properties. The densities of all three glasses are decreasing with accumulated radiation dose, following exponentially saturating curves. The density decrease at saturation is predicted to be about 0.47% for MW and SON68 and 0.65% for PFR116.

The Soxhlet leach-rates of the three glasses have been measured at intervals as the radiation dose has built up and are shown in Figure 1, where they are compared with similar results previously obtained on other glasses. It can be seen that the leach rate is not much affected by radiation but that, if anything, the leach rate of these three glasses decreases with increasing radiation dose.

3. Effect of product quality on the release rate

It is considered that the poorest possible glass would be one in which the calcined waste had not been incorporated into the frit. In order to measure the equilibrium concentrations for such a case, capsules were set up containing calcined waste doped either with Tc or with Np, Pu-239 and Am, OPC(1)/PFA(10), iron filings and water. These were opened after 1,3 and 6 months and the water analysed. The results are given in Table IV where they are compared with the concentrations obtained when the capsules contained well-melted glass. For Tc, Np and Am the results are very similar for the two sets of capsules. For plutonium, the results for the melted glass were about one hundred times lower, but this is thought to be due to the lower inventory of plutonium, as noted above (Section C.1).

3. References

/1/ BOULT, K.A., DALTON, J.T., HOUGH, A., MARPLES, J.A.C., and ROBERTSON G.P., Annual CEC Progress Report for 1988.

/2/ MERTENS, L.A., LUTZE, W., MARPLES, J.A.C., VAN ISEGHEM, P. and VERNAZ, E., in Scientific Basis for Nuclear Waste Management, OVERSBY, V., Editor, Materials Research Society 1990.

/3/ BOULT, K.A., HOUGH, A., MARPLES, J.A.C. and ROBERTSON, G.P., Harwell Laboratory UK Report AERE-R-13369 (1988).

TABLE I: Pu CONCENTRATIONS IN SOLUTION (/10^{-12}M)

Time (/months)	wt.% Pu in glass	Concentrations	
		0.45μm filter	25000 MWCO filter
1	0.12	2000	30
3		7	5
6		40	3
6(a)	6 x 10^{-5}	0.06	0.08
6(b)	0.03	130	
6(c)		10	
Solubility (d)	100 x 10^{-12}M		

(a) In capsules containing Pu-238/1/
(b) For fully-active MW(Magnox) glass/1/
(c) For fully-active MW(THORP) glass/1/
(d) EWART, F.T. and TASKER P.W., in 'Waste Management 87', POST, R.G. Editor, ANS (1987).

TABLE II: Molar concentrations in PFR 273/sea water source term experiment at 60°C.

	Tc-99 (/10^{-8})		Np-237 (/10^{-10})		Pu-239/240 (/10^{-12})		Am-241 (/10^{-12})	
Filter	0.45 µm	25000 MWCO	0.45 µm	25000 MWCO	0.45 µm	25000 MWCO	0.45 µm	25000 MWCO
1 month	4	5	11	16	30	25	1.4	1.6
3	4	4	3	3	130	10	5	3
6	6	5	1	0.6	220	140	1.3	0.9
IN D.I.W. (6 months) /1/	1	1	1.7	1.5	40	3	0.2	0.4
	pH	Eh(mV)			pH	Eh(mV)		
1 month	9.1	-400			9.0	-200		
3	9.2	-420			9.1	-390		
6	10.0	-390			9.7	-150		

TABLE III

Molar concentrations in the supernatant water in the RSST containers at 90°C

		Tc-99				Actinides		Np-237		Pu-239/240		Am-241	
				(/10^{-8}M)				(/10^{-10}M)		(/10^{-12}M)		(/10^{-13}M)	
Water	Time (months)	Filter		0.45 µm	25000 MWCO			0.45 µm	25000 MWCO	0.45 µm	25000 MWCO	0.45 µm	25000 MWCO
		pH	Eh (mV)			pH	Eh (mV)						
Volvic	1	11.7	-500	3	2.5	11.6	-550	8	4	13	10	5	7
	3	11.6	-550	2	2	11.4	-550	15	24	24	23	3	8
	6	10.7	-250	2	2	10.7	-170	2	3	100	18	6	2
/3/	6	8.4	+ 20	1600	1500	8.2	(+150)	5000	5000	300	170	55	40
Sea	1	9.3	-400	2	2	9.4	-400	1.7	1.2	20	20	7	6
	3	9.8	-130	2	1.5	10.1	-150	0.4	0.2	250	5	40	2
	6	10.3	-480	0.4	0.4	10.2	-470	0.1	0.1	35	14	3	2
/3/	6	7.5	N/A	80	70	7.5	N/A	350	360	55	50	37	8
Limiting Concentration				6.7×10^{-8}M				2.1×10^{-10}M		2.3×10^{-12}M		0.47×10^{-13}M	

TABLE IV: Concentrations observed in the presence of unmelted calcine and glass frit at 60°C

Time /months	Tc (/10^{-8}M)		Np (/10^{-10}M)		Pu (/10^{-12}M)		Am (/10^{-14}M)	
	0.45 µm	25000 MWCO	0.45 µm	25000 MWCO	0.45 µm	25000 MWCO	0.45 µm	25000 MWCO
1	20	18	6	3	1200	3	1300	6
3	4	3	4	3	70	2	50	1
6	2	1	1	0.5	20	16	15	30
6(a)	1	1	2	1.5	0.06	0.08	20	30

(a) For similar capsules containing properly melted glass.

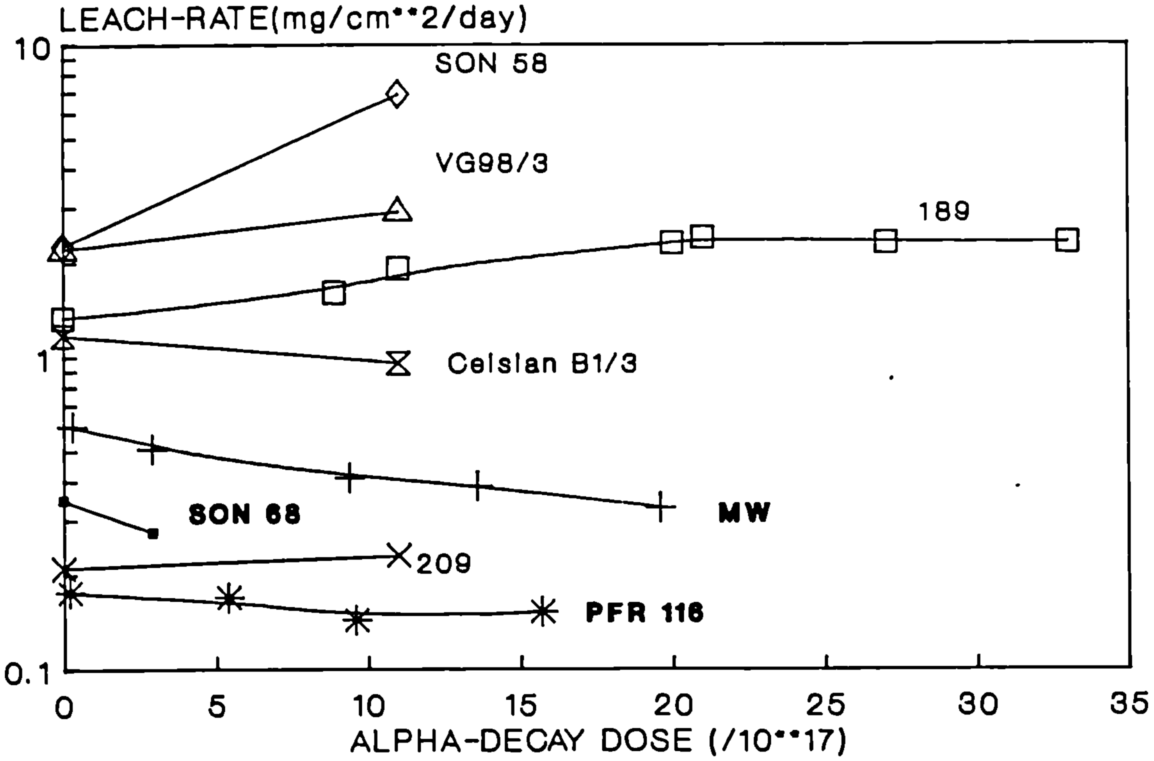


FIG 1. LEACH-RATE vs ALPHA-DECAY DOSE.

LONGTERM BEHAVIOUR OF TRU-WASTE BEARING CERAMICS

Contractor :	Kernforschungszentrum Karlsruhe GmbH / FRG Institut für Nukleare Entsorgungstechnik (INE)
Contract N° :	FI1W/0098-D (B)
Duration of contract :	July 1986 - June 1990
Working Period :	January 1989 - December 1989
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 consists 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 1 E-8 and 1 E-9 g/cm2d after the ISO-draft.

Aim of the current programme is to get information on the long time behaviour of such ceramics with respect to radiation and hydrolytic influences.

Changes in microstructure and hydrolytic stability as a function of long storage time, induced by high alpha-dosis and thus accelerating mutual interactions, will be recorded.

The goal of this programme is achieved by performing "time-lapse" experiments. That means doping the ceramics with a short-living alpha-emitting radionuclide, so the desired high alpha-dose is transmitted to the matrix within short times.

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 (alpha-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 alpha-Dosis required.

C. PROGRESS OF WORK AND RESULTS OBTAINED

1. Synthesis and Preparation of Samples (B.1, B.1.1)

Due to its availability, Plutonium(-238)O_2 with an amount of 20wt.-% 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 simultaneously. 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 E11 Bq/g (2.733 Ci/g)	1.33 E9 Bq/g (0.036 Ci/g)

2. Sample Characterization (B.2)

The ceramographic sample characterization has been performed by means of X-ray-diffractometry, optical and electron microscopy. The crystalline phase compositions has been determined as

- corundum (Al2O3), mullite (Al6Si2O13) and PuO2, considering the ceramic KAB 78 containing 20 wt.-% Pu(238)O2,
- corundum (Al2O3), traces of mullite (Al6Si2O13), (U,Pu)O2, Epsilon-Phase and RuO2 with respect to the KAB 78 ceramics containing 30 wt.-% of original dissolver residues.

During three years the internal absorbed alpha-dose of the Pu(238) ceramics reached 8.3 E 9 Gy. At the beginning, in the middle and at the end of the year the data of the X-ray-peaks of the Pu(238) ceramics were reanalyzed with respect to the d-values, peak aereas, intensity factors and half-width-values. In function of time only slight, but no significant changes of these data could be found so far. No sign of metamictization could be detected.

By means of electron microscopy well selected regions of the "timelapse" sample have been recorded three times with a distance of one year with emphasis on the registration of their pores' and cracks' dimensions and their elemental distributions in function of the increasing internally absorbed alpha-dose. Significant changes within these properties were missing too.

3. Leaching Tests (B.3)

A series of leaching tests after the ISO-draft have been performed, using the KAB 78 Pu(238) ceramics. The average leachrate for plutonium was found to be about 1 E-7 g/cm2d after a total leaching time of 160 days, using Q-brine and distilled water as leaching solutions.

Leaching and corrosion experiments with these samples at 200°C, using Q-brine as well as distilled water and autoclave technique have been performed for an period over more than 200 days.

It seems that the influence of the elevated leaching temperature increases the plutonium leachrate about 1.5 orders of magnitude, whereas the highest values were appointed to the KAB 78 ceramics, containing 20 wt% of Pu(-238)O2 in contact with the Q-brine.

4. Sample Characterization of the irradiated and leached ceramics (B.4)

The Pu-238 doped ceramics KAB 78 has been analyzed after having received a total alpha-Dosis of about 7.5 E 9 Gy by means of differential thermoanalysis aiming to detect a sign of stored enerfgy by the ceramic matrix. By several runs from room temperature to 1300°C no deviation of the DTA-reference curve, respectively no energy storage could be found so far.

The ceramographic preparation of the KAB 78 ceramics containing Pu (-238)O2, respectively original dissolver residues leached under elevated temperatures has been finished.

D. PUBLICATION

Loida, A., Solidification of TRU-Wastes by Embedding into an Aluminiumsilicate Based Ceramic Matrix, 91st Annual Meeting of the American Ceramic Society, April 23-27, 1989 Indianapolis; Advances in Ceramics-Nuclear Waste Management (1989).

Laboratory and in-situ interaction between simulated waste glasses and clay

Contractor : S.C.K./C.E.N. Mol, Belgium
Contract N° : FI1W/0179
Duration of Contract : January 1988 - December 1989
Period covered : January - December 1989
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 (81-84) and the third (first phase, 86-87) CEC R & D programme (contracts n° 302-83-15 WASB, 324-83-55 WASB, FI1W0100). Important progress was realised on the elucidation of the corrosion mechanisms in clay media (claywater with and without clay) of various candidate HLW and TRUW glasses, taking into account such factors as temperature, SA/V (surface area to volume), redox potential. The tests were done at different levels : with inactive glasses, with tracered glasses, in the presence of an external γ irradiation field, or in-situ (in the underground laboratory in clay under the Mol site).

The 88-89 programme aims to conclude about the corrosion mechanisms and the radionuclide release ("source term") of various waste glasses in clay. The presence of canister/overpack corrosion products is considered, as well as the presence of an external γ irradiation field. The corrosion of some fully active glasses in clay will be evaluated, relative to the inactive simulants. The in-situ performance in clay will be further studied. The following waste glasses are studied : the AVH SON68, the Pamela SM513 and 527, and FLK WG124.

B. Work Programme

B.1 Corrosion experiments in various clay media, with attention to the leaching of the matrix components (Si, B, Fe, ...) and of the radionuclides (Pu, Tc, Np, ...). Temperatures are 40, 90 (reference) and 150 °C ; corrosion products of stainless steel, carbon steel and titanium are included.

B.2 Corrosion experiments in clay media with fully active samples of glasses SON68 and SM513 in the reference conditions applied under B.1 (90 °C, reducing condition, SA/V = 100 m^{-1}).

B.3 Corrosion experiments on waste glasses in clay in integrated conditions, (1) in an external γ irradiation field, in the presence of canister/overpack corrosion products and backfill, and (2) following the CEC standard procedure for the repository system simulation test, using active glass.

B.4 In-situ tests in the underground laboratory in clay, at various temperatures (rock temperature, 90 °C, 170 °C) and in two media (humid clay atmosphere and clay).

C. Progress of work and obtained results

State of advancement

The corrosion experiments on inactive glasses (SON68, SM513, SM527 and WG124) and Pu-Cs-Sr doped glasses (SON68, SM513 and SM527) from the 86-87 programme were continued in 1989. The 2 years duration was reached for both inactive and active glasses. For the inactive glasses corroded in CCSICM (500 g clay/l SIC), test durations until 980 days were reached.

Another item of the 86-87 programme, the influence of the surface layer, was evaluated in the previous annual report. By means of electron microprobe X-ray analyses on samples, corroded for 2 years in DCSICM (10 g clay/l SIC) or CCSICM, new information which contributes to a better understanding of the role of the surface layer was obtained in the course of 89.

Several series of new leaching tests have been started :

- Blanks : a new series of blank tests (DCSICM and CCSICM) was initiated, to have a base for comparison with the results of the first series, which seemed somewhat unreliable.
- Inactive glasses : tests at 40 °C and 150 °C in CCSICM ; tests in SIC and a leachate presaturated in Al, Si and Fe at 90 °C ; tests in CCSICM at 40 °C and 90 °C, containing corrosion products from the canister and candidate overpack materials.
- Pu-Sr-Cs tracered glasses SON68, SM513, SM527 and Pu doped glass WG124 : solubility tests on powdered glasses in SIC at 40 °C and 90 °C ; tests at 90 °C with $E_h > 0$ (all other tests are carried out in reducing conditions) ; tests in CCSICM at 40 °C ; tests in CCSICM at 40 °C and 90 °C, containing corrosion products from the canister and candidate overpack materials.

Tests with Np-Tc-Fe tracered glasses will be started during the first half of 1990.

The corrosion experiments in an external gamma irradiation field were continued in 1989, with an irradiation time of max. 180 days at a dose rate of about 0.60E5 rad h^{-1} (test completed in January 1990).

A fully active SON68 sample and fully active SM513 beads were received in the course of 89. Samples for corrosion experiments are being prepared. The actual start of the corrosion tests is planned for March 90.

The in-situ experiments were continued. No results are to be reported w.r.t. the experiment in direct contact with the clay. The tube containing samples in a clay derived atmosphere at 170 °C was retrieved in July 89.

An extension of the contract until mid of 90 was asked, because of the delay in starting corrosion tests on the Np-Tc-Fe tracered glasses and the fully active glasses.

Progress and results

1. Corrosion mechanisms in clay media

1.1 Inactive experiments

- * Blank tests : the first series of blank tests (90 °C, DCSICM and CCSICM) was completed with the last duration (720 days). A new series has been running for over 180 days. The maxima of the elemental concentrations of Si, Al and Fe, observed in the first series, are confirmed, although less pronounced. They are followed by steady state concentrations of about 20 to 60 $mg.l^{-1}$ for Si, 5 to 20 $mg.l^{-1}$ for Al and smaller than 10 $mg.l^{-1}$ for Fe.

- * Corrosion at 90 °C in two clay/SIC media (glasses SON68, SM513, SM527, WG124) : in the diluted clay solution, a residual corrosion seems to

establish for glass WG124, and to a lesser extent for glass SON68. The initial dissolution stage is followed by an equilibrium (apparent saturation) stage, which passes into a final dissolution rate. This is supported by the decreasing Al concentrations in solution with time, which are known to correspond to phase formation and are determinant for the final leaching. A first estimation of the "final rate of dissolution" in DCSICM would yield 0.02 gm^{-2} d^{-1}.
In the concentrated clay solution, the stages during which mass losses increase proportional, resp. proportional with the square root of time, are followed by a further slow-down. This may indicate that corrosion in this medium may tend to some equilibrium value as well. Si steady state concentrations for the various glasses are presented in Table 1.

Table 1 : Steady state Si concentration in solution upon corrosion in clay/SIC mixtures ($mg.l^{-1}$).

Waste glass	DCSICM	CCSICM
SON68	65	20
SM513	120	40
SM527	35	25
WG124	65	80

Electron microprobe (EMP) X-ray analyses, carried out on the samples, corroded for two years in either DCSICM or CCSICM, leads to the following conclusions :

- the absence of a surface layer on glass SM527, which was observed already for a duration of one year, is confirmed for the duration of two years ;
- in general, layers are thicker in the concentrated clay solution ;
- subsurface zones, frequently observed on samples which had been corroded for one year, seem to have disappeared after two years of corrosion.

* Influence of temperature on corrosion (same glasses) : these tests are carried out in CCSICM at 40 °C and 150 °C. The 28, 80 and 180 days tests are finished. Mass losses increase as corrosion temperature increases. The elemental concentrations in the leachate are lower for the tests at 40 °C than at 90 °C, except for Ca. The elemental concentrations of Si, Al, Fe and Ca are however not systematically larger at 150 °C than at 90 °C, which may be related with phase formation.

* Tests in SIC at 90 °C (no clay phase, same glasses) : the 28, 80 and 180 days tests are finished. Mass losses in SIC are smaller than in DCSICM. The difference is however small and even tends to decrease with time.

* Tests in DW (Distilled Water), presaturated with Al, Si and Fe, at 90 °C (only glasses SON68 and SM527) : the 28 and 80 days tests are finished. Mass losses in this medium are smaller than in SIC, but still existing. They decrease however with time in the case of SON68.

* Tests including corrosion products (all glasses involved) : the addition of large quantities of Fe_2O_3 (about 1 g per 3 g clay), leads to a decrease of mass losses with a factor 20 (at 40 °C) to 70 or more (at 90 °C). Small additions (0.01 g Fe_2O_3 or 0.01 g Fe_2O_3 + 0.01 g TiO_2 per 4 g clay) have a negligible effect.

1.2 Radioactive (tracer) experiments

- Source term experiments (glasses SON68, SM513, SM527) : the experimental temperature is 90 °C. Durations up to 2 years are completed. New data however only concern SON68 and SM513. Based on the total Sr inventory, Sr is found to be leaching congruently with the glass matrix in the case of glasses SON68 and SM513. Pu and Cs leaching is however retarded w.r.t. the glass matrix by a factor of 2 to 10. While Pu and Sr stopped leaching beyond a few months for SON68 and SM513, the recent total inventory data reveal that Cs behaves similarly beyond 240 days.
  K_d values (distribution coefficient) for Cs, Sr, Pu and Am generally continue increasing with longer durations.

- Tests in oxidizing conditions (SON68, SM527, PWG124) : $E_h > 0$, experimental temperature is 90 °C, media are CCOSICM for SON68 and SM527 (500 g oxidized clay/l oxidized SIC) and OCWM for WG124 (100 g oxidized clay/l DW). The 27 and 240 days tests are finished.
  In the case of SON68 and SM527, K_d values for Cs, Sr and Pu turn out to be much smaller in oxidizing than in reducing conditions. For PWG124, the opposite is the case. Mass losses are often lower in oxidizing conditions. An exception is SON68 after 240 days, which shows the opposite behaviour.

- Solubility tests on powdered glass (same glasses) : the medium is SIC, temperatures of the experiments are 40 °C and 90 °C. The 27 and 240 days tests are finished. Radiochemical analyses are in progress.

- Influence of temperature (SON68, SM513, SM527) : the medium is CCSICM, temperature is 40 °C. The 27 days test is finished. At this moment, only mass losses are known. They are of the same order as mass losses for inactive glasses in the same conditions.

- Influence of corrosion products (same glasses) : test are running but no results are available yet.

2. Influence of an external gamma irradiation field on corrosion

(See "State of advancement").

3. Corrosion stability of fully active waste glasses

(See "State of advancement").

4. Repository Systems Simulation Test - clay option on Pu-Cs-Sr tracered glass SON68

The tests for 28, 91 and 364 days are finished, but only the results of the radiochemical analyses for 28 and 91 days are available. For none of the tracers the leached amount increased significantly between 28 and 91 days. The amount of Cs and the total gamma in the supernatant even decreases with longer leaching time. The decrease of Cs is much higher than can be caused by its decay. In comparison with the results of the RSST on Pu tracered MW (British glass from BNFL) glass in granite repository conditions, the normalized mass losses for Pu after 28 days are one order of magnitude higher, while the 90 days values are of the same order (a factor of 2 lower).

5. In-situ experiment

5.1 Direct contact with clay : no results are to be reported.

5.2 Experiments in a humid clay atmosphere :

After six months of operation, the tube at 170 °C was retrieved in July. Mass losses of glass samples were measured. They turned out to be very low (of the order of 0.1 to 1 $g.m^{-2}$), compared with mass losses measured in clay-contact experiments.

The tube was reinstalled in August. In the subsequent months, a malfunction of the water evacuation system of the tube caused an accumulation of water. As a result of this, an adequate temperature regulation was impossible. In October it was decided to stop the concerning test and to definitely remove the tube from the gallery.

List of publications

(1) Laboratory and in-situ interaction between simulated waste glasses and clay - Annual Report 1988 (R-2755). Presented at the CEC progress meeting for task 3, sections 2 + 3 (Trisaia, April 1989).

(2) Laboratory and in-situ interaction between simulated waste glasses and clay - Semestrial Progress Report January-June 1989. Presented at the CEC progress meeting for task 3, sections 2 + 3 (Madrid, Sept. 1989).

(3) P. Van Iseghem, K. Berghman and W. Timmermans
The interaction between nuclear waste glasses and clay - II. Paper presented at the XIIIth Intern. Symp. on the Scientific Basis for Nuclear Waste Management, 27 Nov. - 1 Dec. 1989, Boston, U.S.A.

(4) P. Van Iseghem, K. Berghman and B. Neerdael
In-situ testing of nuclear waste glasses in a clay laboratory - results after two years corrosion. Paper presented at the XIIIth Intern. Symp. on the Scientific Basis for Nuclear Waste Management, 27 Nov. - 1 Dec. 1989, Boston, U.S.A.

Part A

RADIOACTIVE SON 68 18 17L1C2A2Z1 GLASS INTERACTION WITH ENVIRONMENTAL MATERIALS

Part B

INVESTIGATION OF IRRADIATION DAMAGE IN GLASS BY THERMOLUMINESCENCE

Contractor:	CEA, CEN-Valrhô, SDHA, F
Contract No:	FI1W-0180 F
Duration of Contract:	January 1988 - December 1989
Period Covered:	January 1989 - December 1989
Project Leader:	N. Jacquet-Francillon

A. OBJECTIVES AND SCOPE

Although the effects of physical parameters (temperature, pH, etc.) on the alteration of nuclear waste glasses in pure water have been widely investigated, interactions between the glass and various materials liable to be present in a geological repository are relatively little known. The environmental materials appear to affect not only the bulk glass corrosion rate but also the actinide leaching behavior.

The objective of this program is to investigate the alteration of radioactive SON 68 18 17 L1C2A2Z1 glass specimens and the characteristics of radionuclide release in the presence of environmental materials from the engineered barrier or the host rock. Parameter studies will be conducted to determine whether the repository environmental materials have a significant effect on actinide containment in the glass. Integral experiments will be conducted to compare interactions (glass corrosion rate, radionuclide release rate) involving both radioactive (α, β, γ) and inactive glass with three types of host materials: granite, salt and clay.

The second part of this program will be carried out jointly with the University of Bordeaux, and concerns the detection of irradiation damage in glass by thermoluminescence (TL) with the intention of revealing an irradiation damage saturation phenomenon at a structural level.

B. WORK PROGRAM

Part A - Radioactive Glass Interaction with Environmental Materials

2.2 Effect of environmental materials on leaching of transuranium nuclides: parameter tests with 7 different environmental materials in contact with 2 radioactive glasses (^{237}Np and ^{239}Pu) after 4 different leaching durations.

2.3 Integral tests in granite, clay and salt:

2.3.1 Inactive tests.
2.3.2 α, β and γ radionuclide release in granite, clay and salt.

Part B - Thermoluminescence Investigation of Irradiation Damage in Glass

2.1 Theoretical investigation of TL mechanisms in the R7T7 glass matrix.

2.2 Experimental thermoluminescence examination of radioactive R7T7 glass specimens.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Part A - Radioactive Glass Interaction with Environmental Materials

The tests conducted to investigate the effect of environmental materials with 7 different media (4 clays, sand, granite and salt) and two different R7T7 glass additives (^{237}Np and ^{239}Pu) over four different durations (3, 6, 9 and 12 months) have now been completed and analyzed. Only the ICP analysis of the saline solutions are still in progress.

The status of the integral tests is now as follows:

- TAV 9 (inactive glass in granite, initiated under contract FI 1W 0096 F) has now been completed after 3½ years; SEM examination of the altered glass is now in progress.
- Two inactive glass tests in Boom clay, one with a fractured glass block and the other with a monolithic glass block, were initiated in February 1989 and will soon be terminated after 1 year.
- Two tests on fractured inactive glass blocks in salt were initiated in September 1989.
- The radioactive glass tests initially planned cannot be undertaken in the remaining time available under this contract.

Part B - Thermoluminescence Investigation of Irradiation Damage in Glass

The following work was accomplished in 1989:

- Development of an irradiation damage model in silicate glass, and extension to nuclear glass formulations
- Implementation of a specific TL device
- Development and qualification of an actinide-doped glass fabrication process
- Proposal of an alternative study on transparent R7T7 glass specimens in case of experimental problems with black R7T7 glass
- Proposal of a model to explain changes in TL properties between crystals and glass.

Progress and Results

Part A - Radioactive Glass Interaction with Environmental Materials

- Effect of environmental materials on leaching of transuranium nuclides

The degree of alteration observed with both ^{237}Np- and ^{239}Pu-doped glass specimens varied according to the nature of the environmental material. The materials may be classified as follows in order of increasing glass alterability in contact with them:

sand ≤ granite < bentonite < salt < illite ≤ smectite < Boom clay

The smectite, illite and Boom clay used for these tests consume silicon released by glass corrosion, and thus temporarily prevent "saturation" conditions from being reached under which the glass corrosion rate becomes extremely low. Conversely, the bentonite tested here tends to favor the rise to silicon "saturation".

Alpha counting and spectrometry measurements of leached activity showed that the neptunium retention factor in the glass alteration film was low regardless of the environmental material, and that the leached neptunium tended to remain in solution: it is not sorbed in large amounts on the environmental materials (Figure 1).

The ^{239}Pu retention factor in the alteration film was satisfactory (Table I), and this nuclide (like $^{238}Pu/^{241}Am$) was also retained in the nearfield environment, mainly in the form of colloidal particles. Clays (except for Boom clay) appear to favor this phenomenon, probably by providing a colloidal fraction (Table II).

- Integral tests in granite, clay and salt

The results of the 3½-year integral test in granite showed that steady-state conditions were achieved after 2 years: the glass corrosion rate was no longer measurable, and was well below the corrosion due to leachate renewal after sampling (5×10^{-7} $g \cdot cm^{-2}d^{-1}$) under the experimental conditions (Figure 2).

Part B - Thermoluminescence Investigation of Irradiation Damage in Glass

- Investigation of α Irradiation Damage Inception in Silicate Glass Specimens

Thermoluminescence and electron spin resonance studies of pure silicate glass behavior under α irradiation showed that Si—O bonds were broken, releasing oxygen atoms that could diffuse in the glass, creating oxygen bubbles as they recombined to form O_2 or O_2^- molecules.

- Investigation of Nuclear Glass Behavior under α Irradiation

A specific thermoluminescence device was installed in a glove box and tested with nonradioactive R7T7 glass specimens irradiated by ^{60}Co. Radioactive glass specimens doped with ^{238}Pu and ^{241}Am will be studied in 1990 in place of ^{244}Cm-doped specimens which could not be fabricated (although development work for producing the latter was completed).

- TL Investigation of Nonradioactive R7T7 Glass Specimens

Thermoluminescence in R7T7 glass is limited by its black color and optical self-absorption properties. The fabrication of transparent R7T7 glass was investigated: this glass would have the same TL properties as the black glass, but would be about ten times more irradiation-sensitive. If the actinide-doped R7T7 glass specimens prove to be too opaque, fabrication of transparent actinide-doped specimens may thus be considered.

- Investigation of TL Properties during Glass Recrystallization Process

The TL intensity increases with the degree of crystallinity of a material, proportionally with the mean free path of the charge carriers released by irradiation. Glass samples were experimentally less thermoluminescent than crystals.

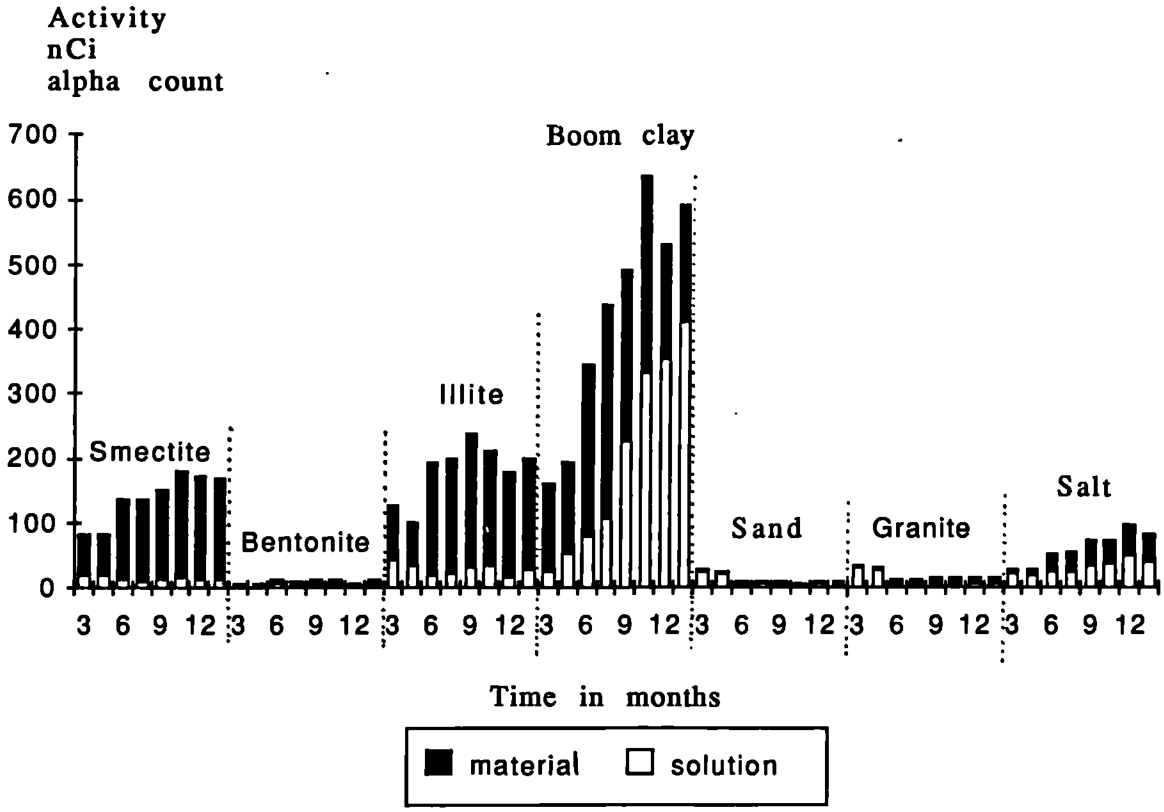


Figure 1 - Activity (in nCi) in Solutions and Environmental Tests with ^{237}Np-Doped Glass

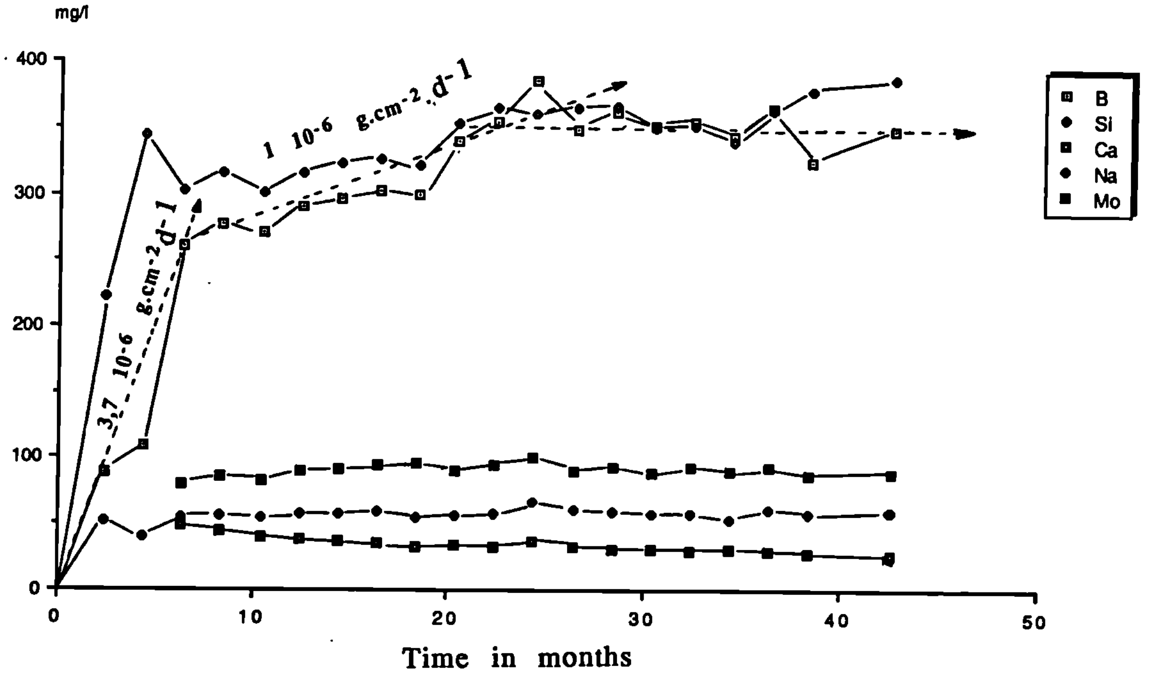


Figure 2 Boron, Silicon, Calcium, Sodium and Molybdenum Concentration Variations in the Leaching Vessel (TAV 9)

	237 Np	239Pu	238Pu241Am
Sand	5-6	33	65
Granite	5	13	26
Smectite	3	75	113
Bentonite	3-4	11	18
Illite	2-3	53	105
Boom clay	1-2	30	20
Salt	nd	nd	nd
Bld.water [5]	8	46	350(241Am)

Table I Mean Actinide Retention Factor in the Glass Alteration Film (NL(B)/NL(ACTINIDE))

	237 Np	239Pu	238Pu241Am
Sand	1,6	226	189
Granite	2	650	542
Smectite	12,5	1700	632
Bentonite	3,5	2650	1178
Illite	10	1800	2027
Boom clay	2,5	227	309
Salt	2	44 (alpha count)	

Table II Mean Leached Activity Retention Factor in Environmental Materials, Colloids and Colloidal Particles
(total recovered activity/ultrafiltrate activity)

CHARACTERIZATION OF THE ITALIAN GLASSES AND THEIR INTERACTION WITH CLAY

Contractor : ENEA CRE-Casaccia, Roma, Italy
Contract No. : FI1W-0181-I
Duration of contract : January 1988 - December 1989
Period covered : January 1989 - December 1989
Project leaders : A. Donato, C. Cantale

A. OBJECTIVES AND SCOPE

A study for an integrated treatment of all the HLW stored in Italy (MCE waste) is currently going on. One of the studied options is based on a pre-treatment of this waste, in order to concentrate the HLW fraction, separating the most part of the inert salts; this work is carried out in the frame of the ECC R&D Programme (Contract No.FI1W-0011-IS, part 1 and 2).

After the MCE waste pre-treatment, the vitrification of the resulting HLW stream is foreseen.

The objective of this research is to select a borosilicate glass composition suitable for this HLW stream and to characterize it with reference to the geological disposal. A comparative characterization of glasses obtained either in laboratory or in a cold plant (IVET) is planned.

B. WORK PROGRAMME

B.1 Preliminary selection of glass compositions suitable for the HLW semi-liquid fraction coming from the separation process.
B.2.1 Optimization of the selected composition with reference to the waste to glass ratio.
B.2.2 Preparation of the glass (lab-scale) using as feed the simulated waste obtained in SERSE cold plant operations.
B.2.3 Physical, physico-chemical and chemical characterization of the glass.
B.3 Production of the glass in the cold IVET pilot plant (full scale) and characterization of representative samples.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The glass composition named BAZ was previously selected /1/.

The physico-chemical, mechanical and chemical characterizations of the glass as prepared in laboratory have been completed.

The chemical durability has been investigated by MCC-1 type static leach tests carried out at 90 °C and both at SA/V = 10 m^{-1} and 100 m^{-1}. Distilled Water (DW), Synthetic Interstitial Claywater (SIC) and a Clay-Water Mixture (CWM), have been used as leachant.

The same glass composition has been used to prepare some blocks of glass in the IVET Plant (ENEA-Trisaia), after the proper plant modifications. The previous characterization programme has been followed using one of these blocks, in order to compare the two glasses and to investigate, in case, the influence of the plant operations.

A delay in the plant glass production has shifted the conclusion of the chemical durability tests. It is foreseen to complete the programme for the end of February.

The general work progress status is as follows:

- B.1 - B.2.1 - B.2.2 were completed last year.
- B.2.3 has been completed.
- B.3 is in progress and it will be completed in two months.

Progress and results

B.2.3 The characterization of BAZ-R glass as prepared in laboratory (conclusion)

The MCC-1 (Materials Characterization Center) standard test, matrix D (maximum duration 91 days) has been used to evaluate the chemical durability of BAZ-R glass in distilled water (DW), Synthetic Interstitial Claywater (SIC), and in a Clay-Water Mixture (CWM, containing 500 g of clay in 1000 cm^3 of distilled water). The test temperature have been 90 °C. Inactive simulated glass specimens has been used and the tests have been carried out at atmospheric conditions.

The results refer to SA/V = 100 m^{-1} using all the three leaching systems. The results concerning SA/V = 10 m^{-1} were reported last year /1/.

Looking at the results obtained in DW, expressed as Mass Loss, it appears that the behaviour of BAZ-R glass is comparable to the BEL 15 glass (see Figure 1).

When SIC is used as leachant, a precipitation of salts on the surface of the specimens occurs at any SA/V ratio, together with a change in the solution composition. A large variability in the results has been observed for those elements that are contained both in the SIC leachant and in the glass. A better evaluation of the glass release in SIC is possible looking at those elements (B, Li and Cs)that

are not contained in the leachant. The normalized elemental mass losses (NL) measured for Boron, Lithium and Caesium, suggest a lower release for BAZ-R glass in comparison with BEL 15 in the same conditions (see Figure 2).
The results obtained in CWM suggest a leaching mechanism of BAZ-R mainly controlled by matrix dissolution, which results in a leaching rate at 91 days higher than BEL 15 one (see Figure 3).

The surface analyses carried out on the leached specimens have not been able to provide relevant information.

In conclusion the glass is good and its performances are comparable to those of the more representative european glasses (see Figure 4) /2/.

B.3 Characterization of BAZ-R glass produced in the cold IVET pilot plant (full scale).

The production of BAZ-R glass in the IVET plant has been quite satisfactory as concern both the plant operations and the glass quality (in terms of homogeneity, chemical composition and vitreous characteristics). The characterization of the glass produced in the plant (identified as BAZ-V-40), has been carried out in order to evaluate the likeness between the laboratory and the plant products and to explain the possible effects of the plant scale, particularly with respect to the chemical durability. The same leaching programme used for BAZ-R characterization, was partially applied to BAZ-V-40 glass, except the tests using SIC as leachant. The tests have been carried out using both remelted glass coming from various parts of the canister and the original glass.

In TABLE I the results obtained in the characterization of BAZ-V-40 glass are summarized and compared to the BAZ-R results.

In Figure 5 the available results, expressed as Mass Loss, in DW at SA/V = 10 m^{-1} and SA/V = 100 m^{-1} and in CWM at SA/V = 100 m^{-1}, up to 56 days, are shown. The tests are in progress; a preliminary comparison between BAZ-R and BAZ-V-40 behaviour suggests a good agreement.

/1/ C.Cantale, S.Castelli, A.Donato, D.M.Traverso
ECC Research Contract n° FI1W-0181-I, Annual Report 1988

/2/ R.Conradt, H.Roggendorf, R. Ostertag
"The basic corrosion mechanisms of HLW Glasses"
ECC Research Contract n° 440-85-53-WAS-D, Final Report

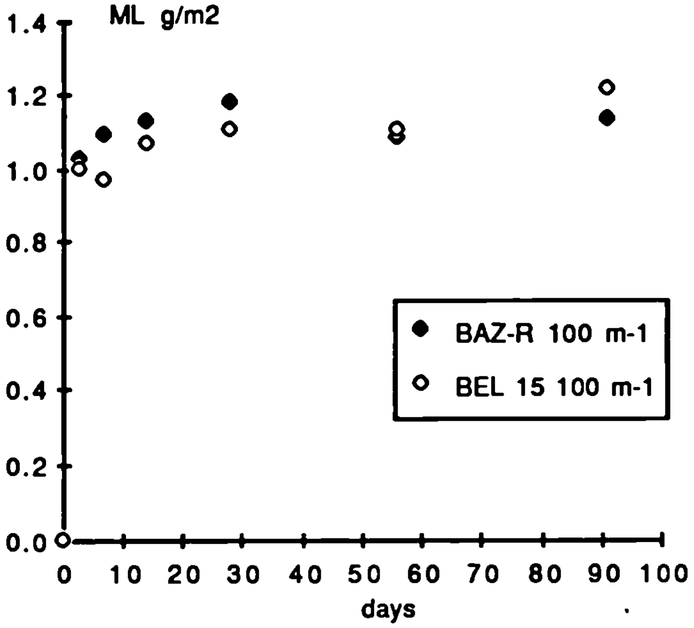


Figure 1 Mass Loss of BAZ-R and BEL 15 glasses leached in DW at 90°C and SA/V=100 m^{-1} as a function of the corrosion time.

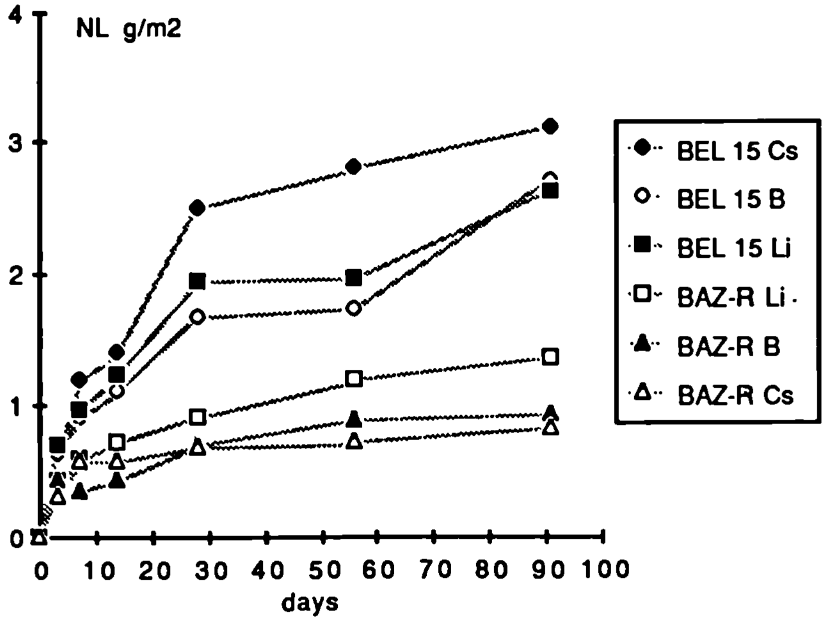


Figure 2 Normalized Elemental Mass Loss of BAZ R and BEL 15 glasses leached in SIC at 90 °C and SA/V = 100 m^{-1} as a function of the corrosion time.

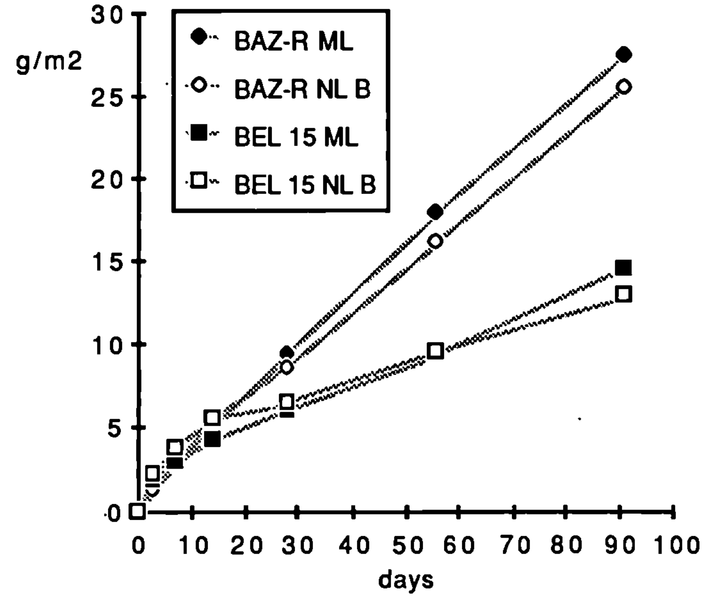


Figure 3 Mass loss and Boron Normalized Mass Loss of BAZ-R and BEL 15 glasses leached in CWM at 90 °C and SA/V = 100 m^{-1} as a function of the corrosion time.

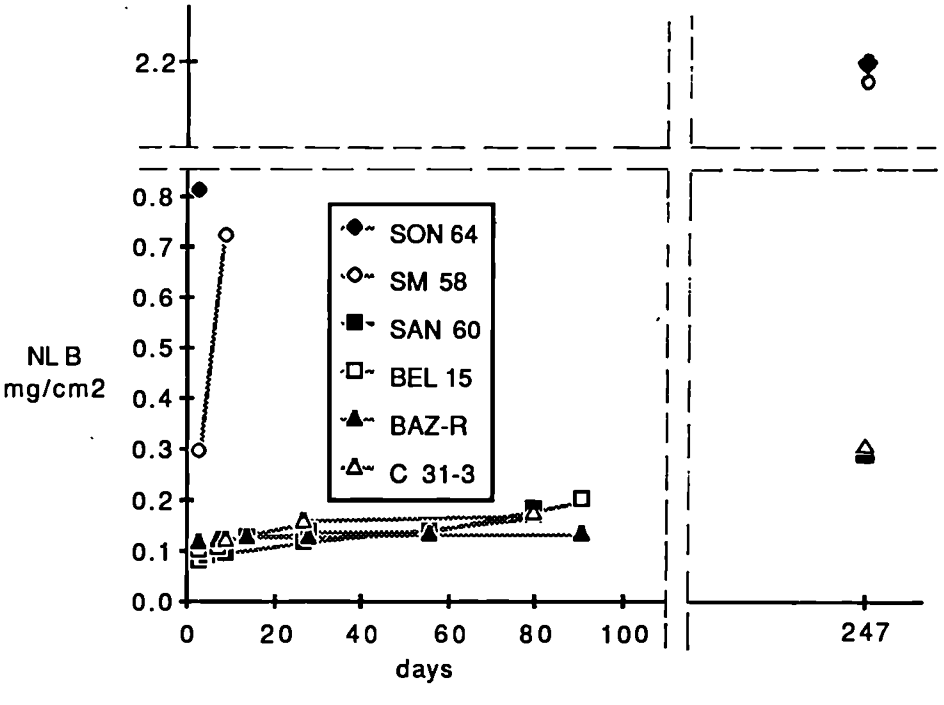


Figure 4 A comparison between Boron Normalized Mass Loss measured in DW at 90°C and SA/V = 100 m^{-1} for BAZ-R and referred data /2/.

TABLE I SOME REPRESENTATIVE DATA CONCERNING THE CHARACTERIZATION OF BAZ-V-40 AND BAZ-R GLASSES.

	BAZ-V-40	BAZ-R
Density (g/cm3)	2.59	2.57
Tg	410°C	430°C
Thermal Expansion Coeff.[1] (E-6 °C-1)	13.97	11.7
Hv[2] (GPa)	6.8	6.7
Elastic Modulus[3] (GPa)	91.6	86
KIC[4] (MPam1/2)	0.87	0.86
Thermal behaviour[5]: devitrification	limited at 700°C	limited range 600-800°C

[1] range 140 - 350 °C

[2] Vickers microhardness

[3] according to the Knoop indentation method

[4] Critical stress intensity factor, according to Evans and Charles eq.

[5] Heat treatments followed by X-rays analyses: 60 h at 500, 600, 700, 800 and 1000 °C.

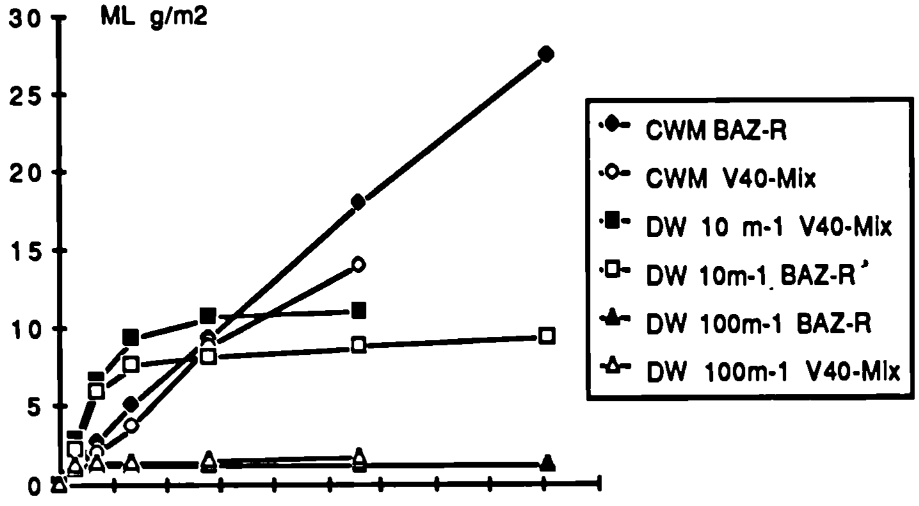


Figure 5 Mass Loss of BAZ-V-40 Mix and BAZ-R glasses leached at 90 °C in DW at SA/V = 10 m^{-1} and 100 m^{-1} and leached in CWM at SA/V = 100 m^{-1}as a function of the corrosion time.

INVESTIGATION OF FULL SCALE HIGH LEVEL WASTE CONTAINMENT GLASS BLOCKS

Contractor:	CEA, CEN-Valrhô, SDHA (France)
Contract N°:	FI1W-0182
Duration of Contract:	January 1988 - December 1989
Period Covered:	January 1989 - December 1989
Project Leader:	J.P. Moncouyoux

A. OBJECTIVES AND SCOPE

This investigation is part of a research program on high level liquid waste containment glass involving industrial scale work applied to the safety analysis of ultimate glass storage, and thus the definition of the glass source term.

The purpose of this work is to quantify the degree of fracturation of industrial glass blocks based on nonradioactive specimens produced in a prototype unit under experimental conditions fully representative of the actual COGEMA vitrification facilities at La Hague.

The project includes a theoretical investigation of fracture-inducing stress distribution in the glass block, as well as an experimental study based on water leach tests at 100°C to evaluate the fractured leachable surface area and on tomographic examinations performed at the BAM in Berlin on full scale canisters containing glass cast at Marcoule.

B. WORK PROGRAM

B.1 Theoretical analysis of the thermal and mechanical conditions liable to induce stresses leading to fracturation of a glass block.

B.2 Experimental study of nonradioactive 400 kg glass blocks 420 mm in diameter fabricated in an industrial prototype facility.

- B.2.1 Measurement of experimental thermal conditions.
- B.2.2 Tomographic examination of 400 kg glass blocks (BAM).
- B.2.3 Assessment of fracturation from the granulometry distribution of glass fragments.
- B.2.4 Assessment of fracturation by leaching in water at 100°C.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

The theoretical investigation of stress-inducing thermal phenomena was undertaken, and the CASTEM code system was implemented for calculation purposes.

The experimental study was limited to containers 420 mm in diameter. The industrial prototype facility was used to produce 200 kg and 400 kg glass blocks for tomographic examination and water leach testing in order to measure the degree of fracturation. Tomography examinations began in 1988 and are still in progress. Dynamic leach tests were conducted on the 200 kg blocks.

Progress and Results

B.1 Theoretical Investigation

A mathematical formulation was developed for the phenomena affecting cooling of the glass/canister system. The thermal evolution of the system is governed by the transient heat equation:

$$\rho \cdot C \cdot \frac{\partial T}{\partial t} = \mathrm{div}(\lambda \nabla T)$$

in which ρ (density), C (specific heat) and λ (thermal conductivity) are temperature-dependent, and thus time- and space-dependent parameters.

The mechanical analysis requires thorough knowledge of the material behavior. Glass is a complex material, considered viscoelastic at temperatures above the transition zone (approx 502°C). Its viscoelastic behavior is represented by a Maxwell model with temperature-dependent variable coefficients.

The total deformation sustained by the glass is reflected in the following equation:

$$\varepsilon^{g,\mathrm{total}} = \varepsilon^{g,\mathrm{elastic}} + \varepsilon^{g,\mathrm{viscous}} + \varepsilon^{g,\mathrm{thermal}}$$

where:

$$\frac{\partial \varepsilon^{g,\mathrm{viscous}}}{\partial t} = M(T) \cdot \sigma^{g}$$

$$\frac{\partial \varepsilon^{g,\mathrm{thermal}}}{\partial t} = - \frac{\partial (\alpha^{g}, T^{g})}{\partial t}$$

$$\sigma^{g} = K(T) \cdot \varepsilon^{g,\mathrm{elastic}}$$

The M(T) and K(T) terms represent the fluidity and rigidity matrices, which depend on Young's modulus E, the Poisson coefficient ν and the glass viscosity η. The four variables in the above equations (E, ν, η and the thermal expansion coefficient α) are temperature-dependent.

Steel is considered as an elastic material, hence:

$$\varepsilon^{s,\mathrm{total}} = \varepsilon^{s,\mathrm{elastic}} + \varepsilon^{s,\mathrm{thermal}}$$

All the thermal and mechanical analysis parameters and their temperature-related variations were determined. The thermal evolution of a waste package was calculated using the CASTEM code system for a simulated

400 kg glass block obtained by casting two consecutive 200kg melts into a metal canister. The wall temperatures were measured and integrated into the calculation as boundary conditions. The thermal results are presented as colored isotherms or cooling curves for certain points in the system.

The mechanical calculation based on the thermal results is now in progress.

B.2 Experimental Study

B.2.1 - B.2.2

A 400 kg simulated industrial glass block was produced from two successive 200 kg melts in a dismountable metal canister and cooled according to the thermal reference scenario adopted for the La Hague vitrification facilities. Two 200 kg blocks representative of the first and second melts in the 400 kg glass package were also produced.

The 400 kg block is being examined by tomographic examination at the BAM. The first examination has been carried out on the canister as cast, and will soon be followed by a second examination after partial dismantling of the canister to relieve canister stresses. A photograph taken during the first examination is now available.

B.2.4

The 200 kg glass blocks were submitted to dynamic leach testing for 21 days in 100°C water. Surface area values determined by chemical analysis of the leachate indicated a minimum fracturation factor of 4.5.

3.3. OTHER ENGINEERED BARRIERS

NEARFIELD BEHAVIOUR OF CLAY BARRIERS AND THEIR INTERACTION WITH CONCRETE

Contractor : CEA, CEN Fontenay aux Roses
Contract n° : FI1W - 0031
Period covered : January 1989 - December 1989
Project leaders : A. LAJUDIE, R. ATABEK

A. OBJECTIVES AND SCOPE

In order to guarantee the safety of underground disposal waste, coming from spent fuel reprocessing, engineered barriers will be implemented as backfill materials in galleries 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

Analyses and preliminary measurements perform on eighteen samples coming from fourteen french clay deposits have led to the choice of two clay materials (ref. 4a and 13) which may be used as constituent elements of engineered barrier. The mineralogy of these two clays is now well defined for further investigations. A vitrified waste disposal in granite is taken as the most constraining scenario as far as engineered barrier is concerned. The buffer material properties which are evaluated are directly related to the engineered barrier requirements : thermal conductivity, permeability, water diffusion coefficient, swelling properties... Moreover results are obtained on temperature effect on clay material microstructure and properties in both cases : without and with water intake.

The study of concrete durability with regard to clay pore water attack is conducted taking into account previous results obtained to ensure LLW disposal safety.

B.1 is finished
B.2, B.3, B.4 are finished
B.5 started in 1988, as planed in the contract.

PROGRESS AND RESULTS

1. Material choice (B.1)

Precise mineralogical analyses, performed on clay fraction (≤ 2 μm), give the main component content of the two selected materials, referred to as 4a and 13, coming respectively from sparnacian and oligo-miocene deposits. For example, the samples of reference 4a clay subjected to hydrothermal degradations (§ B.4) have the following compositions :

o Non phyllosilicate minerals : 13,8 %
  quartz : 5,3 %   organic carbon : ≅ 0,07 %
  calcite : 1,2 % $CaSO_4$, $2H_2O$: 0,4 %
  goethite : 6,6 %   sodalite : 0,3 %
o Phyllosilicate minerals : 86,2 %
  Undifferentiated mixed layer kaolinite/smectite : 81,2 %
  with 50 % of smectite : 15 % L.C. and 35 % H.C.
  Free kaolinite : 5 %

Low Charge smectite formula (L.C.) :
$(Si_{3,71}Al_{0,29})(Al_{1,66}Fe^{3+}_{0,20}Ti_{0,08}Mg_{0,04})O_{10}(OH)_2(M^+_{0,27})$
High Charge smectite formula (H.C.) :
$(Si_{3,40}Al_{0,60})(Al_{1,62}Fe^{3+}_{0,23}Ti_{0,08}Mg_{0,08})O_{10}(OH)_2(M^+_{0,55})$

2. Definition and characterization of clay barriers (B.2)

In the case of vitrified waste disposal in granite which is the french reference scheme, the buffer material being considered is compacted clay materials. The properties of the prepared material have to be determined as a function of parameters such as dry density (ρ_d) and water content (w) of the material, pressure, temperature and salinity of water. The main properties to be measured are thermal conductivity, permeability, water diffusion coefficient, swelling pressure and swelling ability.

Recent results mainly concern hydraulic properties of engineered barriers. Oedometer tests (strain measurements as a function of total vertical load applied to the material) are used to compare the permeability of different swelling clay materials, prepared under very well defined mechanical state. The results presented on Figure 1 allow to conclude that:

- as previously observed, hydraulic conductivity decreases when density increases,
- natural sodic clay - MX 80 (USA) - leads to lowest permeability,
- sodium carbonate treatment induces a decrease in the preselected clay permeability, especially at low density.

3. Temperature effect on clay material properties

It is demonstrated that 4a clay is able to rehydrate after heating (up to 250°C) under dry conditions. New experiments started to investigate H_2O vapor effect on clay properties (COUTURE effect) (/1/,/2/), reveal that the hydraulic conductivity of such treated samples (140°C, 3.5 bars of vapor pressure during 4 days) is higher thant the reference clay, by a factor of two (Figure 1). This bad effect of H_2O vapor is particularly significant at low dry density ($\rho_d < 1.60$).

4. Hydrothermal degradation of clay materials

Water containing ion species and temperature lead to modifications of the clay structure. Autoclave tests are performed at different temperatures (150, 200 and 250°C) to determine which minerals are thermodynamically stable at long time. In the case of reference 4a clay, it appears that without any potassium ion, smectite content increases and correlatively cation exchange capacity. When potassium is present, illite formation is observed but this formation is inhibited by calcium ; the CEC is maintained constant.

It appears that smectite formation requires silica, coming from quartz present as secondary mineral. In practice, silica will come from vitrified waste leachate if no additive is mixed with the clay to prevent glass dissolution. As an example, Figure 2 shows that smectite 4a and illite 6 consume silica at the expense of vitrified waste leachate while bentonite 9 releases silica (present in the clay as soluble amorphous material).

5. T.R.U. waste disposal : study of concrete durability

Concrete durability studies are conducted since 1983 to evaluate the safety of Low Level Waste disposal. Cement pastes of Portland (OPC) and blended cement (named CLC: slag and fly ash cement) are put in contact with salty solutions (chloride, sulfate and carbonic acids). Degradation mechanisms are studied through mechanical strength and porosity evolution as well as microstructure modifications. It appears that pH is the starting parameter of degradation reactions of cement pastes.

In the case of T.R.U. waste disposal, both cement and clay based materials may be used as engineered barriers. It appears necessary to evaluate:

a) the effet of clay pore water on concrete: experimental results show that the pH of water in equilibrium with reference 4a clay is around 8.2-8.5 and governed by calcite dissolution; the cement pastes which were in contact with water saturated clay at its liquidity limit, are under investigation.

b) the cation exchange mechanisms of the clay at high pH: tests are performed to determine cationic exchange isotherms for Ca^{2+}, K^+, Na^+ and Mg^{2+} as a function of pH (6, 8, 10 and 13). It is found that the various isotherms seem to follow the simple relation (20°C, pH = 13):

$$\log[M^{z+}]_{solid} = \log K + \alpha \log [M^{z+}]_{solution}$$

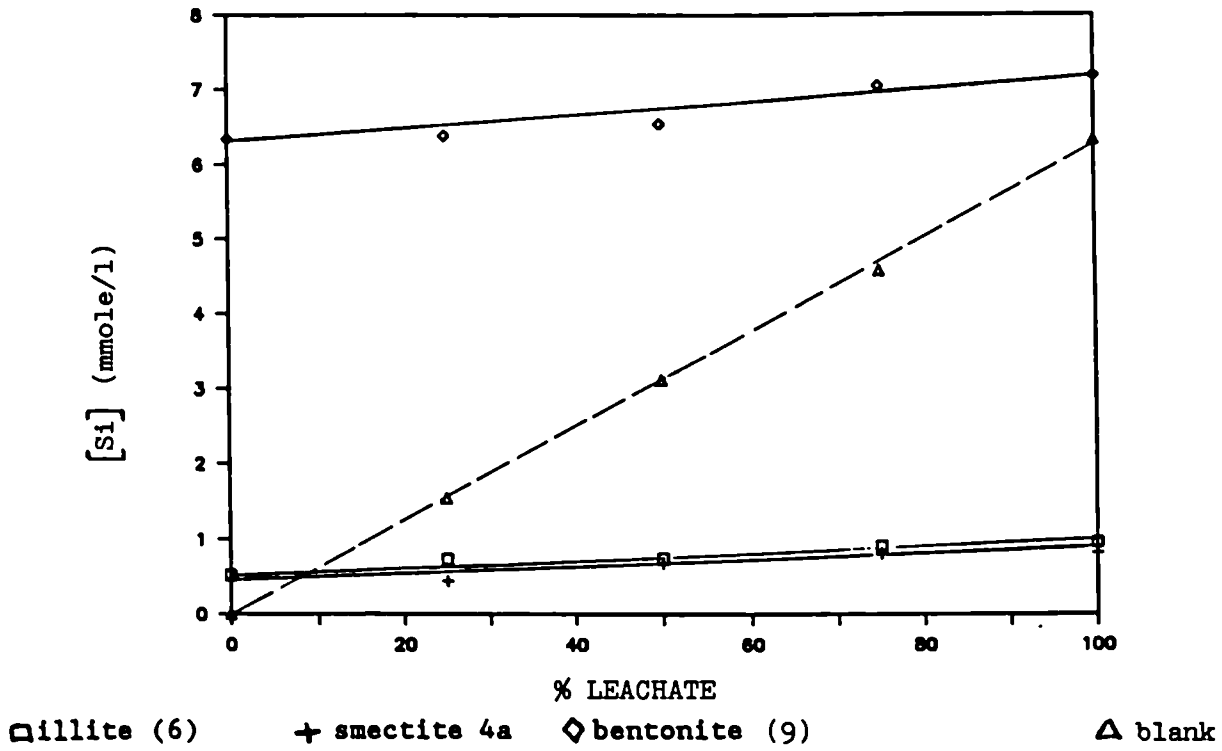
Moreover it is pointed out that the Ca/K exchange is quite well described by the K_d notion ($\alpha \simeq 1$).

REFERENCES

/1/ COUTURE R.A. "Steam rapidly reduces the swelling capacity of bentonite Nature 318, 1985 (pp. 50-52)

/2/ OSCARSON D.W., DIXON D.A., GRAY M.N., "Clay longevity studies for the canadian nuclear fuel waste management program". Workshop on artificial clay barriers for High Level radioactive waste repositories. Oct. 1988.

Figure 2: Silica concentration as a function of vitrified waste leachate dilution (13 months, 90°C)



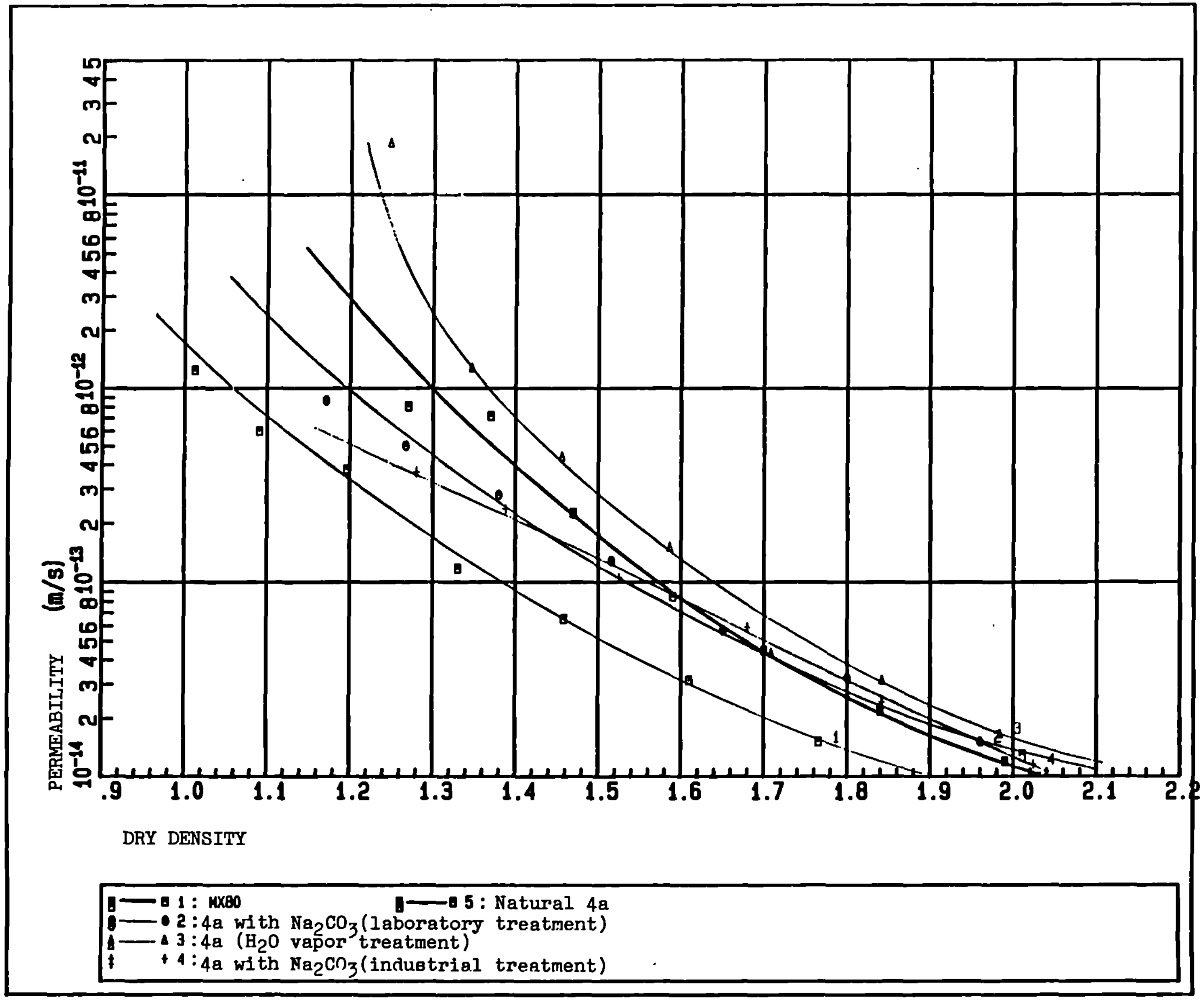


Figure 1: Clay material permeability as a function of dry density.
Oedometer test measurements

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
Period covered: January 1989 - December 1989
Project leaders: E. Smailos, R. Köster

A. OBJECTIVES AND SCOPE

In order to qualify corrosion resistant packaging materials for disposal of high-level waste forms in rock-salt formations, the corrosion behaviour of a number of materials was 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. These steels have exhibited so far only general corrosion so that their long-term corrosion behaviour can be reasonably 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 best suited steel (reference steel) for the fabrication of a long-term resistant HLW packaging and detailed description of the time and temperature behaviour of its corrosion in disposal-relevant corrosion media with and without gamma irradiation.
- Determination of the corrosion behaviour of Hastelloy C4 subjected to high gamma dose rates under the in-situ conditions prevailing in the Asse salt mine. These are investigations performed in order to complete the results available up to now.

B. WORK PROGRAMME

B.2.1 Selective laboratory-scale corrosion studies on the three pre-selected steels, namely fine-grained steel, low-carbon steel, cast steel, with a view to selecting a reference steel.

B.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.

B.2.1.2 With gamma irradiation (10^3 rad/h) at 90 °C in Q-brine.

B.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 B.2.1.1 and B.2.1.2.

B.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 $3x10^4$ rad/h).

B.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.

B.2.4.2 Post-test examination for corrosion attacks of the material specimens and welded Hastelloy C4 tube sections stored in Asse. The testing conditions are similar to those under item B.2.3.

C. PROGRESS OF WORK AND RESULTS OBTAINED

Summary

The corrosion studies performed under this contract on the promising HLW packaging materials unalloyed steels, Hastelloy C4, and Ti 99.8-Pd have been supplemented by laboratory-scale and in-situ corrosion investigations. Besides the materials indicated, also cast iron, Ni-Resists D2 and D4, and Si-cast iron were investigated in order to complete the results available up to now.

In the laboratory-scale experiments the influence was investigated which is exerted by different concentrations (25 mg/l - 200 mg/l) of the thermally released salt impurity H_2S on the corrosion of fine-grained steel and Hastelloy C4 in an $MgCl_2$-rich salt brine at 170 °C and 150 °C, respectively.

In the in-situ experiments conducted in the Asse salt mine the corrosion behaviour was studied of five Fe-base materials, Ti 99.8-Pd and Hastelloy C4 in rock salt at 32 °C rock temperature (reference experiment). Moreover, investigations were performed into the influence of selected characteristics of container manufacturing on the corrosion of cast-steel tubes, which were provided with corrosion protection layers of Ti 99.8-Pd and Hastelloy C4, respectively. The experiments were carried out in rock salt plus NaCl brine at T = 90 °C - 200 °C. Besides these experiments, specimens of different selected materials (steels, Hastelloy C4, etc.) were stored in boreholes for investigations at elevated temperature in a gamma radiation field in the framework of the HLW disposal test.

PROGRESS AND RESULTS

B.2.1, B.2.1.1, B.2.1.2, B.2.2, B.2.4.1 (laboratory-scale corrosion experiments)

Investigations into the influence of H_2S on the corrosion behaviour of fine-grained steel and Hastelloy C4

The influence of the thermally released salt impurity H_2S on the corrosion behaviour of fine-grained steel and Hastelloy C4 was examined in long-term immersion tests in a disposal relevant $MgCl_2$-rich salt brine (Q-brine) in which H_2S was added as $Na_2S \cdot 9H_2O$. Both materials were investigated at an H_2S concentration in the brine of 25 mg/l corresponding to the amount released from a 10 cm thick ring-shaped salt element around an HLW borehole. The fine-grained steel, which had been selected as the reference HLW packaging material, was additionally tested with higher H_2S amounts in the brine, i.e. 100 mg/l and 200 mg/l, in order to determine the influence of the H_2S concentration on corrosion.

The test temperatures were 170 °C for the steel (0.17 wt.% C; 0.44 wt.% Si; 1.49 wt.% Mn) and 150 °C for Hastelloy C4 (15.4 wt.% Cr; 15.2 wt.% Mo; 68.0 wt.% Ni). The maximum test duration was one year. All specimens were examined for general corrosion and local corrosion in the brines by methods of gravimetry, surface profilometry and metallography.

The corrosion results obtained for fine-grained steel and Hastelloy C4 after the maximum test duration in the brine with and without addition of H_2S have been entered in Tab. I. The most essential results can be summarised as follows:

- H_2S in the Q-brine at concentrations between 25 mg/l and 200 mg/l did not significantly influence the corrosion behaviour of fine-grained steel at 170 °C.

- In the H_2S bearing brines - as in pure Q-brine - the steel was resistant to pitting corrosion, and the corrosion rates of 240-300 µm/a roughly corresponded to the value of 235 µm/a obtained in H_2S free brine.
- Hastelloy C4 corroded at 150 °C in the H_2S free Q-brine at a very low rate of < 1 µm/a and was resistant to pitting corrosion. Also in the H_2S bearing brine (25 mg H_2S/l) the general corrosion rate (4 µm/a) was low but severe pitting corrosion (2.3 mm/a) occurred.

B.2.3, B.2.4.2 In-situ corrosion experiments

(a) Investigation of material specimens in rock salt at rock temperature

In a reference experiment five Fe-base alloys (fine-grained steel, Ni-Resists D2 and D4, cast iron and Si-cast iron) as well as Ti 99.8-Pd and Hastelloy C4 were investigated for three years in loose rock salt (96 wt.% NaCl, < 0.1 wt.% H_2O) at rock temperature (32 °C). For this purpose, unwelded and Tungsten Inert Gas (TIG) welded specimens of these materials were stored in small boreholes (D = 50 mm, L = 200 mm) in the Asse salt mine and covered with crushed rock salt. All material specimens were examined for general and local corrosion attacks.

For the materials Ti 99.8-Pd, Hastelloy C4, Ni-Resist D4 and Si-cast iron (15 wt.% Si) no corrosion attack was detected. Also for the other materials - fine-grained steel, cast iron and Ni-Resist D2 - the corrosion rates were negligible (< 1 µm/a). The corrosion attack was uniform and TIG welding did not influence the corrosion behaviour of the materials.

(b) Investigations of cast-steel tubes with corrosion protection made of Ti 99.8-Pd and Hastelloy C4 in rock salt plus NaCl brine at high temperature

An important aspect of the in-situ corrosion studies is the investigation of promising HLW container materials (unalloyed steels, Ti 99.8-Pd, Hastelloy C4) under the combined influence of simulated disposal conditions and selected characteristics of container manufacturing. Corrosion results on an electron beam welded cast-steel tube in rock salt plus NaCl brine have been reported in a previous work /1/.

During the period of reporting two cast-steel tubes provided with a corrosion protection of Ti 99.8-Pd and Hastelloy C4, respectively - applied by electron beam welding and explosion plating - have been investigated. The tubes were stored for 18 months in 2 m deep heated boreholes in rock salt and the 1 mm annular gap between the tube and the borehole wall was filled with 100 ml saturated NaCl brine. The vertical temperature profile in the borehole was in the range of 90 °C to 200 °C; the maximum temperature occurred in the center of the heated zone and the minimum temperature in the upper parts of the tube.

After the testing period the tubes were retrieved by overcoring. Examinations of the tubes with a stereo-microscope and by surface profilometry did not show any corrosion attacks of the plating materials (Ti 99.8-Pd, Hastelloy C4) after 18 months under the test conditions. On the basis of the results available so far it can be stated that the selected characteristics of container manufacturing (hot-rolling, electron beam welding, explosion plating, etc.) did not influence the corrosion behaviour of Ti 99.8-Pd and Hastelloy C4. For longer periods of testing the tubes were stored again in the boreholes.

The results available from laboratory-scale and in-situ investigations under this contract have confirmed that unalloyed steels are promising HLW packaging materials. Nevertheless, further investigations will be necessary to determine the corrosion allowance needed for long-term resistant steel containers. They will focus above all on the clarification of the role which high temperatures ($\leq$ 200 °C) play during corrosion under gamma irradiation and on the performance of statistical in-situ experiments.

References

/1/ SCHWARZKOPF, W., SMAILOS, E., KÖSTER, R., "In-situ Corrosion Studies on Cast Steel for a High-level Waste Packaging in a Rock Salt Repository," Mat. Res. Soc. Symp. Proc. Vol. 127, pp. 411-418. 1989 Materials Research Society.

List of publications in 1989

SMAILOS, E., SCHWARZKOPF, W., KÖSTER, R., FIEHN, B., "Gamma Irradiation and In-situ Corrosion Studies on Unalloyed Steels for a High-level Waste Packaging in a Rock Salt Repository," KfK Report 4529 (1989).

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Table I Corrosion results obtained for fine-grained steel and Hastelloy C4 after one year immersion in Q-brine with and without additions of H_2S

	Corrosion medium	Average general corrosion rate (µm/a)	Maximum rate of pitting corrosion (µm/a)
Fine-grained steel, 170 °C	Q-brine	235 ± 1	-
	Q-brine + 25 mg H_2S/l	240 ± 9	-
	Q-brine + 100 mg H_2S/l	300 ± 2	-
	Q-brine + 200 mg H_2S/l	256 ± 2	-
Hastelloy C4, 150 °C	Q-brine	0.67 ± 0.31	-
	Q-brine + 25 mg H_2S/l	3.87 ± 0.57	2300 1)

- = no pitting

1) on the cutting edges and on the specimen surfaces

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 : from May 1986 to July 1990
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 aggressivity 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 estimate long term corrosion damage. This approach will enable us 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 ratiation field on corrosion rate and mechanism.
5. Electrochemical laboratory experiments in a range of conditions resulting from previous actions.
6. Estimation of long term corrosion damage accumulation.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The main effort during the one-year period covered in this report is situated in the program segments of in-situ experiments B1 and in the segments of laboratory experiments B4, B5 and B6.

One in-situ corrosion test tube (B1) in direct contact with solid clay at 90C has been overcored after an exposure period of 2.3 years. Specimens of Hastelloy C4, Ti/0.2Pd and carbon steel and the clay contacting these specimens have been analyzed chemically and metallurgically. The overall corrosion kinetics were determined and the corrosion mechanisms responsible for material degradation identified.

C-steel, Hastelloy C4 and Ti/0.2Pd specimens have been irradiated (B4) for exposure periods up to 93 days under a gamma radiation field of 10^3 gray/hour. The test medium was solid clay at 90C.

Electrochemical - corrosion potential - measurements (B5) were drafted in the laboratory and subsequently installed in-situ in the underground gallery with carbon steel working electrodes. These measurements resulted in an understanding of the corrosion phenomena observed under B1.

A cooperation with UKAEA Harwell on the subject of mathemathical modelling with the corrosion results, obtained at the SCK (B6) is in progress.

Progress and results

In the UNDERGROUND LABORATORY at SCK/CEN a corrosion test tube in direct contact with clay at 90C was overcored and recovered after 2.3 years exposure at the target temperature regime. The metallic corrosion specimens mounted on the test tube and the solid clay contacting these specimens have been analyzed. The clay slabs were analyzed by ICP/AES for the determination of concentration profiles of alloy elements not normally present in the clay or present in concentrations above clay "background", this as a function of the distance from the original metal/clay interface.
The metal samples were analyzed as follows :
To obtain information on the overall corrosion kinetics, weight change measurements were performed; post-corrosion examination by optical microscopy, metallography, scanning electron microscopy, Auger analysis, X-ray diffraction and electron microprobe were used to identify the effects of localized corrosion and to gain insight in the corrosion mechanisms responsible for the material degradation.
The corrosion results, obtained for carbon steel, Hastelloy C4 and Ti/0.2Pd, gathered from these different analytical techniques performed, are :

Hastelloy C4 has a negligible corrosion rate. No particular interaction between the alloy and the clay environment is perceptible. The metal surface is covered with a 60 Å thick protective reaction layer consisting of chromium and molybdenum oxides.

Ti/0.2Pd also has an extremely low corrosion rate. The reaction layer is relatively thicker (0.1 µm) and somewhat more complex : an important amount of Si from the clay environment is present in the oxide scale, while the primary composition of the scale is most probably based on a mixture of oxides (TiO_2, Ti_2O_3).

Carbon steel has an overall corrosion rate of (7.7 ± 0.8) µm/a. The damage proceeds as uneven general corrosion giving rise to a morphology of dense but undeep pitting.
Two localized corrosion mechanisms are active : deep pitting and lateral

pitting; the maximal depth of this damage is 135 µm and 240 µm respectively for the exposure time considered. The oxide layer on carbon steel (no sulphidation detected) is porous and thus non-protective; chemically it consists of Fe_2O_3, which could be detected in combination with its precursors $Fe_2O_3.H_2O$ and FeOOH. This oxide layer interacts with the contacting clay : the mechanism might be "migration" or the formation of a "modified clay" based on an ion exchange mechanism.

The formation of Fe_2O_3 points to relatively oxic exposure conditions. On the other hand oxygen, introduced into the clay environment when drilling the hole to install the experimental set-up, is known to react quickly with the sulphides (pyrite) present resulting in the formation of sulphates. Therefore, the question arises whether the observed corrosion damage had not accumulated exclusively during the period (4 months) the clay - with entrapped oxygen - needed to establish firm contact with the sample surfaces after corrosion rig emplacement. After establishment of steel/clay contact, corrosion rates may have dropped to extremely low values.

Additional experimental evidence for this hypothesis of a limited active corrosion period are : a) the relatively low pitting rates observed and b) the extremely low general corrosion rate measured in situ on cast iron ER-probes [ASR 1988].

An answer to this question may become available when the second 90C direct contact with clay test-tube will be overcored after an exposure time of 50,000 hours.

In the OVERGROUND LABORATORY electrochemical equipment to measure corrosion potentials of carbon steel specimens as a function of time has been constructed and subsequently installed in the underground laboratory. These in-situ measurements (Pourbaix-diagrams) show an evolution from a E_{corr}, pH-domain where hematite formation is thermodynamically possible to a domain where magnetite formation is possible. In this latter domain the corrosion potential stabilizes. On the other hand the measured values are such that H_2-evolution is not yet possible. In other words during the E_{corr}-traject followed, hematite can be formed, while the magnetite formation is not physically triggered yet. This observation supports the analytical results described for the overcored 90C corrosion test tube.

To evaluate the impact of gamma radiation on corrosion, the RITA facility of the BR2 reactor has been loaded with specimens under different test conditions in solid clay at 90C. A radiation field of 10^3 gray/hour has been applied for an exposure time of 93 days.

On Ti/0.2Pd and Hastelloy C4 no influence on general or localized corrosion can be detected under none of the experimental conditions considered. For carbon steel the overall corrosion rate is essentially not further affected by the irradiation modified chemistry as compared to the results obtained after shorter exposure periods under similar test conditions. The initially high corrosion rate tends to level off with time.

A cooperation with UKAEA Harwell has been started on mathematical corrosion modelling. For this purpose additional information on media and materials is generated to serve as base line data for the existing models at Harwell.

D. LIST OF PUBLICATIONS

/1/ Debruyn W., Dresselaers J., Vermeiren Ph., NIRAS/ONDRAF, R&D programme on radioactive waste disposal, semi-annual report, 1st semester 1989.

/2/ Debruyn W., Dresselaers J., Vermeiren Ph., NIRAS/ONDRAF, R&D programme on radioactive waste disposal, semi-annual report, 2nd semester 1989.

/3/ Debruyn W., Tas, H., Dresselaers J., In-situ testing of candidate container materials in deep argillaceous disposal environments, 9th European congress on corrosion, Utrecht NL, p. EG018.

/4/ Tas H., Debruyn W., Dresselaers J., Vermeiren Ph., In-situ damage rate evaluation of overpack materials in deep argillaceous HLW disposal environments, IAEA-meeting on improvements of structural materials resistance to chemical degradation and irradiation in the back end of the nuclear fuel cycle, Vienna.

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 1989 (extended to July 1990).
Period covered:	January 1989 - December 1989
Project Leader:	K. Brodersen.

A. OBJECTIVE AND SCOPE

Improved understanding of interaction phenomena influencing the near-field 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 the waste through barriers of concrete or clay as influenced by internal or external conditions. The composition of water in equilibrium with various types of waste and concrete is influencing concrete corrosion and the possibility of crack-healing in concrete barriers. The influence of pore type distribution on diffusive transport through concrete has been investigated. SANS-measurements are used to follow the structure of e.g. degrading concrete.

Hygroscopic properties of cemented or bituminized waste containing soluble salts may lead to releases if such materials are disposed of in the unsaturated zone. Relationships between relative humidity in the air and water uptake in the materials are investigated.

Some bituminized waste products tend to swell when exposed to water and may thereby damage the outer barriers. Pressure build-up due to this mechanism is followed. Metabolic products and other effects of growth of micro-organisms on bitumen may influence solubility-controlled leaching and some aspects are investigated. Measurements of flow properties were used to demonstrate ageing effects in the materials.

B. WORK PROGRAM

2.1. Leaching and volume stability.
2.2. Leaching in integral systems.
2.3. Equilibrium extraction from sludges.
2.4. Swelling pressure.
2.5. Self-healing of cracks in concrete.
2.6. Water transport through concrete.
2.7. Water transport through bitumen.
2.8. Water transport through clay.
2.9. Structure of degrading cement paste.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

During the 6. and 7. half-year of the contract more work was done on most of the topics. Experimental work on 2.1., 2.2., 2.5., 2.6. and 2.8. is by now practically finished although interesting phenomena motivating further studies have been identified. The studies of equilibrium extraction from precipitation sludges: 2.3. has not been continued since 1988. Measurements are still in progress on systems related to 2.4. and 2.7. but the main emphasis in the remaining half year of the contract will be on 2.9: the SANS studies of cement paste, which were delayed due to rebuilding of the facility at Risø. Some modelling work connected with 2.2. is also beeing made.

Progress and Results

2.2. Leaching in integral systems

The release behaviour of ^{134}Cs and ^{85}Sr from samples of cemented sodium nitrate (simulated RMA8) through barriers of concrete, kaolin or chalk have been followed for 16 systems representing various conditions. The barrier were of better quality (lower water contents) than the ones employed in similar experiments in 1987, but still inferior to materials which may be used in pratice in waste repositories. The concrete (w/c=0.7) is found to be a better barrier material than kaolin or chalk. An attempt to model the leach data using the one-dimensional multi-barrier model: DIF-MIG is in progress.

2.1. Leaching, water uptake and volume stability of cemented waste

Two samples of cemented ion-exchange resin containing silica fume as additive (cast in Jan. 1987) are still resisting wet/dry cycling. All samples based on Portland cement without additive were broken long ago by this treatment.

Supplementary studies have been made of water uptake from high-humidity air compared with ordinary immersion in water of cemented waste containing soluble salts or ion-exchange resin, i.e. materials aking to RMA1, 3, 8 and 10.

As expected from previous experiments the samples containing $NaNO_3$ or Na_2SO_4 were accumulating solution on the surfaces when stored in a 95 % RH atmosphere. The resulting Na-leaching from the products were about 50 % or 30 % of the leaching by direct immersion. The $NaNO_3$ product swelled about 0.3 vol% under both conditions while the Na_2SO_4-containing product swelled ~0.3 % in water but ~1 % in humid air and was cracked extensively hereby. The other products gave less pronounced results.

Hygroscopic water uptake is thought to be an important safety-related mechanism when waste materials containing soluble salts are disposed of in repositories constructed in the unsaturated zone.

2.6. and 2.8. Water transport through concrete and clay.

Contact to a humid air atmosphere do not have to be direct, but can e.g. happen through porous concrete. The rate of water-vapour transport through slabs of 5 different types of concrete has been measured. The permeability was found to depend primarily on the water/cement ratio.

A preliminar experiment with migration of tritated water through bentonite as such and in contact with concrete have been made but further efforts are needed to obtain reliable results.

2.5. Self-healing of cracks in concrete

An experimental method for demonstration of crack-healing in damaged concrete were developed during 1988. Closing of narrow cracks by deposits of calcium carbonate may take place, when a slow flow of e.g. tap water containing HCO_3^-ions is passed through the crack. However, prolonged experiments with cracks of greater width (up to 0.23 mm) indicate that the closure is incomplete. Parameters such as crack width and length, flow rate, carbonate concentrations and diffusion properties of the concrete are thought to influence the tendency to crack closure. A simple model describing these relationships has been set up but theoretical considerations and a comparison of calculation results with the experimental results indicates that a considerable part of the carbonate must be deposited inside the pores of the concrete without contributing to the closure. Ideas for a more advanced model is beeing developed but is outside the scope of the present contract.

Crack-healing by silicates is also a possibility, but only tentative results are available. A series of experiments to demonstrate material transport between thin plates of two different types of concrete stored in a small amount of water have been finalized. They support to some degree this possibility of crack-healing also in systems without any carbonate present.

2.9. Structure of degrading cement paste (SANS).

Small angle neutron scattering is one method which may be used to characterize the micro-pore structure in hardened cement products. The facility at Risø has been rebuild and can now be operated much more easily and in a Q-range covering a considerably increased range of pore sizes. Some test results with hardening cement paste and with pozzolanic reactions between $Ca(OH)_2$ and SiO_2 have been obtained.

2.4. Swelling pressure in bituminized materials

A simple method has been developed for measurement of swelling pressure due to water uptake through concrete into bituminized waste material containing soluble salts. A test system containing a 60% $NaNO_3$+40% Mexphalte product reached an overpressure of about 2.1 bar in 190 days. The pressure was still rising steadily when the experiment was stopped.

2.7. Water transport through bitumen membranes

A set of experiments with diffusion of tritiated water through 5 and 10 mm thick bitumen membranes cast from pure Mexphalte are in progress. The electrical resistance over the membrane is also followed and has in previous experiments with thinner membranes given interesting information about ion migration through the membrane. The conductivity is still _zero with these thicker membranes even after 5 month.

COLLOIDS RELATED TO LOW AND INTERMEDIATE LEVEL WASTE

Contractor : UKAEA, Harwell, UK
Contract No. : FI.1W 0184 UK(H) Part 1
Duration of contract : from January 1988 to March 1990
Period covered : January 1989 - December 1989
Project Leader : J D F Ramsay

A. OBJECTIVES AND SCOPE

There is a need to improve our knowledge on the possible role of colloids in the transport of radionuclides in groundwater. An understanding of the mechanisms of release of radionuclides immobilised in cement and their subsequent migration processes is necessary for predicting the long-term behaviour of low and intermediate level waste forms. This is an area where the near-field effects of colloids are at present inadequately understood.

Our particular objectives under the present contract are:

i) To characterise and investigate the mechanisms by which colloids may form in cement leachates, giving attention to the composition, age and structure of the cement.
ii) 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.
iii) To assess the radionuclide incorporation of such colloids.
iv) To investigate the possible generation of colloids by the interaction of cement leachate with near-field materials.

The work is seen as providing basic information on cement leaching mechanisms which is relevant to the definition of the source term. Data for the transport modelling of colloids in the near-field environment especially related to their migration, sorption and retention behaviour will also be established.

B. WORK PROGRAMME

2.1 Studies of colloids in cement leachates.
2.2 Characteristics of colloids in repository environments.
2.3 Characterisation of near-field materials in EC repository simulation tests.
2.4 Cement/steel interactions in the near field.
2.5 Colloid sorption behaviour.
2.6 Colloid migration and modelling.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The work has concentrated on two main areas. In the first of these the effects of the near-field cement chemistry on materials typical of those likely to be present in a repository environment have been investigated. Particular emphasis has been given to processes of colloid generation, surface reaction and radionuclide retention in the presence of cement leachates which are characterised by a high pH and Ca^{2+} concentration. Materials typical of host rocks and backfill (sandstone, granite and clay) and steels which may be present as containment or for concrete reinforcement within the repository have been studied.

The second area of work has been concerned with the radionuclide sorption behaviour of colloidal particulates. To gain a more detailed insight into mechanisms of radionuclide sorption initial studies have been made with model single-component colloid systems (eg. montmorillonite, silica, iron oxide) using a cocktail of tracer elements (Cs, Co, Ni, Ce, Eu, Th, U). More extensive studies have also been carried out using silica sols and a single tracer to investigate the effects of such parameters as particle size, specific surface area, pH and Ca^{2+} concentration. The sorption studies have also been extended to include heterogeneous natural colloid systems derived from granite and clay. Such materials are typical of those which may be present in the near field and disturbed zone of a repository site. Our results confirm that such natural systems may be an important source of colloids which will have potential for the sorption and possible transport of radionuclides. Such investigations are necessary in developing a reliable model for predicting the extent of any radionuclide migration involving colloid transport, as well as understanding sorption mechanisms which may contribute to the retardation or retention of some nuclides by immobile phases both in the near and far field.

PROGRESS AND RESULTS

2.2,2.4 Characteristics of colloids in repository environments and cement/steel interactions in the near field

Cement pellets made from pure OPC have been leached for ~500 d at 60°C in the presence of specimens of sandstone (St Bees) and granite (Loch Doon). The leachates were analysed extensively at the end of this period using ICP-ES. The results indicate that little material which may have been leached from the rock specimens as a result of the prolonged contact with the highly alkaline cement leachates remains in a soluble form, apart from enhanced levels of Al and Na when the granite was present. The chief process observed was one of particulate deposition on both the leaching vessel and rock specimen. Such a process which may arise from nucleation of particles in solution followed by deposition is likely to be an important retention mechanism for any radionuclides in solution.

Small samples of sandstone, granite and steel were also exposed to cement leachates at ambient (~25°C) and elevated (60°C) temperature for 12-15 months to provide specimens suitable for subsequent examination by SEM and EDAX. At the lower temperature a scattering of deposited, widely-spaced discrete Ca-rich particles or particle aggregates (typically up to ~10 μm in size) was observed. At the higher temperature the original surface of the rock or steel became completely obscured by the build-up of finely-divided deposits, which were again generally rich in Ca. In the case of the steel (at 60°C) two types of particle morphology could be distinguished, the first consisting of clusters of elongated particles, and the second comprising an apparently underlying coating of finer, granular deposits containing significant levels of Al and Si in addition to the more abundant Ca.

2.5 Colloid Sorption Behaviour

Preliminary investigations were undertaken with model, well-characterised single-component colloid systems (montmorillonite, kaolinite, mica, silica, iron oxide) in order to establish techniques and procedures of measurement. Correlations in the sorption of a range of tracer elements (Co, Ni, Cs, Ce, Eu, Th and U) simulating radionuclides in solution were explored. These elements were added to the colloid suspensions as a spike mixture to investigate competitive sorption effects. The effect of the colloid concentration was also studied. After equilibration the spiked suspensions were centrifuged to remove all particles > 10 nm and samples of the supernates analysed by ICP-MS and ICP-ES. Ranking orders for the sorption affinity of the different tracers were obtained, eg. the montmorillonite at 500 μm ml^{-1} Th>Ce,Eu>U$\gtrsim$Co,Ni>Cs. This affinity sequence reflects the decreasing valence state of the ionic species involved and is in accord with a process of ion exchange. The uptake of the more strongly sorbing elements (Ce,Eu,Th,U) by the various colloid systems studied gave a tentative ranking order for them as follows: montmorillonite > (iron oxide), silica > kaolinite ~ mica.

In a separate study the effects of pH, particle size/surface area and colloid concentration have been explored using a range of model silica sols with well-graded properties (7-80 nm mean diameter, 410-50 m^2 g^{-1} BET surface area and a single spike element (chiefly U as UO_2^{2+}). At pH 4 there was no obvious trend in the sorption of U as a function of particle size. However, at a fixed diameter (~80 nm) a clear increase in the sorption of U was observed as the pH was increased over the range 3-7, with a sharp increase in removal in the presence of silica occurring between pH 4 and 5 compared with silica-free controls treated in the same way.

The sorption studies have also been extended to three natural, multi-component colloid systems derived from a granite (Loch Doon), sandstone (St. Bees) and clay (Mol Boom) respectively. Our results confirm the potential importance of colloid formation with such mineral systems and illustrate their capacity for sorption and retention of radionuclides. Another aspect which has been examined is the effect of Ca^{2+} concentration on both the colloid stability and sorption behaviour.

The granite and sandstone were finely crushed to produce powders with a wide range of particle sizes. These were then dispersed in water. The wet clay was subjected to ultrasonic treatment and dialysis to produce a stable dispersion. Dispersions were also prepared in 10^{-3} mol dm^{-3} $Ca(NO_3)_2$. All the dispersions, together with colloid-free controls were spiked with the same mixture of tracer elements as used earlier with the model colloids, but at a lower level (one-tenth). The spiked preparations were separated into fractions of reducing particle size (hydrodynamic diameter) range using a combination of gravitational and centrifugal sedimentation. These fractions were then analysed as previously. The results obtained with the clay dispersions are illustrated in Figs. 1 and 2. Fig. 1a shows the concentrations of the elements which are major components of the clay and which remain dispersed in the liquid phase after particulates of progressively smaller size are removed by sedimentation. Fig. 1b highlights the marked destabilising effect of Ca^{2+} ions when added to the dispersion (this causes particle aggregation as previously established). This destabilisation effect decreased in the order : clay > granite > sandstone. Fig. 2 illustrates the parallel removal of the sorbed spike elements from the liquid phase as the particle size (and clay concentration) is decreased. Although detailed aspects of sorption mechanisms have been shown to correlate with the nature of the elemental ionic species and the nature of the mineral and colloid size we can highlight qualitatively some of the main findings. Thus with the clay the sorption of all the elements is markedly greater than observed with the colloids derived from sandstone and granite. However in general we observe a similar affinity sequence: Ce~Th>Eu (high); Co,Ni (intermediate); U,Cs (low or insignificant). Thus for high sorption typically $<10^{-3}$ of the initial spike remains in true solution whereas for intermediate sorption this may rise to almost 10^{-1}.

2.6 Colloid Migration

Initial measurements of the permeation and retention of silica colloids in packed columns of granite powder and fine grade high-purity sand are being made. A number of nominal particle size fractions of granite powder have been used to obtain columns of different permeability and effective pore size. Typically the porosity of the resulting wet beds when consolidated lies in the range 49-55%. Permeability cells are also being set up to allow similar measurements on representative specimens of porous rock (eg. St. Bees sandstone).

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3. RAMSAY, J.D.F., RUSSELL, P.J. and AVERY, R.G., Colloids related to low level and intermediate level waste - Progress report for the period 1st January to 31st December 1987, AERE R-12957 (1988).
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5. RAMSAY, J.D.F. and RUSSELL, P.J., Colloids related to low level and intermediate level waste - Progress report for the period 1st January to 30th June 1989, AERE R-13595 (1989).
6. RAMSAY, J.D.F., AVERY, R.G. and RUSSELL, P.J., Physical characteristics and sorption behaviour of colloids generated from cementitious systems, Radiochimica Acta 44/45(1), 119 (1988).
7. RAMSAY, J.D.F., The role of colloids in the migration of radionuclides from nuclear waste, Radiochimica Acta 44/45(1), 165 (1988).

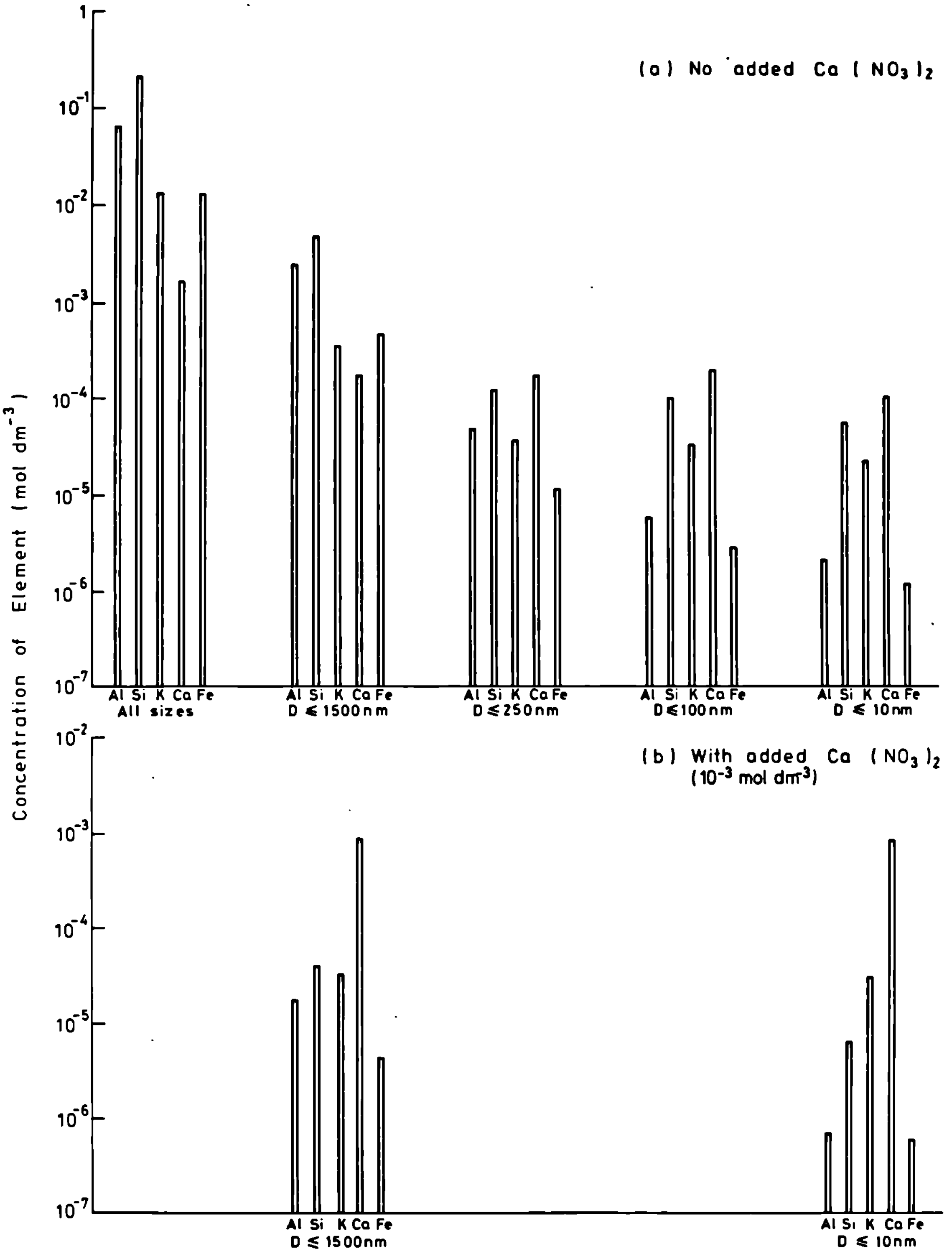

FIG 1 MOLBOOM CLAY DISPERSION : CONCENTRATION OF SELECTED ELEMENTS AS A FUNCTION OF MAXIMUM PARTICLE DIAMETER , D.

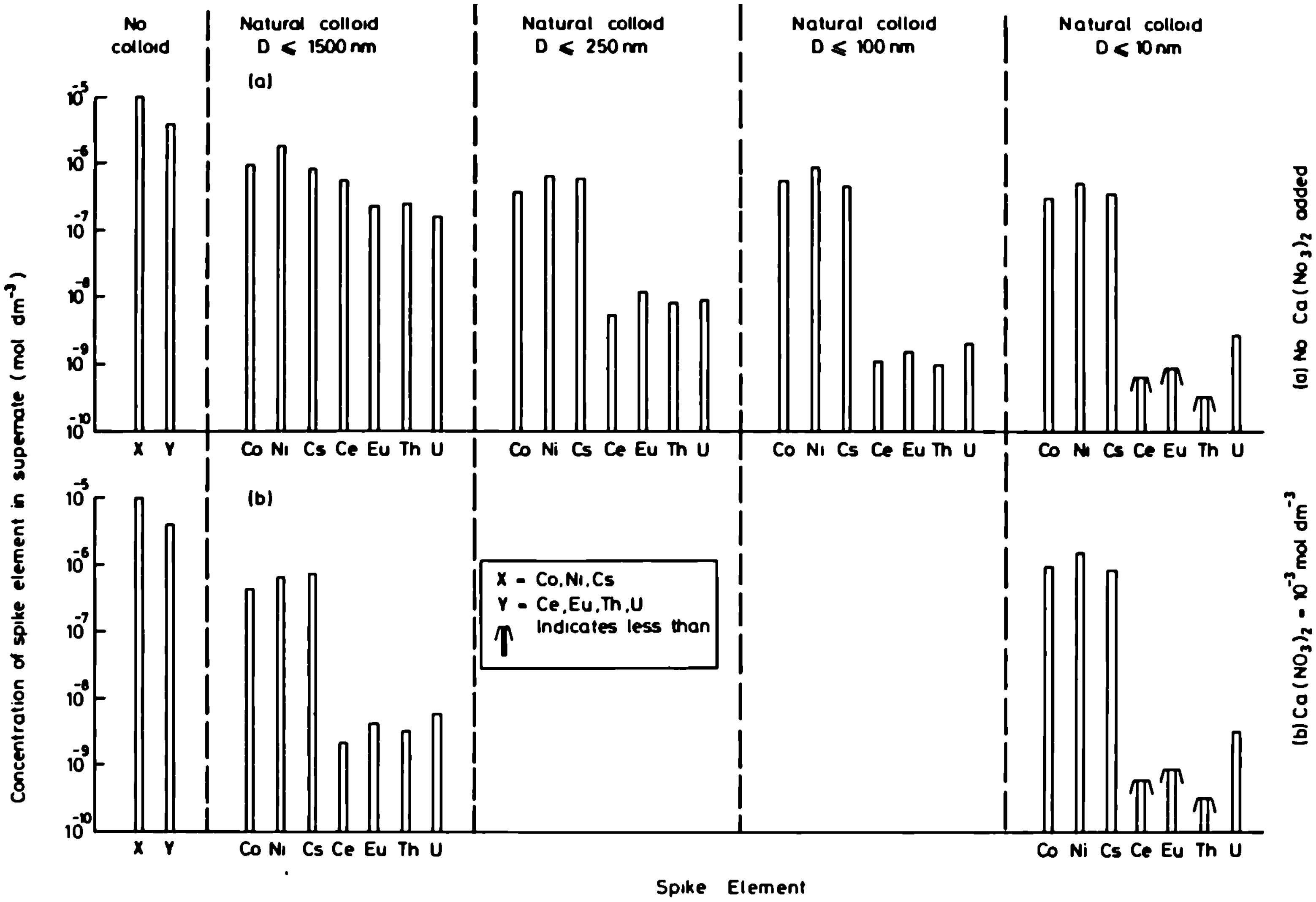

FIG 2 SPIKED *MOL BOOM CLAY* · CONCENTRATIONS OF TRACE ELEMENTS REMAINING IN SUSPENSION AFTER SEDIMENTATION OF CLAY PARTICLES OF PROGRESSIVELY SMALLER SIZE (D).

Note: in (b) $Ca(NO_3)_2$, 10^{-3} mol dm^{-3}, has been added, facilitating particle aggregation.

Near- Field Modelling in cement Environments

Contractor:	Harwell Laboratory, U.K.
Contract No;	FI.1W/0184/00
Working Period:	January 1989 - December 1989
Project Leader:	Dr P.W.Tasker

A. Objectives and Scope

The primary aim of this project is to develop research models of various physical and chemical processes within the near-field of a repository. These research models use experimental data to study areas of repository behaviour in detail to examine assumptions and approximations implicit in assessment models. The assessment models are necessarily relatively simple.

The near field has a complex chemistry which determines the solubility and sorption of nuclides. The chemical environment changes in both space and time throughout the near-field region due to the ingress of groundwater and the degradation of the engineered barriers. The coupling between the chemistry and transport processes is very important in determining the evolution of the near-field. This programme is largely concerned with modelling coupled transport and chemical processes within a cement environment.

B. Work Programme

B.1 Application of CHEQMATE/1/ to the space and time degradation of the cementitious backfill and comparison with experimental results for a number of cement compositions.

B.2 Application of CHEQMATE to the evolution of groundwater chemistry in host rock using experimental data obtained by the British Geological Survey at Bradwell,U.K..

B.3 Participation in the code comparison exercise CHEMVAL.

C. Progress of work and obtained results

State of Advancement.

The CHEQMATE code has been applied to two main topics of importance to the evolution of near-field chemistry:

i) an investigation of the degradation of cement of several compositions in contact with pure water and groundwater; and

ii) the evolution of groundwater chemistry in a host rock. There has also been participation in CHEMVAL with both PHREEQE/2/ and CHEQMATE for the coupled code verification and validation.

Progress and Results

1. Investigation of the Degradation of Cement in a Repository.(B.1)

The current U.K. concept for a low- or intermediate-level nuclear waste repository includes a largely cementitious backfill. The cement provides a high pH environment in which the solubilities of many nuclides is reduced and corrosion rates are low. Cement will degrade due to the leaching of the solid components and attack from aqueous species in the groundwater. A coupled chemistry model of cement degradation has been developed/3/. This model has been used to investigate the effect of interactions with groundwater on the evolution of pH in the repository. Several experimental studies on the evolution of pH for different cement types have been carried out at Harwell/4/. These use a technique called accelerated leaching and aim to simulate the long term effects on the pH on contact with both demineralised water and groundwater. The model predictions are generally in qualitative agreement with results from accelerated leaching experiments. Both the modelling and experiment show that interactions with groundwater species produce a faster fall in pH than leaching by demineralised water. The cement composition affects the evolution of pH and PFA/OPC would appear to be unsuitable for maintaining a high pH in the near field of a repository. The model is sufficiently flexible to consider a range of cement compositions and a number of different groundwaters. It can then be used to consider a number of different repository scenarios and make predictions on the long term spatial evolution of pH.

2. Evolution of Groundwater chemistry in host rock (B.2)

The groundwater chemistry of the rocks surrounding a repository will be perturbed by the engineered barriers in the near-field. In the previous study we investigated the scale of the perturbation to a clay groundwater due to the ingress of alkaline porewater from a cement backfill/5/. The chemical model of the buffering behaviour of the clay has since been refined and this improved description has been incorporated into a model of groundwater evolution based on experimental data provided obtained by the British Geological Survey from the London clay beds at Bradwell/6/. The model is based on a vertical section through the London clay which is in contact with seawater at its upper surface and has a chalk aquifer underlying it. Aqueous species are assumed to diffuse through the clay under the imposed concentration gradients. The boundary aquifers are maintained at constant composition except for a period of 3000 years at a time around 9000 years before the present where knowledge of the site indicates an increase in the salinity of the overlying seawater and this has been included in the model. The predicted chloride profile as a function of depth is in good agreement with that measured in the field.

3. Participation in CHEMVAL (B.3)

CHEMVAL is a code comparison exercise with the object of verifying and validating the chemical codes used in radioactive waste modelling. Final reporting of Stage 2 of the project, which aims to validate the static speciation codes against both field and laboratory data, is now nearing completion. The results from this stage showed some good agreement with data from laboratory experiments in many cases, but comparisons with field measurements were less satisfactory. A number of reasons have been suggested including insufficient problem definition and formation of colloidal species, which none of the codes currently include.

Encouraging results have been obtained from the third stage of CHEMVAL which aims to verify the coupled chemical-equilibria and transport codes. The verification exercise was divided into two stages; firstly the transport and chemistry parts of the codes were tested separately and then fully-coupled test cases were attempted. As the codes use different grids, time-stepping methods and solvers, exact numerical agreement between the codes cannot be expected in this stage of the project but the results obtained showed very close agreement in their predictions.

List of Publications

1.A.Haworth, S.M.Sharland and C.J.Tweed
Proc. 13th Int. Symposium on The Scientific Basis for Nuclear Waste Management, MRS, Boston 27th-30th November 1989.

References

/1/ A. Haworth, S.M. Sharland, P.W. Tasker and C.J. Tweed.
Nirex Safety Studies Report NSS.R113

/2/ D.L.Parkhurst, D.C. Thorstenson and L.N. Plummer
U.S. Geological Survey, Water Resources Investigations, 80-96

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Proc. 13th Int. Symposium on The Scientific Basis for Nuclear Waste Management, MRS, Boston 27th-30th November 1989.

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Harwell Laboratory Report R12961

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Nirex Safety Studies Report NSS.R111

/6/ A.H. Bath et al
International Symposium on Hydrogeology and Safety of Radioactive and Industrial Hazardous Waste Disposal, Orleans, France(1988)

MIGRATION AND RETENTION OF RADIONUCLIDES IN THE NEAR-FIELD, PART C, SORPTION MECHANISMS IN THE NEAR-FIELD

Contractor:	Harwell Laboratory
Contract Number:	FI.1W.0184/UK
Duration of Contract:	April 1988 - March 1990
Period Covered:	January 1989 - December 1989
Project Leader:	Mr F T Ewart

A. OBJECTIVES AND SCOPE

The sorption of radionuclides onto solid phases in a radioactive waste repository can be a very important mechanism for the reduction of radionuclide source terms. One of the advantages of using cementitious materials as components of the near-field, is that they provide a large surface area on which sorption may occur. Many empirical studies are underway to determine the distribution ratios for radionuclides between solid and solution phases. However, as the safety performance of the repository has to be assessed over very long timescales (10^6 years), such empirical data may be of limited usefulness unless the mechanisms of the sorption processes are understood.

The objective of this research programme is to understand the processes and reactions which may take place when actinides are sorbed onto a cement surface.

B. WORK PROGRAMME

(i) To acquire sorption data for actinides on to some single mineral phases which are present in mature cement.

(ii) To study the crystallography of calcium silicate hydrate and its capacity to incorporate actinide ions within the lattice.

(iii) To study the surfaces on which sorption has occurred in order to obtain information on the chemical state of the sorbed actinide.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The programme of work is approaching completion. All three tasks will have been completed substantially in accordance with the original proposal. A significant advance this year has been the application of EXAFS to the study of the chemical state of the sorbed species. These initial scoping studies show that analysis by this method should be possible.

The preparation of the cement phases has been completed during this year. The question, which had arisen during this year, of the need to choose between hydrogarnet and tobermorite as suitable long term phases has been settled. Both phases have been used for the sorption studies, but it has not proved possible to prepare tobermorite in the presence of lanthanum.

Progress and results

i) Sorption Measurements

Samples of all the phases required by the project: C-S-H, Hydrogarnet, Ettringite, Gehlenite Hydrate, Tobermorite and the last three with lanthanum additions have been prepared and characterised by TGA and XRD. The preparation of tobermorite in the pure state was achieved satisfactorily, but in the presence of 2% lanthanum the product was found to be largely xonotlite.

The pH dependence of the solubility of lanthanum has been determined. The speciation of lanthanum, deduced from the trends of these results, closely resembles that of americium. It was therefore considered safe to proceed with the programme using lanthanum as an inactive analogue for americium.

The sorption of lanthanum, americium and plutonium onto the CSH phases, ettringite and tobermorite has been determined. The sorption coefficients were all greater than the detection limit for the experiment (2000 ml/g) and higher than expected. During the last six months sorption measurements on all of the prepared phases have been made in experiments designed to allow the determination of higher Kd values. The results for those materials for which the experiments have been completed are given in table I.

ii) Crystallographic Studies (University of Oxford)

Crystals of the hydrates ettringite, hydrogarnet, tobermorite and gehlenite hydrate, prepared both in the presence and absence of lanthanum, have been examined and microanalysed in the TEM. The possibility of carrying out high resolution TEM of crystalline hydrates has been evaluated.

Ettringite (AFt) crystals supplied by the University of Aberdeen were found to damage very rapidly in the electron microscope and so were entirely unsuitable for high resolution work. Microanalysis in the TEM of crystals prepared in the presence of lanthanum, detected lanthanum within large areas of fine crystals but not within large, well-developed crystals. The remaining hydrate phases, tobermorite, gehlenite hydrate and hydrogarnet were much more stable in the electron beam and at moderate magnifications (say x 50K) could be studied for long periods without evident loss of crystallinity or other damage. In the cases of tobermorite and gehlenite hydrate a study was made of the feasibility of carrying out high resolution TEM studies. Using a magnification of x 300K, lattice fringes could be identified on a monitor as a transient phenomenon, but the rate of loss of crystallinity made systematic work almost impossible. It is considered that the study of structure images in sufficient details to show effects such as foreign atom adsorption or substitution would be impossible in these materials. After the initial loss of lattice fringes from the hydrate crystals as it damages, a more stable high resolution image develops but it is considered that this represents a decomposition product of the initial hydrate. The microanalysis of tobermorite and gehlenite hydrate crystals prepared in the presence of lanthanum, as supplied by the University of Aberdeen, revealed no lanthanum within well-developed hydrate crystals (Figure 1) even when these were adjacent to lanthanum hydroxide particles, indicating a level no greater than ~ 0.1% from the sensitivity of the technique. Hydrogarnet crystals formed by hydrating a 2.94 CaO Al_2O_3 0.7 SiO_2 0.03 La_2O_3 glass showed no lanthanum on microanalysis although an aluminosilicate hydrate gel formed at the same time, has a Ca:La ratio of about 5.

iii) Chemical State of Sorbed Species

Samples of CSH that had been equilibrated with aqueous solutions of neodymium or lanthanum have been analysed by X-ray photoelectron spectroscopy (XPS) and by electron probe analysis (EPA). The lanthanum signal was just above the noise level in the XPS analysis, but it was considered that it was unlikely that reliable chemical information could be obtained by this technique. The sorbed species were not detected in the EPA.

Recent scoping studies using EXAFS (Extended X-ray Absorption Fine Structure) have shown that the signal from the lanthanum can be detected at very low concentrations in a BFS/OPC cement. The results should provide information on the chemical form of the lanthanum. These initial data are being interpreted.

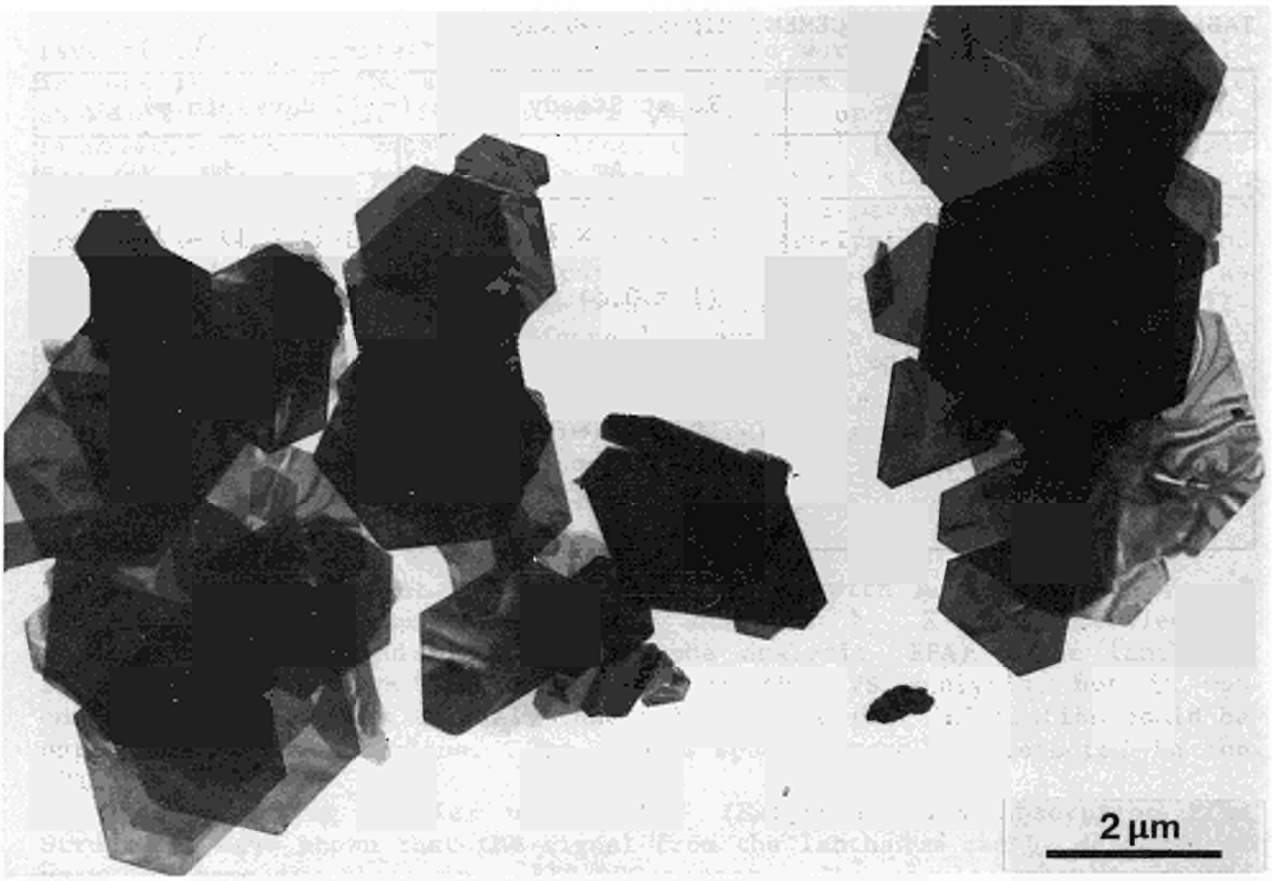
<u>List of publications</u>

F T Ewart, F P Glasser, M L Jenkins, P T Moseley, S A Roger and J L Smith-Briggs, 'Migration and retention of radionuclides in the near-field Annex 3, Part C Sorption mechanisms in the Near-field', Annual Report 1 April 1988 - 1 January 1989. AERE R 13337

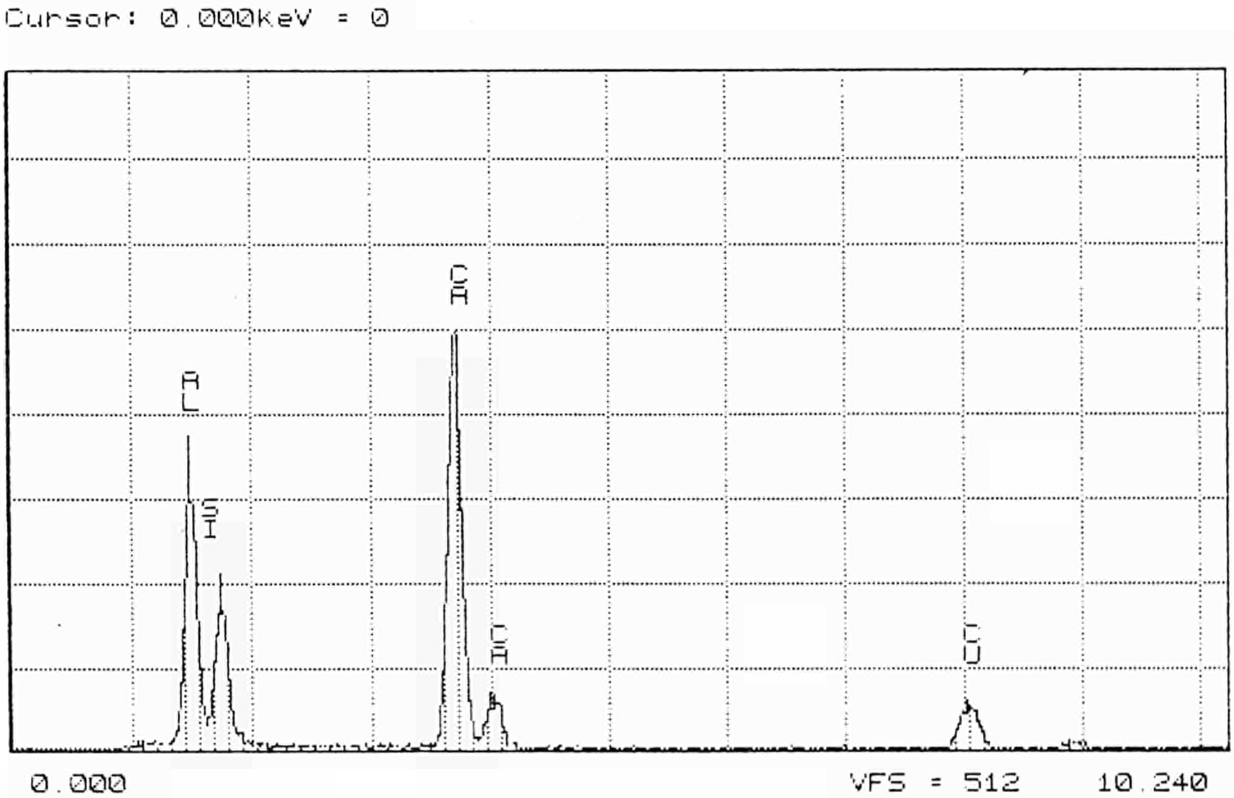
I G Richardson, S A Roger and G W Groves, 'Microstructure of ggbfs/OPC Hardened Cement Pastes and Some Effects of Leaching', Mater. Res. Soc. Proc. <u>176</u> (1990) (to be published)

TABLE I: SORPTION ON CEMENT MINERAL PHASES

Sorbing Solid	Rd at Steady State (≈ 25 days) in ml.g^{-1}	
	Am	Pu
9:1 BFS/OPC	(3 ± 1) x 10^3	(3 ± 1) x 10^3
Ettringite	(1 ± 0.5) x 10^5	(1 ± 1) x 10^4
Normal Tobermorite	(2 ± 1) x 10^4	(4 ± 0.5) x 10^5
CSH	(6 ± 2) x 10^4	(2 ± 1) x 10^4
Hydrogarnet	(1 ± 0.5) x 10^5	(8 ± 3) x 10^4



Crystals of gehlenite hydrate (with 2% La).



EDXA spectrum from one of the above crystals. No lanthanum peaks are present.

CORROSION AND GAS TRANSPORT IN CONCRETE BARRIERS

Contractor:	Harwell Laboratory, AEA Technology, Didcot, Oxon, UK
Contract No:	FI 1W.0187.UK(H)
Duration of Contract:	1st January 1988 - 31st March 1990.
Period covered;	1st January 1989 - 31st December 1989
Project Leader:	Dr A Atkinson

A. OBJECTIVES AND SCOPE

Effect of Anaerobic Reinforcement Corrosion on the Concrete Barrier in Low and Intermediate Level Waste Repositories (Corrosion Studies)

The programme is aimed at studying the corrosion of carbon steel (as waste container or structural reinforcement) in concrete under the anaerobic conditions which are expected to develop in repository near-field areas after a few years. This corrosion is important because the principal products, H_2 and low solubility ferrous oxy-compounds, may accumulate at the metal/concrete interface. Such accumulations could ultimately cause cracking of the concrete near-field barrier.

The aims of the work are to evaluate the rate of anaerobic corrosion at different hydrogen over-pressures and to investigate the nature and distribution of solid corrosion products. These data can be used with existing mass transport models to assess the likely accumulation of solid corrosion products and the build up of a hydrogen pressure in the near-field.

Transport of Gases Through Concrete (Gas Transport)

Gases, such as hydrogen, could potentially accelerate water movement through a repository, or even damage the engineered barrier system. The objective of this work is to measure the rate of gas transmission through candidate cementitious materials for repository construction and to quantify the effect of the following factors on the rates: Type of cementitious material, type of gas, degree of water saturation of the material, gas pressure and potential short circuits (joints,interfaces).

In addition it is intended to provide a theoretical interpretation of the results and to use the gas generation rates from the corrosion studies to assess the likely effect of the gas on the repository structure.

B. WORK PROGRAMME

Corrosion Studies

B1. Investigation of the influence of hydrogen over-pressure up to 100 atmospheres on the electrochemical kinetics of the anodic and cathodic reactions constituting the corrosion cell.

B2. Long term corrosion tests under oxygen free conditions with carbon steel specimens cast into 6 different cement or concrete mixes with subsequent characterisation of the surface corrosion products by XRD.

Gas Transport

B.3. Establishment of test methods to measure the transmission of gas through cementitious samples at a constant humidity. Two types of apparatus are required, one to measure at low pressures (up to 2 bar) and one for high pressures (up to 30 bar).

B.4. Gas transport measurements on a selected range of materials and gases to provide the necessary data to ascertain the sensitivity to the key variables.

B.5. Water absorption, mercury intrusion and ionic conductivity tests.

B.6. Calculations of the effect of the gas on the repository.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Corrosion Studies

Facilities for pursuing both aspects of the programme have been constructed and commissioned, and all the specimens for the long term tests in anaerobic concrete or cement have been produced and monitored for between 10 and 20,000 hours. Electrochemical measurements of the anaerobic corrosion rates of the carbon steel specimens in the various cement mixes have indicated corrosion rates ranging from 0.3 to 5.5 μm/a. The rates at the higher extreme of this range were measured in cement or concrete mixes deliberately contaminated with chloride, while the lower rates refer to chloride free specimens. Electrochemical studies at various hydrogen over-pressures, in saturated $Ca(OH)_2$ solution, have indicated that the active (anaerobic) corrosion rate is reduced by a factor of about 4 when the pressure is increased from 1 to 80 atmospheres. The final phase of the programme which involves breaking the steel samples out of these concretes and grouts to measure corrosion weight loss and identify the corrosion product has started and should be completed by 31st March 1990.

Gas Transport

The apparatus for low pressure transport measurements was already in use at the start of the year and a high pressure cell was completed and used during the year. The bulk of the measurements have now been completed. The remaining work consists of measurements on the new backfill material and a small number of other tests necessary to complete the programme. The measurements of water absorbtion and mercury intrusion are now also substantially complete.

Progress and results

Corrosion studies

Long term anaerobic Corrosion Tests

Anaerobic corrosion tests have been underway for approaching two years with carbon steel samples embedded in three different concrete/grouts chosen as typical components of a repository: a structural concrete, a canister infill grout and a repository backfill grout. The mix proportions are listed in Table I. Corrosion potentials continue to indicate anaerobic conditions, Table II. A number of steel samples are soon to be broken out of the concrete/grouts, initially within the anaerobic facility, to calculate the corrosion weight loss and analyse the form of the corrosion product.

During the year corrosion rate measurements by linear polarisation and A.C. Impedance have continued to indicate low rates of corrosion with the chloride contaminated samples continuing to indicate a slightly higher corrosion rate.

To accelerate attainment of anaerobic conditions the steel samples were lightly abraded immediately before being cast into cement to disrupt the passive film. During the year further tests have been carried out on steel samples with purpose-grown corrosion films of either Haematite or Magnetite. In the case of the former the corrosion potential plateaued at approximately 150mV positive of anaerobic conditions. For samples with a Magnetite film no such arrest was apparent, anaerobic conditions being attained as quickly as for the lightly abraded samples. This result indicates that aerobically corroded drums may locally hold the repository oxidation potential positive of anaerobic conditions for some period.

The Influence of Hydrogen Over-pressure

The attainment of equilibrium anaerobic conditions within the autoclaves used for these tests has been found to take a long time necessitating the commissioning of further autoclaves. Cathodic reduction of the steel has been used to remove the oxide film. It is interesting to note that the platinum electrode in the autoclave cell takes up to an anaerobic potential more easily and of a more negative value than the steel. Potentiodynamic scans have been made on steel under anaerobic conditions both in 0.1M potassium hydroxide and potassium hydroxide plus 10,000ppm chloride. The Tafel slopes (figure 1) measured for the cathodic reaction are around 70mV/decade of current and extrapolation of the tafel lines to the equilibrium potential for the H_2O/H_2 reaction at 100 atmospheres of pressure yields exchange current densities (in Amps/cm^2) of 7.3 10^{-7} for potassium hydroxide solution and 1.8 10^{-6} for the same solution with a chloride addition, Table III.

Discussion

The attainment of consistent anaerobic conditions continues to present difficulties especially in the solution phase experiments. Even when negative potentials are achieved on the steel the potentials are still approximately 20mV positive of platinum, suggesting that there is some residual oxide-related electrochemical couple present which is polarising the steel.

The corrosion rates as measured or estimated are low. There does appear to be an effect of hydrogen overpressure on the corrosion rate although this does not appear to be of a large enough magnitude to reduce the corrosion rate significantly at the pressures likely to be encountered in the repository.

Conclusions

1. Long-term tests with carbon steel in anaerobic concrete have been running for approaching 20,000 hours. The rest potentials are all consistent with anaerobic conditions although they are approximately 20mV positive of platinum metal under the same conditions.
2. Exact corrosion rate measurements are rendered difficult by the very slow corrosion which is occuring. There continues to be an indication that the chloride contaminated samples are corroding at twice to four times the rate of the chloride free samples.
3. Experiments in autoclaves indicate that there is an effect of hydrogen pressure on the anaerobic corrosion rate but it is not of a magnitude significant enough to halt corrosion under presently calculated repository.

Gas Transport

2.2 Provision and Characterisation of Materials

Three mix designs are currently in use in this programme. A PFA concrete with 300 kg/m^3 OPC, 100 kg/m^3 PFA and a water/cementitious ratio of 0.475, a 9:1 BFS:OPC grout with a water/solids ratio of 0.4 and a 2:1 lime:OPC grout with a water/solids ratio of 0.9. Before testing the samples are either dried or equilibrated at target humidities of 75%RH or 100%RH. The results for mercury intrusion and weight loss on sample conditioning are in tables IV and V.

2.4 Gas transport measurements

The work programme defines five sets of tests to be carried out to determine the sensitivity to key variables. The conclusions which may be drawn from the results which are currently available are as follows:

2.4.1. Type of concrete

The results show a difference between the PFA concrete and the Lime Grout of almost two orders of magnitude for the dry samples and about four orders of magnitude for the wet samples. The BFS grout is an order of magnitude more permeable than the PFA concrete.

2.4.2. Type of gas

A total of five gases have been used on the low pressure system because it will probably not be possible to use the flammable gases (H_2 and CH_4) at high pressure. The comparison at low pressure will be used to obtain estimates for the high pressure values for the flammable gases from the values for the non-flammable gases. The PFA concrete has been tested with all five gases at 0 and 75% RH. The results indicate that the permeability falls slightly with increasing molecular weight of the gas.

2.4.3. Degree of water saturation

The results for the PFA concrete at 0%, 75% and 100% RH for Argon indicate that the permeability falls considerably with increasing humidity. The high pressure tests have not shown the gas to be able to expel water from the pores.

2.4.4. Gas pressure

The low pressure tests have revealed a substantial increase in permeability at low pressures but virtually no change at pressures above atmospheric up to 100 atmospheres.

2.4.5. Potential short circuits

The results obtained for the reinforced samples lie within the range of the corresponding unreinforced samples.

Publication

Atkinson,A., Claisse,P.A., Harris,A.W. and Nickerson,A.K.
"Mass Transfer in water saturated concretes", to be published in Mater. Res. Symp. Proc. (Scientific Basis for Nuclear Waste Management, Boston, November 1989).

Table 1 - Composition of cement/concrete Mixes being investigated

MIX 1	75% OPC/25% PFA concrete with limestone aggregate (max 20 mm) W/C = 0.45
MIX 2	As 1 but with 2% chloride added (by weight of mix water)
MIX 3	90% BFS/10% OPC grout W/S = 0.35
MIX 4	As 3 but with 2% chloride added (by weight of mix water)
MIX 5	66% lime/33% OPC W/S = 0.9
MIX 6	As 5 but with 2% chloride added (by weight of mix water)

OPC	Ordinary Portland Cement
PFA	Pulverised Fly Ash
BFS	Blast Furnace Slag
W/C	Water/Cement Ratio
W/S	Water/Solids Ratio

Table II - Average values of the steady rest potentials and their associated standard deviations for the various cement Mixes under investigation

Mix No	Storage Condition	Test Time (h)	Average Steady Rest Potential (mV vs SCE)	Standard Deviation (mV)
1	Immersed	17088	-980	± 4
2	Immersed	16920	-984 Cl^-	± 6
3	Immersed	16200	-946	± 2
4	Immersed	16056	-958 Cl^-	± 4
5	Immersed	13152	-935	± 46
6	Immersed	13152	-922 Cl^-	± 32
1	> 95% RH	16440	-980	± 6
2	> 95% RH	16416	-1000 Cl^-	± 6
3	> 95% RH	15912	-988	± 5
4	> 95% RH	15864	-1010 Cl^-	± 4
5	> 95% RH	13152	-945	± 28
6	> 95% RH	13152	-890 Cl^-	± 78

Table III

Electrochemical Kinetic Parameters for the Water Reduction Reaction on Carbon Steel Derived from the Polarisation Curves

Solution	Sweep Rate (mV/min)	b_c	α	i_o (amps/cm^2)
0.1M KOH	100	68.4	0.861	7.30×10^{-7}
"	10	76.0	0.774	1.78×10^{-6}
"	10	77.8	0.756	2.03×10^{-6}
0.1M KOH	100	114	0.516	4.56×10^{-6}
+ 10,000 ppm Cl^-	10	131	0.449	7.90×10^{-6}
	10	101	0.583	3.39×10^{-6}

Table IV

	Intruded Volume mm^3/g	Density g/cc	Porosity %	Average Pore radius micron
PFA concrete	48	2.4	11.5	0.011
BFS grout	191.1	1.55	29.6	0.011
Lime grout	679	0.855	58	.6973

Summary of results from mercury intrusion.

Table V

Control solution	Initial Condition	Equilibrated 75% RH NaCl	Equilibrated 100%RH Water
BFS GROUT			
As cut	-	.32	-.19
Saturated	-.02	.24	-.16
Dried	23.46	11.19	4.24
PFA CONCRETE			
As cut	-	.33	.03
Saturated	-.01	.41	.07
Dried	5.9	2.82	.31
LIME GROUT			
As cut	-	35.87	24.24
Saturated	.15	36.93	23.91
Dried	45.44	37.96	28.33

Percentage weight losses from samples after different initial treatments.

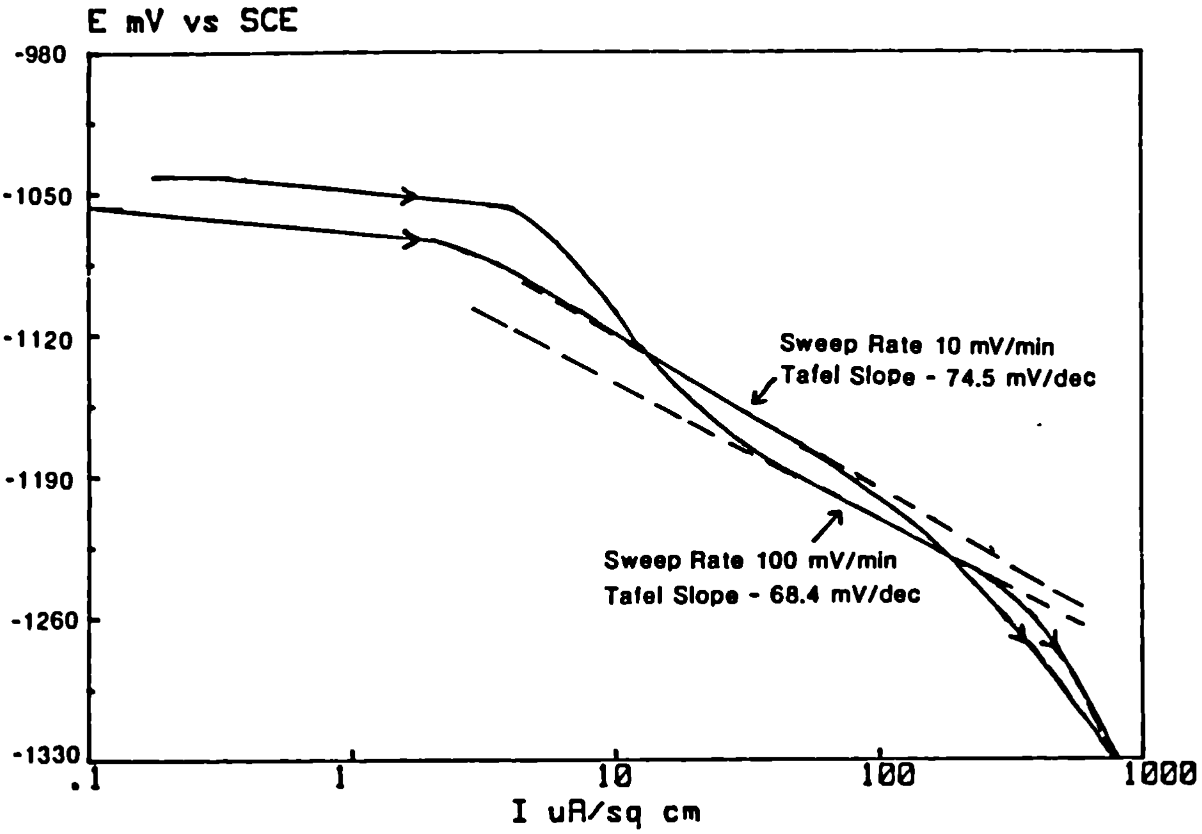


Fig 1 Cathodic polarisation curves for a carbon steel specimen in 0.1M KOH (100 atmospheres hydrogen pressure).

LIMITING SOLUBILITIES OF RADIOELEMENTS IN INTERSTITIAL BUFFER MATERIAL WATERS OF WASTE DISPOSAL

(Solubilités limites des radioéléments dans les eaux interstitielles de matériaux de voisinage et de remplissage des stockages de déchets)

Contractor : CEA Fontenay-aux-Roses, FRANCE
Contrat No : FI1W-0190-F (CD)
Duration of contract : from 1st January 1988 to 31st December 1989
Period covered : 1989
Project Leader : P. VITORGE

A. OBJECTIVES AND SCOPE

The migration of actinides inside cement (or concrete) is very slow, even when the material is saturated with water : precipitation of actinide hydroxide explains this retention phenomenon. The aim of this work is to measure Am solubility in aqueous solutions equilibrated with CPA55 cement to :

- compare it, with thermodynamic predictions ;
- correlate it to (future) migration measurement of Am through cement disks.

B. WORK PROGRAMME

2.1. Modelisation of the interstitial water of cement.
2.2. Preparation and lixiviation of cement.
2.3. Am solubility in aqueous solutions equilibrated with cement.
2.4. Comparison of Am diffusion and its solubility.
2.5. Modelisation of Am solubility.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The following measurements and calculations planed in this two years studies :

- calculation of the main components of the interstitial water of cement and its experimental verification,
- solubility measurements of Am(III) and Am(V) in lime water as a model of its behaviour in cement water,
- Am(III) and Am(V) solubility measurements in cement water,
- thermodynamic calculations on Am solubility in alkalin media,

have been performed ; but (as stated initially), only partial migration measurements have been done since solubility equilibration in the upper compartments of diffusion cells where too much time consumming and the solubility (in the upper compartments) lowered the amount of Am that could migrate.

Results

2.1 Cement water is modelised as lime water since Am solubility results show (§ 2.3 and 2.5) only small differencies between the two media hence :

- carbonic gaz (from the air) reacts with lime to product calcite, and when the system is closed, the two solids (lime and calcite) maintain (very low) constant carbonic gaz pressure ;
- only hydroxide and eventually carbonate anions react with the americium cations ;
- potash addition increases hydroxide and carbonate concentrations and also ionic strength (and then modifies formal complexing constants),

2.2. Cement preparation is performed according to NFP15 401, NFP15 402 and NFP15 411 norms. To verify the composition of its interstitial water, after a curing time of one month, a part of this cement is lixiviated (during 72 days). The results of chemical analysis of this water are in accordance with the known behaviour of CPA55 cement.

2.3. Am solubilities in aqueous solutions equilibrated wit cement are measured in the upper compartment of diffusion cells filled (3 months after the preparation of the cement) with synthetic cement water (§ 2.2) where solid lime (excess) and potash (0 to 10 M), are added. Different chemical species are used to add americium :

- Am(III)
  - * acidic solution (lnM to lμM),
  - * hydroxide solid,
  - * carbonate solid,
- Am(V) potassium carbonate solid.

Am solubility is also measured in batches where only lime and potash are added. Solubility equilibria are achieved within less than 6 months (at least 3 months) :

- when potash concentration is less than 1 M, Am(III) solubility is 0.01 nM in lime water and a little higher (0.03 nM) in cement water, if Am has been initially oxidised, solubility is slightly higher : 0.02 and 0.05 nM respectively (for lime and cement waters).

- at higher potash concentrations, Am solubility increases.

2.4. **Am migration** through cement disks have been detected after one year ; but this could not be correlated to solubility since the solubility was not constant at the begining of the migration ; hence it seems that at least one more year is needed to detect again significant amount of americium in the lower compartment. Soluble anionic hydroxide, carbonate or oxidised complexes are not stable enougth to significantly increase Am solubility in cement water : this has been used to study Pu migration (this is not a part of this contract).

2.5. **Thermodynamic modelisation** of the above solubilites are peformed using :

- thermodynamic equilibrium constants,
  - * AERE or our data bank could give Am solubility predictions,
  - * Allard, EIR, Kim, UWIST, CHEMVAL data banks overestimate the stability of some anionic Am complexes wich leads to very poor prediction ;
- activity coefficients,
  - * Specific Interaction Theory is precise enougth,
  - * Pitzer equations are too complicated and empirical to be used, when there are too many ionic complexes.

ANNUAL SUMMARY REPORT

Contract CCE No. FI 1W-0191-E (TT)

CHARACTERIZATION OF CLAY (BENTONITE)/CRUSHED GRANITE MIXTURES TO BUILD BARRIERS AGAINST THE MIGRATION OF RADIONUCLIDES : DIFFUSION STUDIES AND PHYSICAL PROPERTIES

No annual summary report ´89 has been received for this contract

3.4. DEVELOPMENT OF STANDARD TEST METHODS

ALL WORK IN THIS SECTION WAS COMPLETED BEFORE SUMMER 1989 AND THEREFORE NO REPORTS ARE INCLUDED HERE.

3.5. DEVELOPMENT OF TESTS FOR QUALITY CONTROL AND QUALITY INSPECTION PURPOSES

Annual Summary Report 1989

Quality Assurance of Radioactive Waste Packages by Computerized Tomography

Contractor: BAM, Berlin, Germany
Contract NO: FI 1W-0037 / FI 1W/0193
Working Period: January 1989 - December 1989
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. bitümen, 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. The objectives of the new contract are an extension of the dimension of the waste packages to be investigated as well as the variety of the physical properites to be investigated.

B. Work programme

1. Choice and acquisition of a radiographic linear accelerator, installation and acceptance test
2. Development, construction and testing of a HECT detector

3. Investigation of the crack formation in non-radiactive HAW glass simulate
4. Nondestructive evaluation of the internal surface of a glass cylinder
5. Investigation of cemented cladding waste
6. Investigation of swelling, shrinking and segregation in LAW and MAW containers
7. Nondestructive evaluation of the compressive strength of cemented waste
8. Evaluation of the activity distribution in MAW-containers by combination of ECT and TCT-measurements
9. Combination of simulated HAW-measurements with TCT-measurements
10. Investigation of supercompacted waste packages
11. Investigation of HIP-treated HAW-simulate

C. Progress of work and obtained results

State of advancement

During the working period the new electron linear accelerator (X-4000) has been delivered and installed in the CT-scanner. The acceptance measurements showed that the contracted specifications are fulfilled. The investigation of the crack formation of HAW glass simulate was continued. It was the first time that the behaviour of a glass block was tested non destructively before and after a drop test. The emission CT measurements could be finished. It turned out that for dose rates higher than 200 mrad/min at the surface of a package the background caused by backscattering from the surrounding walls is too high in our installation. For lower dose rates at the surface we obtained clear ECT tomograms (cf. 1988 Report). An extensive investigation of the compressive strength of various concrete mixtures was performed. From the tasks of the extended work programme preliminary results of the investigation of HIP treated HAW simulate are presented. HIP treatment is a new scope of the advanced conditioning technique research with the aim to maintaine the first barrier around the HAW glass block as long as possible.

Progress and results

1. Choice and acquisition of a radiographic linear accelerator, installation and acceptance test

The new LINAC (X-4000) has been delivered in January 1989. The acceptance measurements showed that the contracted specifications are fulfilled. The machine was the first time used for the inspection of a supercompacted waste package.

3. Investigation of the crack formation in non-radioactive HAW glass simulate

In the framework of the leakage test of the ASSE-TB-container which is intended for a long term storage test of real HAW-glass in the ASSE salt mine a 9 m drop test was made at BAM. The 80 l container filled with glass simulate was dropped twice, the first time with shock adsorber, the second time without. It turned out that the welding seam of the cover was leakproof after both 9 m drop tests.

Additionally tomograms at various heights were measured to study the behaviour of the glass block under heavy shock loads.

In another test together with CEN Valrho a dismantable container will be investigated and hopefully improve the understanding of crack formation and propagation in vitrified waste simulate.

5. Emission CT

To test the ability of our CT scanner to measure emission tomograms, we chosed a 50 l drum of bitumized MLW with a total activity of 0.37 TBq, housed in a standard 200 l barrel. The activity was nearly homogenously distributed within the 50 l drum. For the measurements we used the same scan parameters as we would do for the transmission CT. Nevertheless the counted activity in the outer channels is not zero (background is less than 10 counts). However, due to the fact that the large volume of the 50 l activity produces a very high background radiation, which is not shielded by the collimator which was constructed for a well collimated point source in front of it. The net signal of the drum itself is less than 10 % of the background radiation. Further more the intensity of the background radiation varies with the vertical distance from the detector.

The conclusion is that with our detector system, as it is built up by now, emission CT on MLW drums is not possible: The signal to noise ratio is too large. The collimator setup has to be changed and the shielding of the detectors in every direction has to be improved (at least 20 cm of lead).

6. Investigation of swelling, shrinking and segregation in LAW and MAW containers

The BAM tomograph is limited to objects with a maximum diameter of 1 m and 1000 kg weight. The largest object which was measured with the HECT detector is a 870 l waste drum (CEN/Cadarache, diameter 985 mm) containing a source of low activity. The first measurements on this drum were made with the old LINAC.

The outer steel container contains three different parts of concrete shielding, an inner part of concrete and bore holes filled with concrete. The shielding has a density which is 5 % higher than that of the inner part, where as the density of the filled bore holes is about 7 % lower than the density of the inner part.

The average linear attenuation coefficient of the concrete is 0.054 [1/cm] and the average attenuation factor is about 220. In the shadowgraph the maximum attenuation factor is more than 10000 in these areas where the steel reinforcements are penetrated.

The investigation of this drum will be continued with the new LINAC to localize the low activity source.

7. Nondestructive evaluation of compressive strength, structural information and composition of cemented waste packages

7.1 Structural information

Several examples for the nondestructive evaluation on structural details have been presented in earlier reports of this project: the voidless incapsulation of radioactive metal parts in cement matrix, the detection of free water, the verification of the homogeneity of waste-cement-mixtures. A new example deales with the integrity of a storage cask for irradiated AVR-fuel elements, type COCON, scale 1:3 model.

A 1:3-scale model of a storage cask type COCON (designed for the intermediate storage of irradiated AVR-reactor fuel elements) was tested at BAM within the scope of the design licence procedure.

The cask was investigated before and after the 9 m drop test with CT. So it could be verified that the internal structure of the container was not damaged by the shock load.

7.2 Compressive strength of cemented waste

From safety considerations for the final repository it was derived that cemented waste packages must have a minimum compressive strength of 10 N/mm^2. So, it would be very helpful to have a method to verify non-destructively whether a package meets this condition or not. For this purpose a series of waste-cement-water mixtures were prepared and analysed for density and compressive strength. KFA-Jülich send the waste simulate "MAW 300", BAM prepared the cement-waste-mixtures and measured compressive strength, density by weight, and CT-density of the standard sized samples (10 x 10 x 10 cm^3). Between the gravimetric density and the CT-density there was found a very strong correlation.

The result of this investigation can be summarized as follows:

- the density of cemented radioactive waste can be measured non-destructively by CT, also in sealed packages. For a measuring time of 30 min per tomogram there results a density resolution of 5 %. The measuring time can be reduced considerably at the cost of density and/or spatial resolution. The minimal measuring time for a tomographic slice with 255 x 255 pixels of a 200 l drum with 60 cm diameter is 7 min.
- For a constant cement/waste ratio the compressive strength increases with increasing density,
- for a density > 1.7 g/cm^3 the compressive strength is always > 10 N/mm^2,
- within the density range 1.5 - 1.7 g/cm^3 the compressive strength may fall short of the 10 N/mm^2 limit.

11. Investigation of HIP-treated HAW-simulate

Until now heat generating vitrified HAW from the nuclear fuel reprocessing units is poured into cylindrical stainless steel containers which are then leakproof sealed and stored in an intermediate storage facility. The further and final storage procedure has not yet been decided. One aim of the advanced conditioning technique research is to find means to maintain the first barrier around the glass block (= the steel container) as long as possible. It is expected that the container will implode under the ground pressure once the steel barrier is corroded through if there is a large hollow space in it caused by incomplete filling.

Therefore KfK developed a HIP (= hot isostatic pressure)-method for the conditioning of the sealed glass containers. The containers are packed into a thick walled steel overpack.

The complete package is then treated with HIP ($T = 1000^\circ C$, $p = 1000$ bar) with the aim to remove any hollow space. The tomographic investigation of the first run revealed a rather inhomogeneous glass matrix. Therefore in the second experiment the high pressure was maintained at medium temperature for a longer period. This improved cooling procedure resulted in a much more homogeneous glass block. No cracks in the glass could be detected in both experiments. This indicates that the HIP-packaging might be an advantageous conditioning technique for filled and sealed HAW-containers.

QUALITY ASSURANCE - PROCEDURES - STANDARDIZATION

Contractor : CEA CEN CADARACHE - FRANCE
Contract N° : FI 1W/0095 Task 5/5
Duration of contract : From August 86 to December 89
Period covered : January 89 - December 89
Project leader : A. SAAS
Executant of task 5 : M. A. SAAS - CEN CADARACHE

A) OBJECTIVE AND SCOPE

The characterization programme led by the CEA laboratories has been focused until end of 1988 on homogeneous embedded wastes. This purpose was treated during the first three items, and typical cases was presented during the fourth item.

The 1989 objective programme has been to present, the schedule of the characterization's procedure of heterogeneous embedded waste and technological raw wastes. That presentation concludes this item's contract programme.

B) WORK PROGRAMME

B.1 - Technological raw wastes procedure.
B.2 - Dismantling raw wastes procedure.
B.2.1 - $\beta\gamma$ measures of raw wastes packages.
B.2.2 - Converting measures.
B.3 - Mass activity measure's procedure of heterogeneous waste packages.
B.3.1 - Restriction and distribution of package's activity.
B.3.2 - Procedure of mass activity measures.
B.3.3 - Valuation's procedure of heterogeneous packages.

C) PROGRESS OF WORK AND OBTAINED RESULTS

The mass activity measures of heterogeneous wast package must given the same expectation and guarantee abou criteria as homogeneous package, in particular concerning :

- in first, the acceptability of the mass activity (embedding level permissible activity),
- in second, the package's activity distribution.

We have used the case of the water filters determination after sheath rupture for B1 programme. The methodology was the determination of the activity by $\beta\gamma$ and X spectrometry with an accuracy of about 25 %. The knowledge of the embedding rate gives then an estimation of the respect or not of the fundamental rules for safety and repository recommendation.

The procedure for raw wastes from dismantling, B2, is also presented with an example support. In this case we must measure, as before, the raw waste's activity, and then we must calibrate the systematic measures as a function of two criteria :

- the waste origin,
- the radionuclide composition of the waste.

The measure of the mass activity of heterogeneous embedded waste, B3, is given often with a bad accuracy, mainly for 3 reasons :

- non equal distribution of the raw waste in the package,
- radioactivity's change from a waste to another,
- radiation's self absorption as a function of the matrix or the overpack thickness.

So, for aged embedded package, the procedure commended must be as following :

- measure of the global mass activity by using probes with different energy and yield,
- if necessary or if the equipment calibration is not obtained, we must core the package and make a γ scanning measurement of the core sample,
- if needful, we take an aliquot, a part, of the core sample for destructive measurements.

All these steps must be authenticated.

Development of Test Methods for Quality Control of LLW and MLW in Cement or Polymers

Contractor:	ENEA, C.R.E. Casaccia, Rome, ITALY
Contract No:	FI1W - 0101 - I(A)
Duration of Contract:	from 1-1-1987 to 31-12-1989
Period covered:	January - December 1989
Project leader:	G. De Angelis

A. OBJECTIVES AND SCOPE

Purpose of the R & D programme is the investigation of the industrial operation of a Mobile Waste Conditionig Plant (MOWA) with regard to quality control.

The application of the proposed controls is evaluated by comparing the product qualities from inactive simulated full scale tests and labo scale preparations.

Expected results are the realization of the proposed quality assurance procedures and the technical improvements of process control.

The MOWA plant operation can be outlined as follows: the simulated waste, as it is or pretreated, is pumped from a storage tank into a metering tank inside the MOWA and checked for temperature, density and volume by means of the external control panel. After stirring it is transferred to the conditioning station, where a 200 or 400 liter steel drum with a non-recoverable stirrer, previously filled with the correct amount of incorporation matrix (cement or polymer), is ready to receive it.

At last the drum is transported away by a fork lift and the final waste form is left to cure and harden.

B. WORK PROGRAMME

2.1 Optimization of recipes for the cementation with MOWA of bead ion-exchnge resins, filter sludges, BWR evaporator concentrates.

2.2 Labo. scale tests in the frame of a quality assurance programme.

2.3 MOWA plant operation and collection of process data to be compared with standard process parameters fixed before.

2.4 Full scale tests.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The characterization programme of the solidified waste continued on a labo. scale basis with the assessment of some leach properties and the improvement of the retention capacity of cement based systems towards BWR evaporator concentrates (Sulphates).
The leach studies were related to the release of Cesium from cemented BWR evaporator concentrates (sulphates) under different experimental conditions.
In particular the variation of the following parameters was taken into account: temperature, initial concentration of the tracer, renewal of the leachant, chemical composition of the leachant, size of the specimen. Each test was made on duplicate samples. Deep crack formation occurred, in more than one case, with direct consequences on the leach data.
The performance of silica fume as blending agent was verified in the solidification of Sulphates, whose incorporation in both Portland and pozzolanic cement had given unsatisfactory results: low leach resistance and crack formation by water immersion had been the main troubles.

PROGRESS AND RESULTS

3.1 Leach studies

The influence of different parameters on the release of Cs from BWR evaporator concentrates was evaluated. On the basis of the results obtained the following conclusion have been drawn.

3.11 Effect of temperature

The leachability is strongly influenced by the increase in temperature, not only as total leached amount, but mainly as leach rate at increasing leach times. Moreover at elevated temperatures (70°C) the leaching mechanisms seem to change, as shown by plotting the cumulative fraction release (CFR) at a given temperature against the CFR at ambient temperature. A straight line is for a constant leaching mechanism, as it is during the first leaching intervals, but a different slope of the curve holds for a different leaching mechanism.

3.1.2 Effect of initial concentration of chemical tracer

The initial concentration of chemical tracer does not seem to have any influences on the leaching data, at least in the range of concentrations which were investigated: 50, 100 and 1000 mg of Cs in cylindrical samples (dia. 5 cm; h. 5 cm; total weight of about 200 g).

3.1.3 Effect of leachant renewal

The leachant renewal also influences the leach rate. Both ANS 16.1 and ISO tests call for leachant replacement at specified times. Actually it has been demonstrated that saturation effects may occur for inadequate leachant replacement frequency, with the consequence of questionable data analysis.

3.1.4 Effect of chemical composition of the leachant

The different chemical composition of the leachant brings to different quantities of Cesium released. Under this respect the comparison between deionized and sea water was of particular interest: the former gave a pH of the leachate of about 11.5, the latter of about 9.5, at least after the first leachant renewals. This, in general, shows that the deionized water is a more efficient solvent for cement than the sea water, as confirmed by the leach data. On the other hand, the high conductivities and the Ca values found for the deionized water leachates show the attack of this leachate on the cement surface.

3.1.5 Effect of size of the sample

The size of the sample influences the leachability according to the ratio between volume of the specimen (V) and external surface area (F). The tests were made with cylindrical samples having the same concentration of Cs and increasing diameter. The diameter/height ratio was kept constant, as well as the ratio between volume of leachant and external surface area of the specimen. In this way the ratio between volume of leachant and volume of sample varied together with V/F.

3.2 Cementation of BWR evaporator concentrates (Sulphates) by addition of silica fume.

Samples in which 15-20% of cement had been replaced by silica fume were prepared and examined under various test conditions.
Mechanical properties (compressive, tensile and flexural strength; ultrasonic pulse velocity, elastic modulus, shear modulus, Poisson's ratio), thermal properties, expansion in both humid atmosphere and in tap water, uptake of water, hydraulic conductivity and leachability were satisfactorily evaluated. Also freezing-and-thawing cycles (from +40 to -40 °C within 24 hours), which had been reported to prove deleterious in some cases were successfully withstood.

LIST OF PUBLICATIONS

G. CAROPRESO and G. DE ANGELIS, "Evaluation of the properties of cemented low level wastes through an extensive characterization programme", presented at the 1989 Joint International Waste Management Conference, Kyoto (Japan), 23-28 October 1989. Proceedings, volume 1, pp. 421-429.

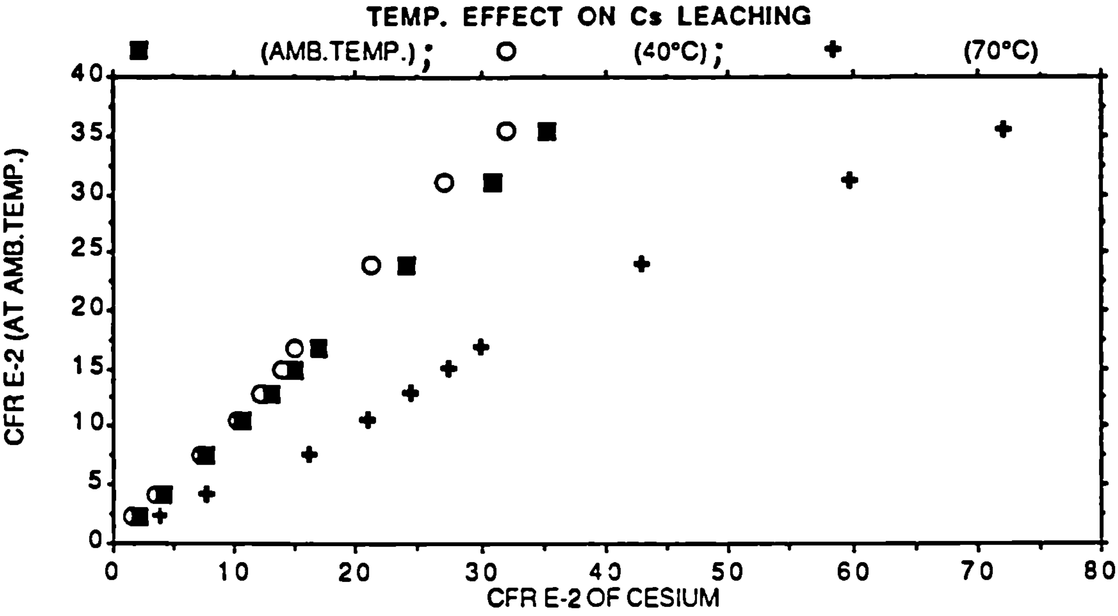


Fig. 1 Effect of temperature on Cesium leaching

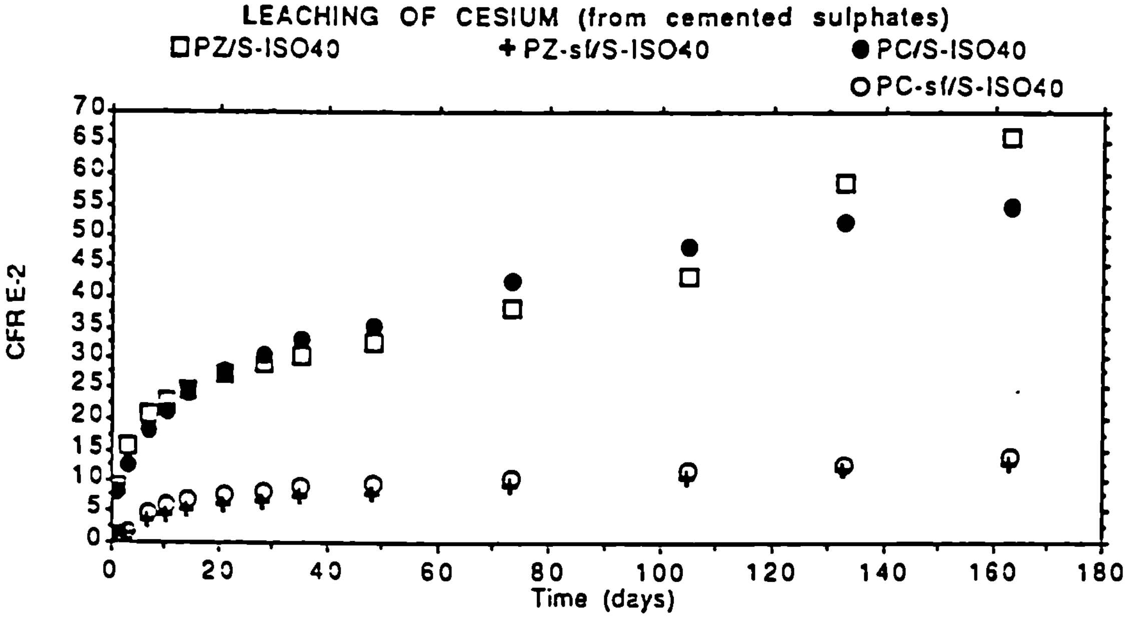


Fig. 2 Leaching of Cesium on cemented Sulphates (Portland and pozzolanic cement, with and without silica fume)

RADIOACTIVE WASTE PACKAGE ASSAY FACILITY

Contractor:	Taylor Woodrow Construction Ltd, Southall, UK
Contract Nos:	FI.IW.0102, 0244 UK(H)
Duration of Contract:	January 1987 to July 1990
Period Covered:	January 1989 to December 1989
Project Leader:	Mr T V Molesworth

A. OBJECTIVES AND SCOPE

Neutron and gamma interrogation of drums of radioactive waste may be used to determine actinide content. A linac, with appropriate targets, provides powerful gamma and neutron sources yielding the potential for a very sensitive technique for actinide determination.

The objective of the work is to provide information which will enable an integrated assay facility, incorporating a number of examination techniques, to be designed. The present programme is directed at research to determine the feasibility and sensitivity of a linac driven interrogation system in the assay of the contents of 500 litre drums of cemented wastes and the development of methods by which signals generated in the experiments may be processed.

The programme is led by TWC supported by the Harwell Laboratory, Plessey Controls Ltd* and Ray Technologies Ltd.

*formerly Fisher Controls Ltd

B. WORK PROGRAMME

Stage 1 (Feasibility Study)

B.1.1 Investigate suitability of linac and neutron target for active neutron interrogation.

B.1.2 Determine and evaluate the performance and limitations of combined active neutron and active gamma interrogation chamber, and compare with separate chambers. Consider compatibility of chamber with passive neutron examination.

B.1.3 Establish data processing model and test against available calculated and experimental information.

Stage 2 (Main Experimental programme)

B.2.1 Provide suitable components for an experimental assay system.

B.2.2 Commission experimental system.

B.2.3 Operate system in neutron and gamma interrogation modes and measure initial responses.

B.24 Make preliminary evaluation of system and modify accordingly.

b.2.5 Operate system in neutron and gamma interrogation modes and measure responses under different conditions.

B.2.6 Evaluate characteristics of common neutron and gamma interrogation system and identify development needed for use in an integrated assay facility.

B.27 Develop data processing model and check against test results.

Stage 3 (Application to practical assay facility)

B.3.1 Evaluate performance of integrated assay facility.

B.3.2 Consider engineering and systems developments required for an integrated assay facility.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Substantial progress was made with Stage 2 of the programme. The experimental composite assembly for active neutron and active gamma interrogation was constructed at Harwell. Bremsstrahlung and neutron generating targets and associated equipment were produced, and suitable modifications made to the existing HELIOS linear accelerator LE beam line.

Over 200 numbered runs and other experiments were carried out in both neutron and gamma interrogation modes, using ^{235}U,^{nat}U and D_2O as the sample materials placed in a simulated CAGR 500 litre cemented waste drum. Counter detection efficiencies were measured using a ^{252}Cf neutron source.

Measured responses were generally consistent with previously predicted responses, with a satisfactorily linear relationship between response and actinide mass for both interrogation modes. There are some discrepancies for which suitable explanations are proposed, leading to a refinement of calculation methods.

A poster paper was presented to the BNES conference on radioactive waste management, held in Brighton during May /1/. A paper was also presented to the CEA/CEC meeting on non-destructive assay, held at Cadarache during November /2/.

A start was made on the creation of a mathematical model, linked closely to the experimental facility. Further investigation of the methodology indicated that a full process model dealing with all variables could not be developed within the present programme.

Progress and Results

Feasibility study (B.1.1, B.1.2)

Already completed. The suitability of a linac and neutron target for active neutron interrogation was established. Responses were predicted for a conceptual composite assay arrangement.

Data processing (B.1.3)

The general model was defined /3/. Model testing has been reprogrammed to be carried out as part of the Stage 2 work, using the results obtained from the experimental assay facility at Harwell.

Experimental assay system (B.2.1)

The experimental assembly was built during the first half of the year, a detailed description being given in the intermediate progress report /4/.

The entire assembly can be translated from one position to another by means of the air pads which support the steel table carrying the assembly. The affected area of cell floor was covered in stainless steel sheet to allow smooth air reaction operation.

A turntable, operated at 0.5 RPM, carries a borated concrete shielding block of variable height, which, in turn supports the drum. Antimony free lead was used for shielding the 100mm diameter vertical neutron counter channels. 48 separate borated concrete pieces provided the main shield round the drum and detectors. These were keyed to prevent shine through.

A common beam line is used for both modes of interrogation. Modifications were made to the LBW3 branch so that it could be decoupled from the rest of the LE beam line. Deflectors have been arranged to permit deflection of the beam in any direction.

A variety of neutron detector packages was assembled to permit measurement of both fast and thermal neutrons at different points. These also included one position inside the drum for thermal flux and another outside the chamber, for fast neutrons emitted by the target. Assemblies of 4 x 25mm diameter 300mm long ^{3}He counters have been provided, as an alternative to single counters, in one or more channels.

An electronic data acquisition system was set up around a multi-input, multi-shot time digitiser. The digitiser has 8 separate inputs each with 1μs time channels extending to 2ms. At each linac pulse, the digitiser clock is started, and the times of occurrence of neutron detector signals recorded.

Commissioning of experimental system (B.2.2)

All components of the system were tested to ensure proper functioning. Preliminary experiments were carried out using a simulated 500 litre CAGR waste drum, in which a ^{235}U sample was placed. These showed that the system functioned satisfactorily. Also highlighted was the need for tight shielding around the drum and the desirability of recording the off-axis component of the electron beam, using the collimator. Additional borated cement grout contained in polyethylene bags was packed into gaps between some of the main shielding pieces.

Initial operation in neutron and gamma interrogation modes (B.2.3)

Over 200 numbered runs and several unnumbered ones were carried out including some with a ^{252}Cf source to measure neutron detector efficiencies. For neutron interrogation, ^{235}U foil samples 0.05mm thick were placed at different locations within the drum. 17 counters were used to measure fast and thermal neutrons (Fig.1). The target absolute neutron output was determined by measuring the ^{41}Ar activity induced in sachets of K_2HPO_4 located at 50mm intervals on a line from the target.

For gamma interrogation, 275g ^{nat}U cylinders 19mm diameter, and 64g D_2O samples were placed at different locations in the drum. 4 counters were used to measure the fast and thermal neutrons (Fig.2).

Typical time spectra are shown in Fig.3. In neutron mode, the effect of introducing fissile material is obvious and the 135μs i/e die-away time of this component agrees with the die-away time of the thermal flux.

The responses as a function of actinide mass are shown in Fig.4, corrected for background. Responses are satisfactorily linear in both modes. For neutron interrogation, the small deviations are attributed to spatial distribution of the ^{235}U.

The absolute response at drum centre is 0.2×10^{-10} counts (per g ^{235}U per interrogating neutron), lower than the predicted 1×10^{-10}. It is believed that this may be due to a lower than predicted thermal neutron flux.

Target neutron output is consistent with that calculated for a larger target. The measured dependencies on azimuthal angle are in good agreement with those calculated. For gamma interrogation with ^{nat}U, the measured and calculated responses at drum centre are $2x10^{-4}$ and $4x10^{-4}$ counts respectively (per g ^{nat}U per microcoulomb) for 7MeV electrons. The discrepancy is believed to be due to use of inappropriate detection efficiencies in the calculations. Measured dependencies on azimuthal angle are in such good agreement with those calculated. Measured and calculated responses with D_2O are not in such good agreement ($0.7x10^{-3}$ and $4.4x10^{-3}$ counts at 5MeV; $5x10^{-3}$ and $17x10^{-3}$ counts at 7 MeV). The discrepancy is attributed to the softer neutron energy spectra from deuterium, and at 5 MeV.

Preliminary evaluation (B2.4)

Results to date show that there are no serious unexpected difficulties in the system as designed. The overestimate of neutron interrogation response is being investigated. It is expected that calculation methods can be refined to understand the behaviour of the assay process. Further work is planned on Magnox and PCM wastes. Various changes may be made to counter arrangements and to other aspects, to determine effects on performance.

Develop data processing model (B2.7)

The work sequence has been redefined into a series of tasks, which are equated with the boxes in the model construction block diagram /1/. Work has commenced on the first three tasks which covers the definition of signals, definition of the deterministic model, and the definition of radiological data.

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/2/ MOLESWORTH, T.V., BAILEY, M., FINDLAY, D.J.S., PARSONS, T.V., SENÉ, M.R., SWINHOE, M.T., "Development of an integrated assay facility". CEA-CEN Meeting, Non-Destructive Assay of Radioactive Wastes, Cadarache, 20-22 November 1989.

/3/ WISE, M.O., LALIES, A.A., Radioactive Waste Package Assay Facility, Data Processing Model. Plessey Controls Report TECH 9615 A2, (1989).

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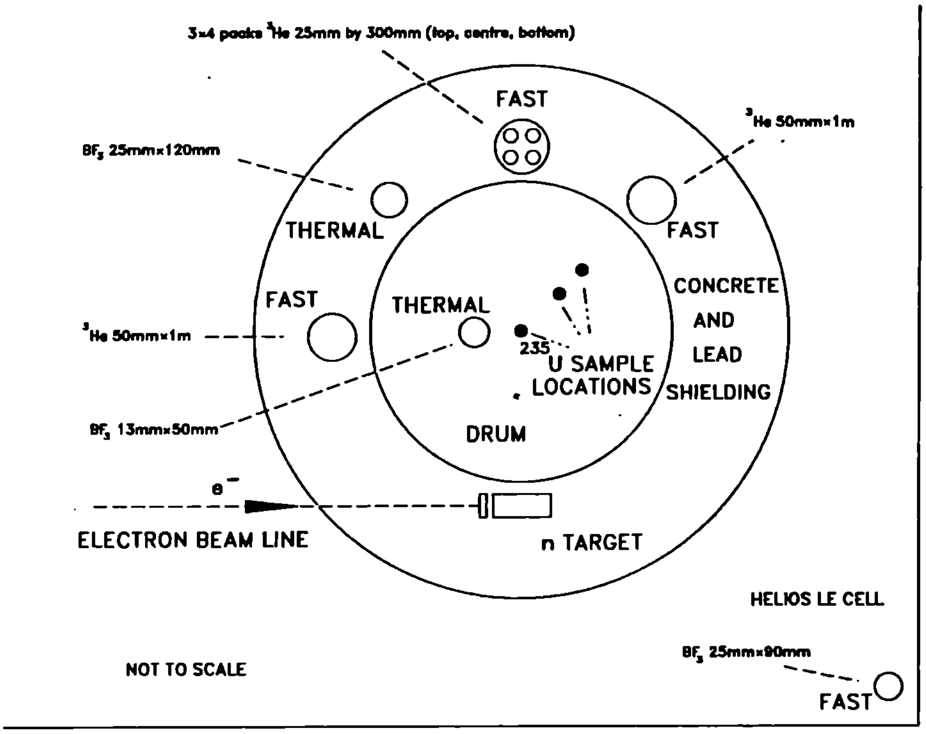
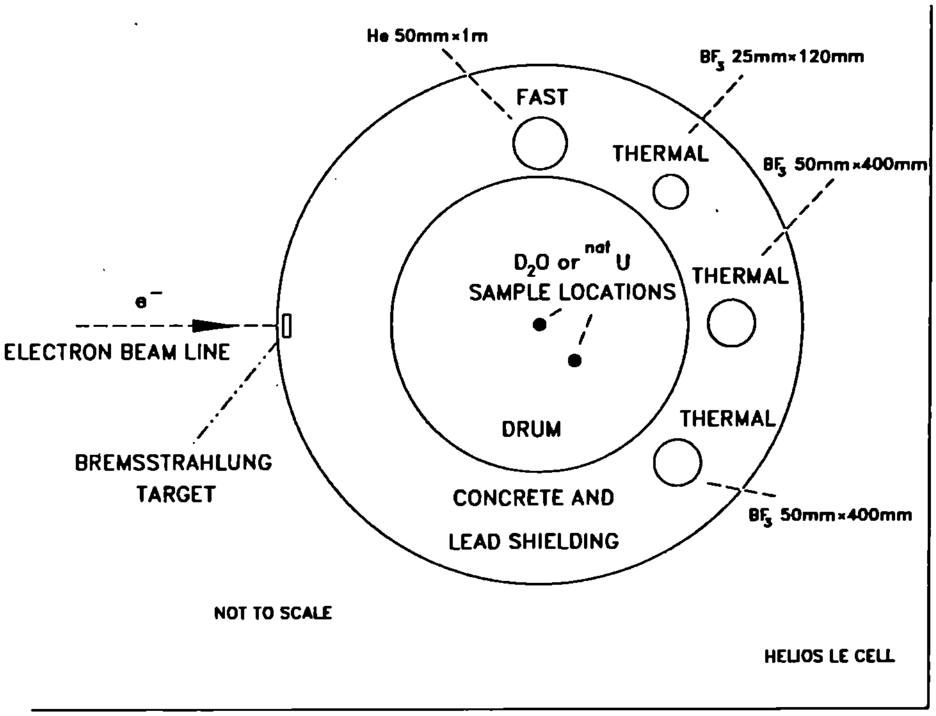


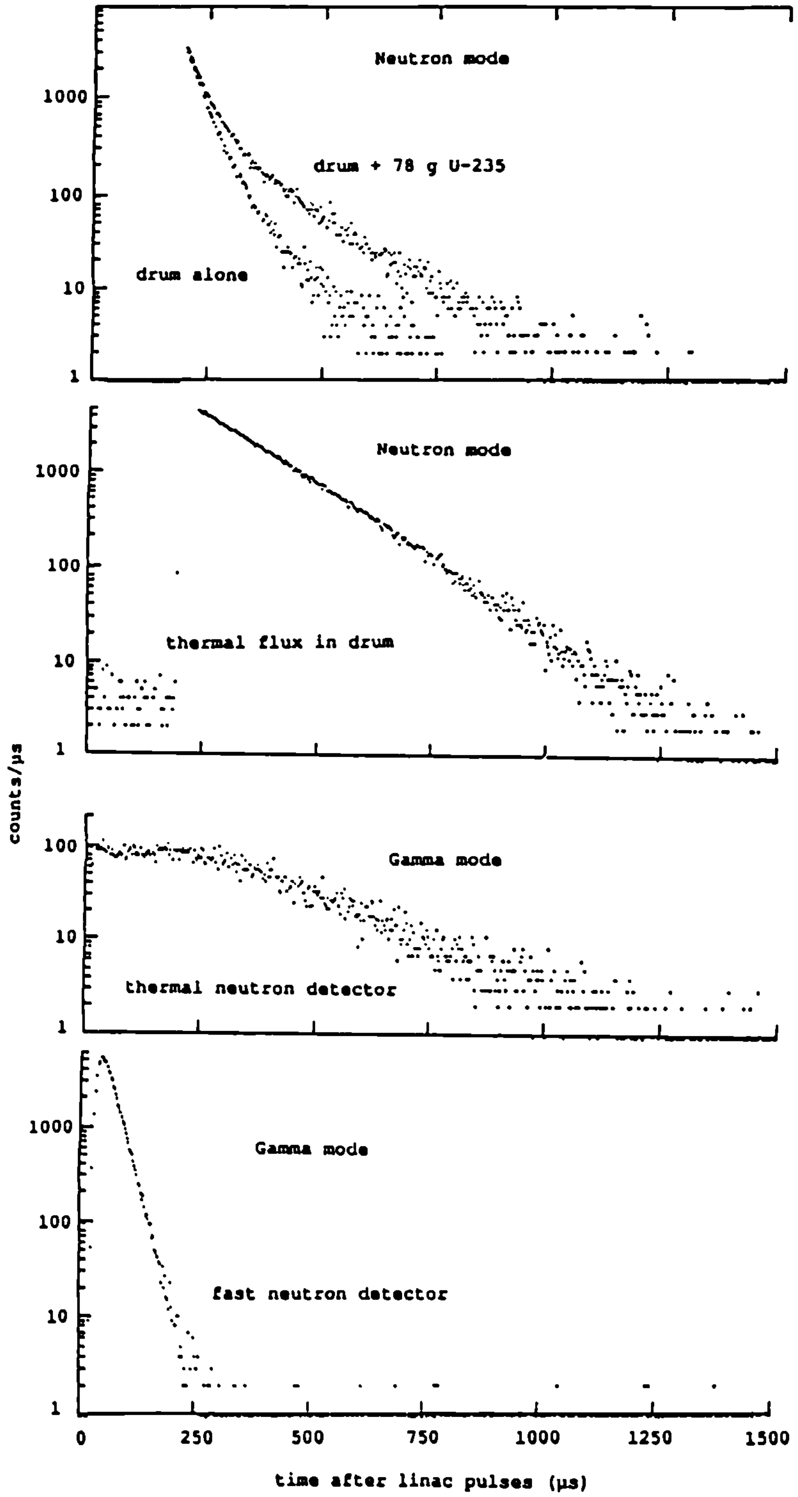
EXPERIMENTAL ASSAY ASSEMBLY – NEUTRON COUNTER LOCATIONS
(ACTIVE NEUTRON INTERROGATION MODE)

FIGURE 1



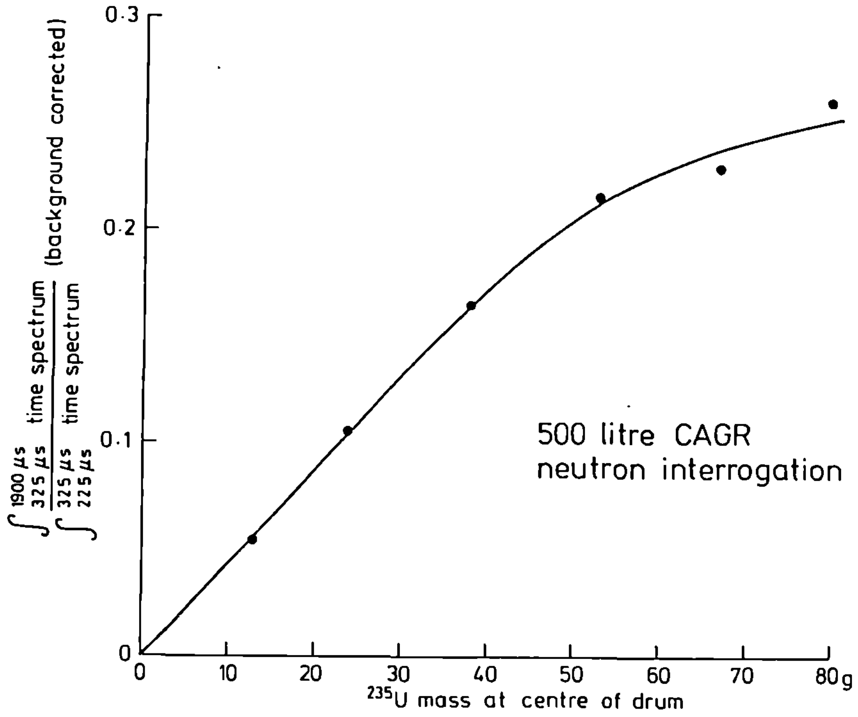
EXPERIMENTAL ASSAY ASSEMBLY – NEUTRON COUNTER LOCATIONS
(ACTIVE GAMMA INTERROGATION MODE)

FIGURE 2

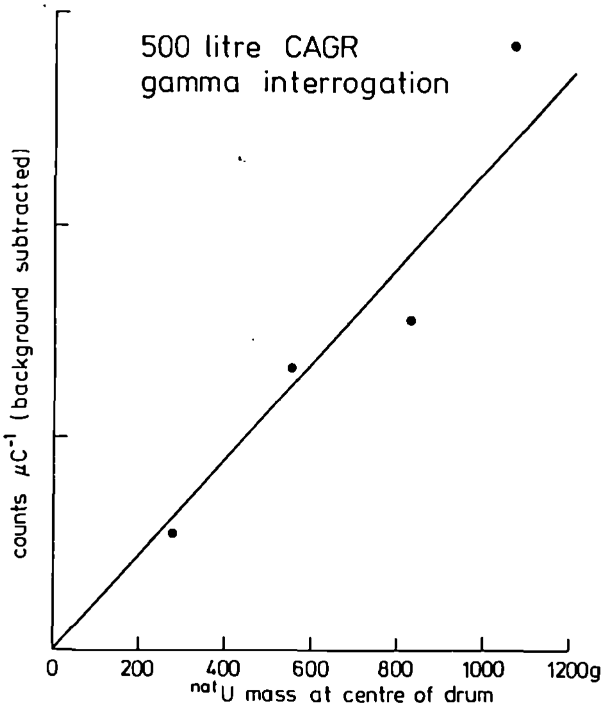


Time dependences of signals from detectors in neutron and gamma modes. Top: in neutron mode, from mid-plane 4-pack fast neutron detector, with (upper) and without (lower) 78 g ^{235}U at the centre of the drum. Second top: thermal neutron flux in drum measured using small 13 mm $^{10}BF_3$ counter described in the text. Second bottom and bottom: in gamma mode, from 225° thermal neutron and fast neutron detectors respectively as described in the text.

FIGURE 3



Variation of the response of the system in neutron mode with fissile mass at the centre of the drum. The quantity plotted is the ratio of the 325 - 1900 μs region of the time spectrum from the mid-plane 4-pack to the 225 - 325 μs component as described in the text. The line is a fit to the data points.



Variation of the response of the system in gamma mode with actinide mass at the centre of the drum. The quantity plotted is the total count from the 225° thermal neutron detector per microcoulomb of charge delivered to the radiator. The line is a fit through the data points.

FIGURE 4

EXPERIMENTAL STUDY OF GLASS SAMPLING DEVICES

Contractor: CEA, CEN-Valrhô, SDHA (France)
Contract N°: FI1W-0192
Working Period: October 1987 - December 1989
Period Covered: January 1989 - December 1989
Project Leader: A. Jouan

A. OBJECTIVES AND SCOPE

The properties and characteristics of the high level waste containment glass in the process developed and implemented in France are ensured by maintaining process parameters at their specification values and by monitoring the material throughput. French nuclear safety authorities have expressed the desire that additional glass samples be taken at the moment of casting from the melting furnace into the metal waste canister.

The proposed sampling program envisages two hypotheses:

- Development of a system that can be directly implemented in existing facilities with minimal modification work.
- Development of a new system requiring provisions in the design of future waste conditioning facilities.

B. WORK PROGRAM

The work for each development program involves designing, manufacturing, testing and qualifying the proposed technique, and ensuring reliability by demonstration in nonradioactive industrial facilities.

B.1 Device No 1
  B.1.1 Design study
  B.1.2 Device optimization
  B.1.3 Equipment manufacturing
  B.1.4 Preliminary operation testing
  B.1.5 Modification and qualification testing

B.2 Device No 2
  B.2.1 Design study
  B.2.2 Device optimization
  B.2.3 Equipment manufacturing
  B.2.4 Preliminary operation testing
  B.2.5 Modification and qualification testing

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Device No 2 was designed and built in 1989 for testing during 1990. It is only applicable to facilities now in the design stage or currently under construction, as the sampling system is an integral part of the furnace. Glass samples are taken by using an external device to move a graphite vessel into position beneath the molten glass stream. The external device consists of two automatically operated mechanical transfer systems: one horizontal (to move the sampling vessel beneath the casting stream) and the other vertical (to install and recover the vessel using a simple telemanipulated system).

Progress and Results

Samples are taken using a graphite vessel with two compartments, one above the other.

The sampling mechanism comprises a horizontal tunnel at right angles to the tube connecting the furnace and the canister. The tunnel contains a fork-type carrier mechanism for moving the sampling vessel beneath the glass casting stream. The mechanism is driven by an electric actuator mounted parallel with the tunnel.

Vertical motion is ensured by a floating worm screw system driving a yoke that slides inside a machined tube. A sampling vessel support arm is mounted on the yoke. The arm is guided by a straight ramp with a spiral portion at the lower end of the tube that causes the yoke and arm to pivot 90° for easier sample recovery.

Temperature control is obtained using a furnace to cool the sample vessel at the desired rate, and to preheat the vessel if necessary before sampling.

The control system includes two subsystems:

- The transfer sequences used to move the sampling vessel vertically and place it on the fork carrier, and to lower the vessel after sampling and cooling in the furnace, are manually initiated.
- A programmable controller, connected to a dedicated computer that integrates the glass casting flow rate, provides two programming options for sampling:
  - the horizontal transfer actuator operates at a fixed rate, and the computer controls the time during which the sampling vessel is held beneath the glass stream according to the glass flow rate;
  - the actuator travel speed is adjustable; the vessel transfer rate is determined by the computer according to the glass flow rate so the vessel is constantly in motion (it is never held in a fixed position beneath the glass stream).

  The controller also ensures sample cooling from about 500°C to room temperature at a rate of about 50°C per hour.

The horizontal electric actuator has an operating speed range of 5 to 60 $mm \cdot s^{-1}$ and includes a manual emergency control provision.

Vertical motion is ensured by a trapezoidal-thread worm screw driven by a gear motor.

The preheating and cooling furnace is an Inconel 600 tube heated by 1200 W electric resistors sealed inside ceramic collars.

The units will be assembled, and the complete sampling device will be tested during the first half of 1990.

OPTIMIZATION AND VALIDATION OF SAMPLING PROCEDURES

Contractor CEA : CEA CEN CADARACHE (FR)
Contract n° : F1W/0220 - Task 1/6
Duration of contract : From December 88 to April 90
Period covered : January 89 - December 89
Project leader : A. SAAS
Executant of task 1 : A. RAYMOND - CEN CADARACHE

A) OBJECTIVES AND SCOPE

The embedded waste characterization involves the optimization of a sampling procedure because it is necessary to be sure of the representativity of the samples to be analyzed.

More often, chemical transformations are needed for some determinations (α - and β - emitters for example) and sample amounts have to be kept to a minimum for safety purposes.

The objective of this study is the determination of sample amounts required to have a good representation of the full-scale drum in the case of homogeneous embedded wastes.

B) WORK PROGRAMME

Tests will be carried out on real embedded nuclear wastes in cement and in polymers.

The proposed tasks are as follows:

B1) Primary sampling - It will be defined the minimum of core numbers for a good representativity of the package. It will be established the data dispersal as a function of the sampling.

B2) Secondary sampling - From a representative core it will be defined the secondary sampling masses in the purpose of confirmation measurements.

B3) A correlation will be established between the measurements of 1 or 2 chemical elements and β measurements like ^{63}Ni.

B4) Determination of the homogeneity factor of some standard packages. Setting up of the level of confidence of the data.

B5) Optimization of the sampling procedure.

C) PROGRESS OF WORK AND OBTAINED RESULTS
- STATE OF ADVANCEMENT

During the first part of 1989, we started this programme by developing a mathematical model aimed to evaluate the influence of the different factors involved in the two-level sampling of small, representative specimens from full-size packages. Numerical applications were made with data from two real cement-embedded packages.

During the second semester, we set up a statistical criterium aimed to determine the homogeneity of waste forms and we tested it on the same two cement packages.

These works correspond to B.1, B.2, B.4 and part of B.5 items of this programme.

Progress and results

1) Representative sampling of small specimens in full-size packages.

Usually, this operation is made in two steps : primary sampling of cores through the total height of the package and secondary sampling of specimens at different levels of each core.

The factors influencing the global precision of the sampling procedure were identified as :

- the number and the diameter of each core,
- the number and the weight of each secondary specimen,
- the package homogeneity,
- the analytical precision.

The respective influence of all these parameters was evaluated through theoretical calculations ; it was found that in the case of 220 l drums, the optimum core diameter was 80 to 110 mm whereas the optimum weight for the secondary specimens was 5 to 10 grams.

A mathematical model was developed for practical applications with the aim to :

- calculate the minimum number of cores and the size of secondary samples to achieve a preset global precision,

- evaluate the global precision of measurements as a function of the number of primary and secondary samples, of the analytical precision and of the package homogeneity.

The application of that model to two cement-embedded evaporator concentrates led to the conclusion that in the case of homogeneous packages, a relative precision better than 25 % (2 σ) for the activity of major radionuclides could be expected from a sampling procedure involving 3 cores and 3 specimens per core.

2) Statistical evaluation of homogeneity

An analysis of variance was found useful for testing the homogeneity of waste forms, providing that a sufficient number of measurements is available. In the case of cylindric packages, it is necessary to sample a minimum of two cores and three specimens per core. Moreover, each measurement must be duplicated.

Classical calculations for an analysis of variance lead to numerical values which are compared to limits found in the Snedecor table. When these numerical values are larger than the Snedecor limit it is concluded that an heterogeneity is highly probable ; furthermore, it is possible in this way to measure the homogeneity along each direction as well as an eventual interaction between these directions.

This test, when applied to two 220 l - drums of cement-embedded evaporator concentrate, led to somewhat contradictory conclusions : one package was found heterogeneous for Co-60 but axially homogeneous for Mn-54 whereas the second package was found heterogeneous for Sr-90 but homogeneous for Cs-137. Such behaviour discrepancies were possibly related to different solubility properties ; in this respect, it will be interesting to compare these results with those obtained on polymer matrices, as it is planned for the next progress report.

MEASUREMENT OF ALPHA AND BETA-EMITTING RADIONUCLIDES IN FULL-SIZE EMBEDDED NUCLEAR WASTES

Contractor CEA	**: CEA CEN CADARACHE (FR)**
Contract n°	**: FI1 W/0220 - Task 2/6**
Duration of contract	**: From December 88 to April 90**
Period covered	**: January 89 - December 89**
Project leader	**: A. SAAS**
Executant of task 2	**: P. LOCOGE, A. RAYMOND - CEN CADARACHE**

A) OBJECTIVES AND SCOPE

The analysis of alpha and beta-emitting radionuclides in embedded nuclear wastes requires a quantitative mineralization of the samples in order to obtain homogeneous liquid solutions.

This operation leads to complicated matrices and a continuous adaptation of existing methods has to be undertaken for alpha and beta-emitting radionuclides in cement, bitumen and polymers.

B) WORK PROGRAM

In real embedded waste samples (bitumen, cement and polymers) :

B1) Determination of volatile radionuclides (^{3}H, ^{14}C).

B2) Study of specific methods for measurement of alpha-emitting radionuclides by alpha-ray spectrometry.

B3) Optimization of a special procedure for measuring ^{241}Pu by liquid-scintillation counting.

B4) Development of special procedures for pure beta-emitting radionuclides such as ^{36}Cl, ^{90}Sr, ^{129}I, ^{135}Cs, ^{93}Zr.

C) PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

During the first part of 1989, we started this programme by the development of a rapid procedure for the measurement of Sr-90 in nuclear waste solutions involving the use of crown-ethers as specific extractants.

During the second semester, we have focused on an other important and difficult to measure radionuclide, namely plutonium-241.

These works correspond to B.3 and B.4 parts of this programme.

Progress and results

1) Sr-90 determination in nuclear waste solutions

A rapide analytical method, applicable for the selective separation and determination of Sr-90 in MAW, was developed. Sr was extracted from the aqueous sample by dicyclohexano 18 crown 6 (DCH 18 C 6) in 1,1,2,2 tetrachloroethane. The beta activity of the organic extract, containing Sr-90, was measured by means of liquid scintillation counting.

The optimum conditions for Sr extraction from nitric-acide containing solutions were found as follows :

- HNO_3 concentration : 0,5 to 1 mol.l^{-1},
- NO_3^- concentration : 1,5 to 2 mol.l^{-1},

- DCH 18 C 6 concentration : 0,05 to 0,1 mol.l^{-1},
- $V_{org.}/V_{aq.}$: 0,5,
- Sr^{++} (carrier) concentration : 20 mg.l^{-1}

Finally, this procedure was successfully applied to the analysis of a real MAW sample from La Hague reprocessing plant. In this case, the separation yield was 91 %.

2) Determination of Pu-241

The importance of determining Pu-241 in radioactive wastes is emphasized by the long half-life and the high energy of some of its daughter isotopes. In that respect, two procedures were developed in our laboratory, both of them involving liquid scintillation counting as the measuring technique :

- a complete method, applicable in every case, based on a specific Pu extraction on anion-exchange resin, allowing the quantification of not only Pu-241 but also of the alpha activity,

- a simplified method based on liquid-liquid extraction with T.T.A in these cases where the total alpha activity is larger than the beta/gamma activity.

The application of these two procedures was demonstrated through the analysis of Pu-241 in four different types of samples :

- cement-embedded radioactive wastes,
- bitumen-embedded chemical sludges,
- incineration ashes,
- leachates of embedded incineration ashes.

In all these samples Pu activities equivalent or even larger than that of the other Pu isotopes were observed. The separation yields were 90 to 95 % as measured from Pu-239 or from a Pu-236 tracer.

NON DESTRUCTIVE ANALYTICAL PROCEDURE FOR ALPHA AND LONG-LIVED BETA NUCLIDES IN EMBEDDED WASTE

Contractor : CEA Cadarache, France
Contract n° : FI1W-0220 task 3/6
Duration of contract : 1st December 1988 to 30 April 1990
Period covered : 1st December 1988 to 31 December 1989
Project leaders : A. SAAS
Executant of task 3 : J.F. MONTIGON

A/ OBJECTIVES AND SCOPE

The purpose of the programme is to develop non-destructi techniques for determining the amount of alpha and long-liv beta radionuclides in embedded waste. The following work i scheduled :

- qualification of an alpha evaluation procedure usin passive neutron measurements,
- feasibility study on non-destructive beta measurements.

B/ WORK PROGRAMME

2.2 - Alpha experiments programme with a device of CEA make comprising 18 sensor He-3 tubes, driven by a microcomputer and performing passive neutron counting :

2.2.1 - Experimental study of the influence of the position of fissile material inside measurement cell;

2.2.2 - Experimental study of the influence of the isotopic composition of fissile material on the device's response.

2.3 - Beta experiments with a commercial beta analyzer (NOVELEC, France) wich will be backed by a gamma-spectrometry unit (CANBERRA, USA) :

2.3.1 - Detection of pure beta emitters through substracting measurements made with a gamma detector from the beta + gamma measurements performed with the beta detector;

2.3.2 - Identification of pure beta emitters through measurements of maximum beta energy by differential shielding.

C/ PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The feasibility study on beta nuclides non-destructive measurement on samples of solid waste has begun. The beta detector has been calibrated in a range of energies spreading from 150 keV to 2300 keV.

The alpha measurements programme has not yet started.

Progress and results

2.3 - The beta measurements unit (maker : NOVELEC) has been started and its electronics has been adjusted. The detector has then been calibrated (determination of the detector yield, depending upon the source energy, for each distance allowed by the device). The reference sources employed are listed below :

Isotope	E max (keV)
C-14	156,5
Co-60	317,9
Cs-137	511,5
Na-22	545,5
Cl-36	709,5
Tl-204	763,4
Sr+Y-90	546 and 2284

DETECTION AND MEASUREMENT OF GAS GENERATION FROM RADIOLYSIS BY WASTE/MATRIX INTERACTION (BITUMEN)

Contractor : CEA Cadarache, France
Contract n° : FI 1W-0220 task 4/6
Duration of contract : 1st December 1988 to 30 April 1990
Period covered : 1st December 1988 to 31 December 1989
Project leaders : A. SAAS
Executant of task 4 : J.F. MONTIGON

A/ OBJECTIVES AND SCOPE

This programme aims at qualifying the existing prototypes of monitoring device designed for 200 l bitumen drums.

These devices allow :

- the monitoring of pressure and temperature inside the atmosphere of the drum,
- the sampling of this atmosphere by coupling a reference capacity in which vacuum has been made,
- the evaluation of bitumen swelling by measurement of the final pressure in the reference capacity.

B/ WORK PROGRAMME

2.2 - Experimental checking of gas-tightness of the device.

2.3 - Study of the sweeping gas : optimization of the sweeping gas and evaluation of the efficiency of sweeping.

2.4 - Study of the representativity of the gas samples taken out of the atmosphere of the drum by means of the device.

2.5 - Testing the monitoring device on some 200 l drums of industrial bitumized waste.

C/ PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In 1989, no significant achievements have been obtained on this item because the laboratory has undertaken in priority the work on task 3 and 6 of the contract.

Progress and results

2.2 - The experimental checking of gas-tightness of the device has begun.

DETECTION AND MEASUREMENT OF EXTERNAL GAMMA IRRADIATION - INDUCED GASES EVOLVED BY BITUMINISATES. EVALUATION OF THE PART OF RELEASED AND TRAPPED GASES IN ORDER TO PREDICT FULL-SIZE DRUMS SWELLING.

Contractor : CEA - CEN CADARACHE - FRANCE
Contract n° : FI 1W/0220 Task 5/6
Duration of contract : from December 88 to April 90
Period covered : January 89 - December 89
Project leader : A. SAAS
Executant of task 5 : S. CAMARO - CEN CADARACHE

A - Objectives and scope

The aim of this program is to study the following phenomena :

- production and evolving of radiolytic gases
- transfer ability of these gases by diffusion
- swelling and identification of the responsible gases

by the evaluation of the following parameters :

- radiolytic yield
- diffusion coefficient
- swelling rate definited as the volume's increase in regards to the initial volume.

These data will be useful for the modelisation step of full-size drums swelling.

B - Work programme

B1. Gamma induced swelling of pure bitumen and bituminisates type A (CoS process) and B (Te-Cu process)

B2. Releasing of gamma induced radiolytic gases

B3. Development of an extraction procedure of gamma induced trapped gases.

C - PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The program items 1 and 2 have been achieved : under gamma-irradiation, bitumen (80/100) and bituminisates (A and B) swelled in different manner according to the wasteform type. The gaseous evolving also varied as a function of waste nature.

A trapped-gases extraction procedure was performed. This study proved more awkward than previously projected and the amount of gases responsible for the swelling was so small in regards to the evolved gases that we don't propose any further development on this program item. On the other hand, we chose to study in more detail the diffusion ability (additional item 4).

This new orientation cancels the previous proposal relative to the influence on swelling and gaseous evolving of parameters such as nature of wasteform or bitumen, dose-rate ...

Progress and results

In order to simulate the behaviour of bituminisates under gamma-irradiation, lab samples issued from inactive industrial drums of two types (A (CoS process) and B (Fe-Cu process)) and pure bitumen (80/100) were submitted to external gamma-rays (^{60}Co). The initial filling was 50 %.

Under gamma-irradiation, the samples swelled. Swelling was followed by introducing water in the free-left volume. Swelling of bituminisates was different from that of pure bitumen and varied as a function of the nature of wasteform.
A serrated swelling varying around the midvalue of 15 %

(amplitude 5 %) was observed for pure matrix. Bituminisates A and B had different initial kinetics (B > A) but tend both to reach the same limit of 45 %. These initial variations may be explained in either of two ways : either by a more important radiolytic gaseous evolving or a smaller transfer ability for type B than A.

The repartition of bubbles in the heart of samples was heterogeneous : appearance of small bubbles down the samples and big ones (probably issued from coalescing phenomena due to ascending migration) at the top.

A new device for swelling measurement is being studied in order to allow :

- irradiation in less oxydant and more representative of full scale drums conditions

- simultaneous analysis of radiolytic gases

Gaseous analyses performed on samples (bitumes, bituminisates type A and B) irradiated in gastight vessel showed up the appearance of :

- H_2 for type B
- $H_2 + CO_2$ for type A

A time-lag was observed on H_2 evolving curves, probably due to a preliminary step of gaseous sorption into bituminisates. The evolved H_2 quantity - expressed in ml TPN/kg bitumen - is :

- about seven times lesser for type A
- a little more important for type B

than for pure bitumen

Some components of wasteform, appearant in waste of type A and (partially or completely) exempt from type B seem to inhibit swelling (they act as hydrogenation catalysts).

CO_2 evolving, directly proportional to the dose, probably originated from area interactions between atmospheric O_2 and bitumen.

The procedure of extraction of trapped-gases responsible for swelling was developed on both types of bituminisates. The results - expressed in terms of difference "irradiated minus non-irradiated" - showed up :

- positive values (but negligible towards evolved gases) for H_2 and hydrocarbons, evidencing radiolytic origin.

- negative values for N_2, N_2O and CO_2, disclosing thermolytic or reactional source.

The trial was operated under vacuum at temperature included between 20 and 120°C by steps of 20°C, on blank and irradiated samples.

This study proved more awkward than previously projected and became tricky by the following facts :

- gases were already trapped (by sorption or dissolution) in non-irradiated samples

- low kinetics rate reactions happened as soon as 80°C

- nature and reactivity of gases depended on nature of the wasteform.

MEASUREMENT OF LIQUID IN FULL-SCALE DRUM

Contractor : CEA Cadarache, France
Contract n° : FI 1W-0220 task 6/6
Duration of contract : 1st December 1988 to 30 April 1990
Period covered : 1st December 1988 to 31 December 1989
Project leaders : A. SAAS
Executant of task 6 : J.F. MONTIGON

A/ OBJECTIVES AND SCOPE

The goal of this programme is to develop an experimental technique for evaluation of the water content in embedded waste.

A commercial moisture measurement unit will be employed; it uses an isotopic neutron source. The back-scattered neutrons are counted to give an evaluation of the hydrogen content in the object being tested, thus the water content after calibration experiments.

B/ WORK PROGRAMME

2.2 - Tests on cemented waste

2.2.1 - Tests with one type of detector, designed to be put into a hole drilled (without water) in the package.

2.2.2 - Tests with another type of detector, designed to lay upon the outer surface of the package.

2.2.3 - Evaluation of the ability of both types of detectors, for :
- the scanning of water content in the package,
- the determination of relative water content by comparison between reference drums.

2.3 - Determination of a methodology (based on the tests of § 2.2) for the control of the water content in cemented waste with a neutronic moisture meter.

2.4 - Extension of the methodology to other matrixes :

2.4.1 - Test measurements

2.4.2 - Trends for the extended methodology.

C/ PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In 1989, the two neutronic moisture meters required for the study were supplied and their calibrations began.

Progress and results

2.2 - The depth gauge : NARDEUX "SOLO 40" and the surface gauge : LINDQVIST "TROXLER" have been supplied.

2.2.1 - The determination of the constants for cemented waste, from which the SOLO 40 will compute automatically the water content, is under way.

2.2.2 - The calibration of the TROXLER gauge has been achieved on layers of wet sand inside a 200 l drum. The range of thicknesses investigated spreads from 50 mm to 800 mm; three water contents were used : 5%, 10% and 15% (in weight); three counting times were tested : 7,5 s - 15 s - 60 s.

SAMPLING METHODS AND NON-DESTRUCTIVE EXAMINATION TECHNIQUES FOR LARGE RADIOACTIVE WASTE PACKAGES

Contractor:	Taylor Woodrow Construction Ltd
Contract No:	FI1W 0223 UK(H)
Duration of contract:	September 1988 - February 1990
Period covered:	January - December 1990
Project Leader:	Dr T H Green

A. OBJECTIVES AND SCOPE

The UK Department of Environment (DoE) has indicated that the overall Quality Assurance Programme for the management of radioactive wastes will probably involve the Quality Checking (QC) of full-scale waste packages. DoE-funded programmes have therefore been set up to establish the availability of destructive (DT) and non-destructive (NDT) test methods for both encapsulated Intermediate Level (ILW) and Low Level (LLW) waste packages. This research programme (jointly funded by CEC/DoE) was designed to augment the scope of the above programmes.

The objectives of the project are:

- To provide experimental data on the destructive sampling and analysis of encapsulated ILW
- Comparison with similar European CEC-funded programmes
- To provide experimental data on NDT examination of LLW packages.

The results will be used as input to the design of facilities in the UK for QC of both ILW and LLW packages.

B. WORK PROGRAMME

The work programme consists of seven tasks:

1. To identify and develop techniques which may be used for the extraction of material from waste packages by coring techniques.
2. To compare the conclusions from the coring programme with those from similar CEC programmes (Kfa, West Germany; CEA/CEN-Cadarache, France; and SCK/CEN-Mol, Belgium).
3. To prepare test pieces and representative samples from the extracted cores in (1) for chemical and physical analyses.
4. To assess the importance and relevance of changes to the sample arising from modifications engendered by the coring processes.
5. To develop rapid, non-labour intensive methods for the dissolution of powdered samples of cemented intermediate level waste.
6. To investigate the use of beta/gamma correlations as an aid to determining the radionuclide inventory of cemented intermediate level waste.
7. To assess the potential of X-ray video imaging techniques for the determination of spatial distribution and partial identification of the contents of drummed low level waste.

C PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

This report covers the period January - December 1989. The main achievements are:

- Demonstration of remotely-operated vertical and horizontal mode coring techniques using either air or water coolant for destructive sampling of 3:1 Blast Furnace Slag: Ordinary Portland Cement (Task 1).
- Development of techniques for dissolution of active BFS:OPC samples using fusion techniques (Task 5).
- Comparison of X-ray techniques for NDT examination of drummed LLW (Task 6).

1. IDENTIFICATION AND DEVELOPMENT OF TECHNIQUES FOR EXTRACTION OF MATERIAL FROM WASTE PACKAGES BY CORING TECHNIQUES

Work has continued on the coring and extraction of cored samples from drums of simulant ILW cement matrices (BFS:OPC) using a specially-designed coring rig. The rig contains remotely-operated water-cooled and air-cooled core bits which can operate in a horizontal as well as a vertical mode.

The experiments conducted to date have demonstrated the feasibility of coring and core extraction by remote-controlled methods with both the drum and the coring equipment in either horizontal or vertical mode. The advantages and disadvantages of vertical and horizontal coring are summarised in Table 1. Based on this work, the preferred orientation of the drum and equipment is the horizontal position.

2. COMPARISON OF UK CORING PROGRAMME AND CONCLUSIONS FROM THOSE FROM SIMILAR CEC PROGRAMMES (Kfa, WEST GERMANY; CEA/CEN-CADARACHE, FRANCE; SCK/CEN-MOL, BELGIUM)

Two technical visits have been made:

- Visit to UK (QC Laboratory, Winfrith, Dorset) by German and French representatives.
- Visit to Germany (Jülich) by UK representatives.

The visit to France (Cadarache) is scheduled for early March 1990.

3. PREPARATION OF TEST PIECES AND REPRESENTATIVE SAMPLES FROM EXTRACTED CORES FOR CHEMICAL AND PHYSICAL ANALYSES

Cemented homogeneous waste cores have been sectioned using a hacksaw without the use of a lubricant. Tests have been conducted (using hollow drill-bits and a vacuum collection system) to extract powdered sub-samples from 100mm diameter cementitious cores.

4. ASSESSMENT OF IMPORTANCE OF CHANGES TO SAMPLES ENGENDERED BY WATER-COOLED CORING OPERATIONS

Trace levels of inactive species (Na, K, Cs, Sr, Fe, Co) have been added to BFS:OPC and cores made up and allowed to cure for periods in excess of 3 months. The cores have been exposed to water for varying times and sub-samples analysed to determine whether leaching has occurred. The results are currently being assessed.

5. DEVELOPMENT OF RAPID, NON-LABOUR INTENSIVE METHODS OF DISSOLUTION OF POWDERED SAMPLES OF CEMENTED INTERMEDIATE LEVEL WASTE

Dissolution methods have been developed for powdered 3:1 BFS:OPC samples. The best technique is fusion at 850 - 1000°C, using lithium metaborate flux, and quenching in 3M nitric acid. The radioactivity (Cs-137 and Co-60) either stays with the sample, or is contained in the nitric acid vapour trap. The technique is capable of dissolving samples weighing several grams, and the process is currently being optimised to increase sample throughput.

6. INVESTIGATION OF THE USE OF BETA/GAMMA CORRELATIONS AS AN AID TO DETERMINING THE RADIONUCLIDE INVENTORY OF CEMENTED ILW

Small test BFS:OPC samples containing a variety of beta- and gamma-emitters (Co-60, Cs-137, Sr-90) are currently being dissolved and analysed to provide information on the reproducibility and accuracy of beta/gamma ratio measurements.

7. ASSESSMENT OF POTENTIAL OF VIDEO X-RAY FLUOROSCOPY FOR NDT OF LLW DRUMS

Five different X-ray methods were evaluated for NDT of contents of 200 litre drums of low level waste. The Rolls Royce video X-ray fluoroscopic system is the preferred technique.

Table 1: Comparison of Vertical and Horizontal Coring Modes

	Vertical Coring	Horizontal Coring
Shielded Facility	Requires a high working ceiling in the cave line	Normal working height but requires a larger plan area than for vertical coring
Mechanical handling of waste drum	Drum lifting and positioning is difficult using conventional cranage	Drum has to be tilted through 90° but can be easily handled using conventional cranage
Maintenance of coring machinery	Equipment will be difficult to remove for maintenance (because of height)	Removal of equipment for maintenance will be straightforward
Water coolant	Water will be retained in core hole	Water will drain out of core hole
Coring equipment	Self feeding for homogeneous wastes	Requires positive drive on core drill carriage
Core removal	Core difficult to extract and could slip out of core tool during removal from the waste drum	Cores are easy to extract and remain in coring tool barrel during removal from the waste drum

INVESTIGATION ON THE DETERMINATION OF DISPOSAL CRITICAL NUCLIDES IN WASTE FROM PWR POWER PLANTS.

Contractor : ONDRAF/NIRAS, Brussels, Belgium
Contract No : FI1W-0225-B (TT)
Duration of contract : September 1988 - December 1989
Period covered : January 1989 - December 1989
Project leader : J.M. DECONINCK

A. OBJECTIVES AND SCOPE.

Safety studies related to the disposal of low- and intermediate-level waste indicate that the long-term risk is determined by the presence of longer-lived nuclides such as C_{14}, Ni_{59}, Ni_{63}, Sr_{90}, Nb_{94}, Tc_{99}, I_{129}, Cs_{135}, Cs_{137} and transuranium elements. As most of these nuclides are very difficult to measure, the correlation between these nuclides and other easily measurable nuclides has been investigated for some typical waste streams, e.g. waste from the operation of PWR power plants, and correlation factors have been proposed by several authors. The range of these factors is, however, relatively large for certain nuclides, and some of them are recognized to be plant-specific.

The objectives of this investigation are :

1) to verify the validity of the correlation factors on the relatively homogeneous range of PWR power plants operated in Belgium,
2) to establish the necessary techniques to assay, both in a practical and reliable way, the concentrations of these nuclides in typical waste streams arising from the operation of PWR power plants.

B. WORK PROGRAMME.

2.1. Investigation on non-conditioned waste.

2.1.1. Determination of appropriate sampling methods and collection of selected representative samples of primary water, evaporator concentrates, ion exchange resins and filter cartridges in the different power plants operated in Belgium.

2.1.2. Preparation and radiochemical analysis of the samples in order to measure their content of C_{14}, Ni_{59}, Sr_{90}, Nb_{94}, Tc_{99}, I_{129}, Cs_{135}, Cs_{137} and transuranium elements.

2.1.3. On the basis of the results, determination of an analysis method that can be industrially applied.

2.1.4. Preliminary investigation of the possible variations in the radiological composition of the waste as a function of plant-specific parameters.

2.2. Investigation on conditioned waste.

2.2.1. Preparation of a set of ten full-scale packages containing representative samples of cemented evaporator concentrates, I-X resins and filters. If possible, the packages are prepared from the same waste batches as those analysed in the first part of the programme.

2.2.2. Non-destructive examination of the waste packages by gamma-spectrometry with the aim of measuring the quantity of Cs_{137} and Co_{60} included.

2.2.3. Assay of the disposal critical radionuclides included in a selection of these packages by destructive analysis (core drilling and analysis as per 2.1.2. above).

2.3. Comparison of the results obtained by destructive analysis on non-conditioned waste, non-destructive and destructive analysis on conditioned waste packages. Verification of the applicability of correlation factors.

C. Progress of work and results obtained.

With the exception of part of the ion exchange resins, the collection of non-conditioned waste samples, and the fabrication of conditioned waste drums provided for in the experimental section of the work have been completed. The various sample preparation and analysis techniques have been defined and tested.
The analysis of the primary water and evaporator concentrate samples and of the available resin samples has almost been completed. Major difficulties were encountered with the analysis of the evaporator concentrates, owing to the presence of an insoluble solid fraction.
Before being destructively analysed, the selected filter cartridges were examined by Y-spectrometry in view of determining their ^{60}Co and ^{137}Cs content. The special equipment required for their destructive analysis has been installed and the analyses are in progress.
The Y-spectrometry equipment for the non-destructive examination of the conditioned drums has been calibrated and automated, and the examination of the selected drums is in progress. The equipment necessary for sampling these drums in view of their destructive analysis has been installed and cold tested.

2.1. Investigation of non-conditioned waste.

2.1.1. Collection of a selection of representative non-conditioned waste samples.

The collection of the primary water, evaporator concentrate and filter cartridge samples, selected at the power plants of Doel and Tihange, was completed. For the collection of the resin samples at Tihange, a special sampling equipment was installed at the end of the year and a first set of samples was taken.

2.1.2. and 2.1.3. The radiochemical analysis of the primary water samples has been completed. The analysis method used, and the main results are summarized in table 1. For certain nuclides, major differences exist between the samples analysed.
For the analysis of the evaporator concentrates, difficulties were encountered with the separation and the analysis of the solid fraction present.

The samples were finally separated in three fractions, each of them being analysed separately : centrifuged solution, soluble fraction of the centrifuging residue, and insoluble fraction of this residue. An appropriate flux was required for the analysis of this last fraction, which essentially consisted in silicate compounds. As illustrated in table 2, considerable differences exist both in the physical and radiochemical composition of the samples. As a consequence, most of the separation and analysis techniques used for determining the different critical isotopes had to be recalibrated for each sample analysed.

A special ultrasonic cleaning/dissolution equipment was built for the destructive analysis of the filter cartridges. The preliminary tests showed that the activity is not distributed homogeneously over the filters, and that the activity deposited on the filters cannot be removed successfully by ultrasonic cleaning. Figure 1 illustrates the non-uniform distribution of ^{60}Co and ^{137}Cs along the height of the filter, as measured by Y-scanning. As a consequence, it was decided to dissolve the whole filter material using boiling nitric acid. This work is in progress.

2.2. Investigation of conditioned waste.

2.2.1. Preparation of representative full-scale cemented waste packages.

Seven packages (on the ten provided) were prepared. The other three packages with cemented resins are expected to be prepared in the coming months.

2.2.2. Non-destructive examination of the waste packages by gamma-spectrometry.

The method employed is a variant of the widely used method of segmented gamma scanning. An important effort was made to improve the reproducibility of the measurements by automating the whole system. The system was also calibrated in function of the geometry and of the content of the drums to be analysed, both on a theoretical and experimental basis.

2.2.3. Destructive examination of a selection of these drums.

A core drilling machine has been installed and cold tested. The dissolution method necessary to prepare the samples for analysis has been set up on simulated inactive material.

TABLE 1 - RESULTS OF THE α, β,γ MEASUREMENTS ON THE PRIMARY REACTOR WATER SAMPLES (Bq/l)												
Nuclide	Analysis method	Detection limit	Sample									
			KCD_1	KCD_2	KCD_3	KCD_4	CNT_1	CNT_2	CNT_3	$CNT_{1'}$	$CNT_{2'}$	$CNT_{3'}$
^{60}Co	direct Y-spectrometry	150	286	170	115	215	1600	3200	420	1761	17316	2945
^{137}Cs	direct Y-spectrometry	150	800	2420	42600	28300	43500	3250	550	3833	< 230	1228
^{94}Nb	direct Y-spectrometry	150	a)	a)	a)	a)	a)	a)	a)	a)	a)	a)
^{14}C	acidolysis + LSC	1	800	220	260	793				392	271	2732
^{59}Ni	separation + X-ray spectrometry		a)	a)	a)	a)				a)	a)	a)
^{63}Ni	separation + LSC	10	a)	100	a)	a)				a)	4100	a)
^{89}Sr ^{90}Sr	separation + ^{90}y counting	1 1	 4	 a)	 1	 2				820 13	72 1.4	370 3.9
^{99}Tc	separation + LSC	50	1300	270	1700	530	a)	320	a)	330	a)	300
^{129}I	separation + LSC	5	21.2	6.1	21.6	17	a)	17.4	8.5	a)	35.4	a)
^{135}Cs	separation + mass spectrometry	0.2	a)	a)	a)	a)	0.2	a)	a)			
Total α	α -counting	30	a)	a)	a)	a)	a)	a)	a)	a)	a)	a)

Note : a) below the detection limit.

TABLE 2 EVAPORATOR CONCENTRATES - DISTRIBUTION OF THE β-γ ACTIVITY OVER THE DIFFERENT FRACTIONS PRESENT										
Sample n°	Quantity of centrifugation residue (g/l)		Activity (Bq/l)							
	Total	Insoluble	Centrifugate		Soluble residue		Insoluble residue		Total	
			^{60}Co	^{137}Cs	^{60}Co	^{137}Cs	^{60}Co	^{137}Cs	^{60}Co	^{137}Cs
1	60.70	1.62	$4.66.10^5$	$4.89.10^5$	$7.5.10^6$	$8.29.10^4$	$1.94.10^5$	$< 7.10^2$	$8.16.10^6$	$5.72.10^5$
2	64.91	6.32	$9.37.10^4$	$5.37.10^5$	$2.09.10^7$	$5.45.10^5$	$2.2.10^6$	$< 4.10^3$	$2.32.10^7$	$1.08.10^6$
6	1.84	0.25	$4.26.10^4$	$5.28.10^4$	$1.59.10^6$	$3.26.10^3$	$1.15.10^5$	$< 2.10^2$	$1.75.10^6$	$5.61.10^4$
8	3.52	0.23	$6.4.10^4$	$4.55.10^4$	$1.17.10^6$	$7.2.10^3$	$1.04.10^5$	$< 2.10^2$	$1.33.10^6$	$5.27.10^4$
9	5.45	0.29	$5.53.10^4$	$8.28.10^4$	$1.68.10^6$	$8.0.10^3$	$2.71.10^5$	$< 4.10^2$	$2.01.10^6$	$9.08.10^4$
10	1.98	0.21	$1.43.10^5$	$7.5.10^5$	$6.51.10^4$	$8.91.10^3$	$4.62.10^3$	$< 3.10^1$	$2.13.10^5$	$7.59.10^5$

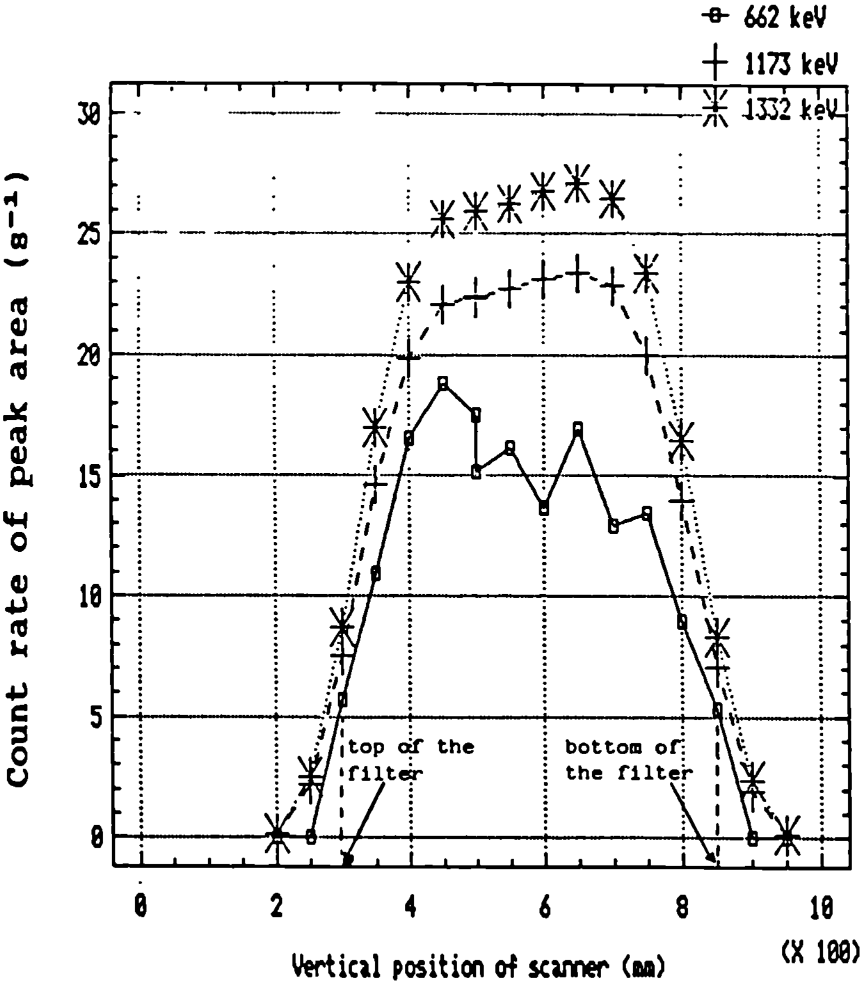


Fig. 1 : Filter cartridge LWC-FR-07 - distribution of the activity along the height (The data for ^{137}Cs are multiplied by 100).

DEVELOPMENT OF A NON DESTRUCTIVE METHOD AND A CALCULATION PROCEDURE FOR THE IDENTIFICATION AND QUANTIFICATION OF GAMMA EMITTER RADIONUCLIDES IN PACKAGES CONTAINING LRW & MRW

Contractor:	CIEMAT, Spain
Contract No.:	FI 1W.0226.E
Duration of contract:	Oct.1988-March.1990
Period covered:	1989
Project leader:	J.A.Suárez G. del Rey

A.OBJECTIVES AND SCOPE

The purpose of this research is the development of an experimental technique and a calculation procedure for the identification and quantification of gamma emitters in drums containing low and medium level radioactive wastes.

The objectives of the project are:

* To study and to stablish several methods to quantify gamma radionuclides in drums containing homogeneous matrices of cement with liquid radioactive wastes, heterogeneous matrices in several cases and radiactive sources in concrete that allow us the determination with the lowest posible margin of error.

* To develop a methodology and computer codes to quantify the activity and to determine the geometrical distribution of gamma radionuclides in drums containing real radwastes.

B.WORK PROGRAMME

1.3 Design of the collimator for the detection system. Determination of the solid angle of measurement.

2.1 Preparation of homogeneous packages. Standard and known activity packages.

2.2 Preparation of compacted and uncompacted heterogeneous solid wastes in drums.

2.3 Preparation of compacted and uncompacted heterogeneous solid wastes in drums, with previously armered interiors.

2.4 Preparation of drums with a special concrete shield for cartridge-filters. Preparation of standard cartridge-filters.

4.1 Quantification of homogeneous packages. Loss efficiency due to dead time. Attenuation factors due to the density. Homogeneity test.Calibration curves

4.2 Quantification of compacted and uncompacted solid heterogeneous packages. Influence of position, collimation, form and size of the wastes.

4.3 Quantification of packages with cartridge-filters.

C. PROGRESS AND OBTAINED RESULTS

The main tasks carried out during this period were focused in preparation of standard radioactive packages in the different geometries programmed and its measurement to perform the efficiency calibration curves.

Several methods were developed to quantify the gamma emitters in each geometry. A large number of parameters That were not considered in the initial program have been find.

This is the cause of a short delay in the schedule along with the exahaustive control of all variables that we were programmed to achieve the quantification with a minimum of error.

1.3 Design of collimator.

A collimator was designed as a set of lead pieces, the central one is changeable in order to test several forms and sizes of collimation. A study of the real solid angle seen by the detector was carried out. The results show that the theorethical values are coincident with the experimental values obtained with a maximun error of 7%.

2.1 Preparation of homogeneous packages.

The standard radioactive packages were prepared with Eu-152 and the margin of densities tested was 1.7 to 2.0 g/cc. From the dificulties found to prepare the extreme values in real scale, mock-up scale packages were prepared that allow us a larger range of densities and an easier preparation due to their smaller size.

2.2.2.3 Preparation of heterogeneous packages with and without concrete shields.

The difference between these packages is a 7 cm thickness armored concrete shield that one of them presents.

To prepare these kinds of packages a system to place the radioactive standards was designed. The system allows to place the sample in several positions in the 3 dimensions of the drum.

The densities to be tested are in the range of 0.10 to 1.00 g/cc. The matrices of wastes were simulated using paper (one of the matters that we can find in these packages) except the density of 1 g/cc which was simulated with water.

The radioactive samples were prepared in paper with Eu-152 to calibrate and with Mn-54, Co-60 and Cs-137 to carry out the quality control of the calibration.

2.4 Preparation of cartridge filters packages

A drum with a special design for cartridge filters was prepared. It consists of a drum with a concrete shield 18.5 cm thickness that provides a cylindrical hole of 55 cm in height and a 20 cm diameter where a maximun of 4 cartridge filters can fit.

Two type of cartridge-filters were prepared: standard cartridge filters with Eu-152 to calibrate, and a known activity cartridge filter to check the calibration.

4.1 Quantification of homogeneous packages

To quantify the packages with homogeneous matrices it was first necessary to determine the efficiency loss due to the dead time to transform the obtained results (Fig 1). The second step was to establish the efficiency loss due to the matrix density which depends on the photopeak energy (Fig 2). Another parameter was the determination of the homogeneity of the package calculating with a rotation of the drum in 8 vertical steps and measuring the standard deviation of the peak areas into the measurement. if $\sigma\%\leq 10\%$ then the package is considered homogeneous.

Finally the calibration was done using the mock-up scale packages prepared in 2.1 since these provide us with the same results as full scale when multiplied by 8 (Fig3).

4.2 Quantification of compacted and uncompacted Heterogeneouus packages

The preliminary tests were carried out to determine the influence of several variables in the efficiency calibration.

The first was the form and size of the radiactive sample simulated by a paper with Eu-152. Using 7 shapes and 4 sizes in a rotating measurement of 8 vertical segments, we showed that the shape and the size do not influence in the measurement.

The second study concerned the position of the sample in the drum and it was studied in function of the colimation diaphragm and the drum-detector distance (variable solid angle).

The study was performed using static and rotating counting, in Fig 4. we can see that there is an efficiency loss with static counting and a gain of efficiency as the sample moves away from the drum surface to the center in rotating measurement. In this way we can establish counting conditions to determine these packages where the position in the drum has either no influence on the efficiency or an influence lower than the experimental error.

4.3 Quantification of packages for cartridge filters.

The quantification was carried out by first testing the influence of the concrete matrix due to the possible eccentricity of the central hole. After that we determine the influence of the number of filters and their position in the hole. 11 geometries were designed as the more probable geometries and their deviation from the average was estudied then, the geometries of 2 filters were selected as the standard since they are the closest to the average.

The calibration was performed using 2 collimators diafragms;5.0 cm and 2.5 cm diameter, for high counting rate and low counting rate respectively.

The calibration curve is illustrated in Fig 5.

List of publications

* "Desarrolo de un sistema para la identificacion y cuantificacion de radionucleidos en bultos". J.A. Suárez,G. Piña y M. Rodriguez. - Ponencia XV Reunión anual Soc. Nuc. Española. Alicante (España)-.

* " Development of a non destructive experimental method for the quantification of gamma emitter radionuclides in packages ". J.A. Suárez & G.Piña -Non destructive assay of radioactive Waste Cadarache (FRANCIA).

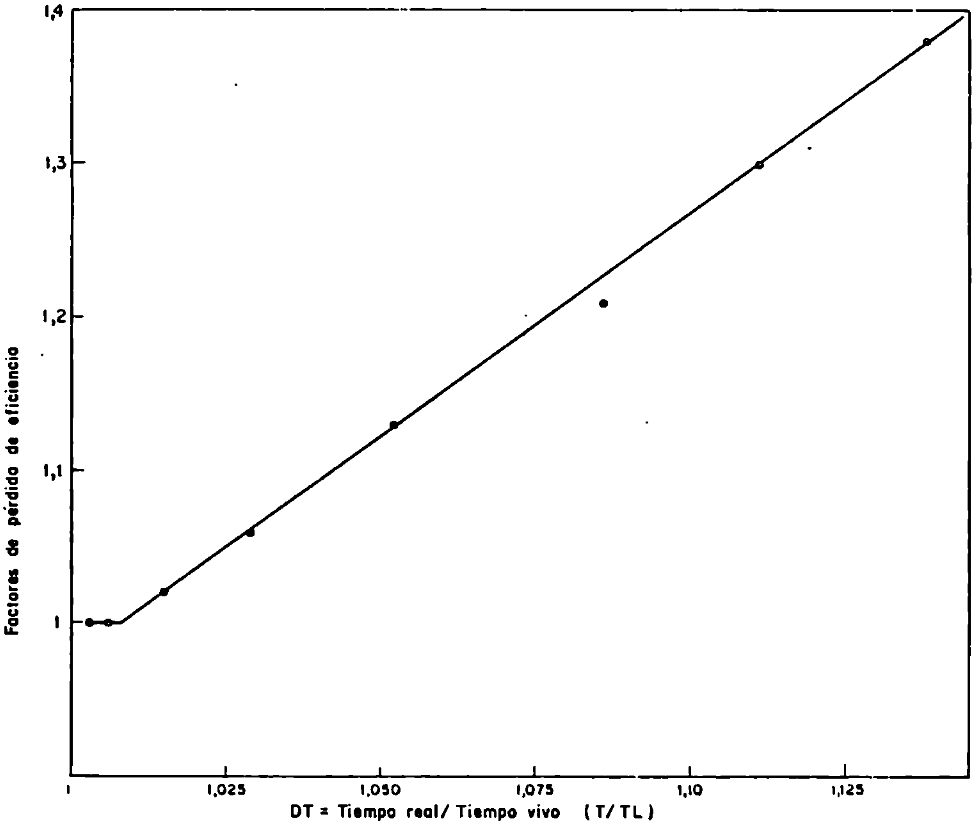


FIG. 1 - EFFICIENCY LOSS FACTORS FOR Ge(ReGe) DETECTOR IN FUNCTION OF THE DEAD TIME (DT)

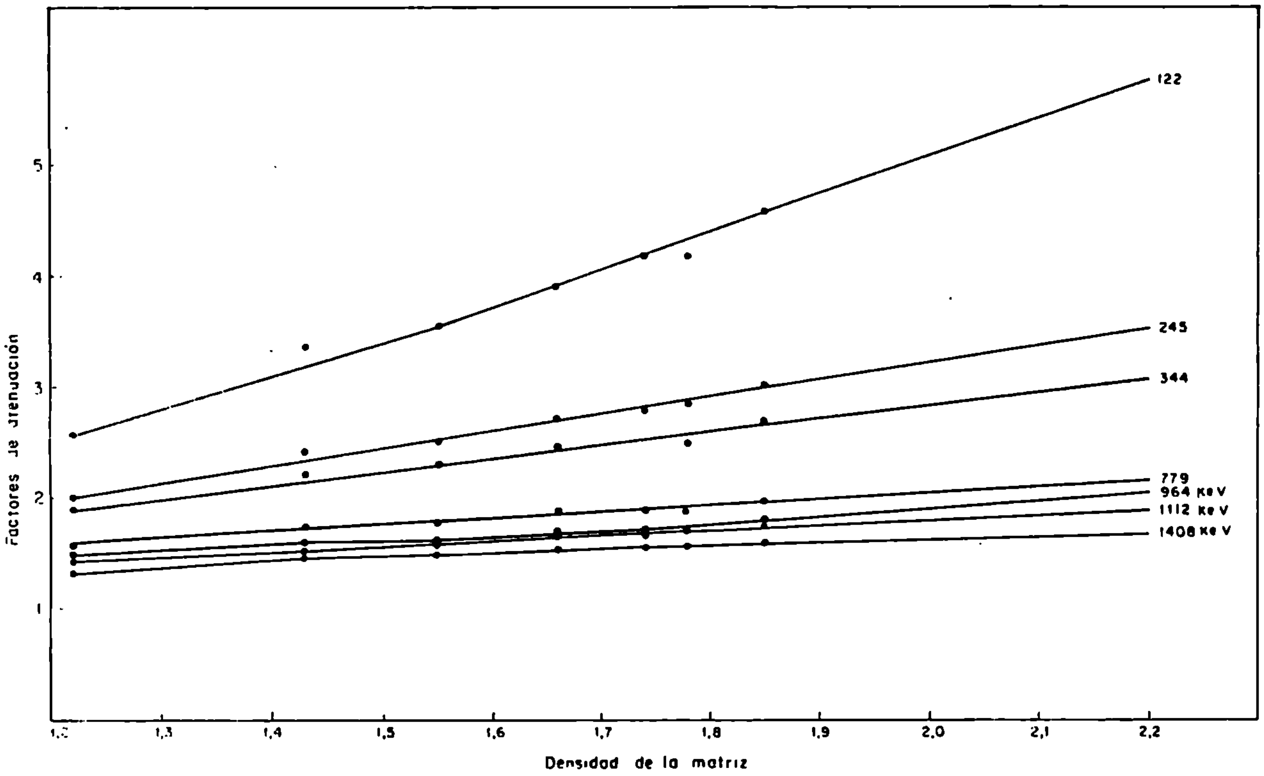


FIG. 2 - ATTENUATION FACTORS IN FUNCTION OF THE CEMENT DENSITY

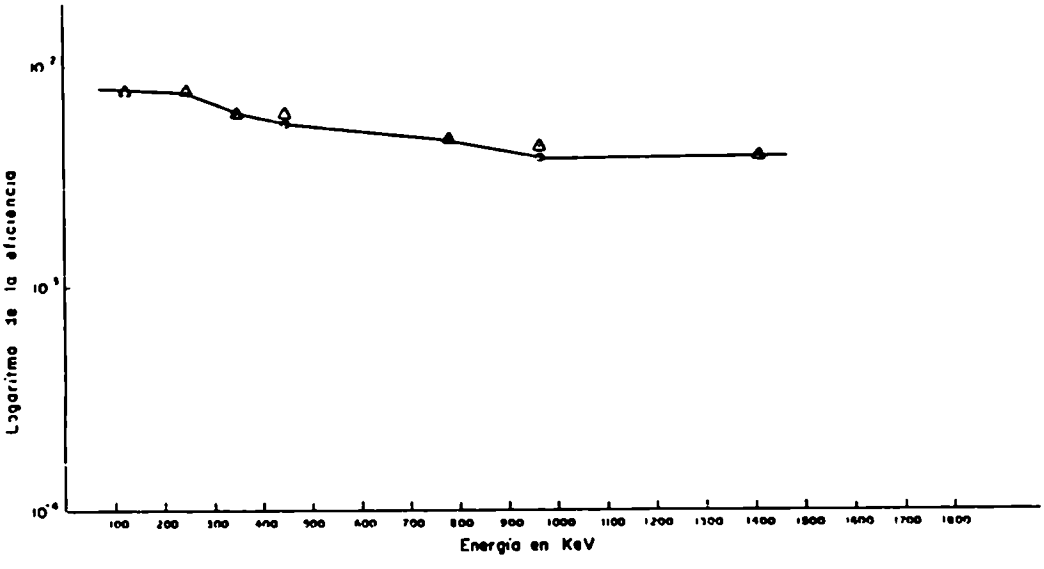


FIG. 3 - FULL SCALE EFFICIENCY CURVE. Eu-152 STANDARD

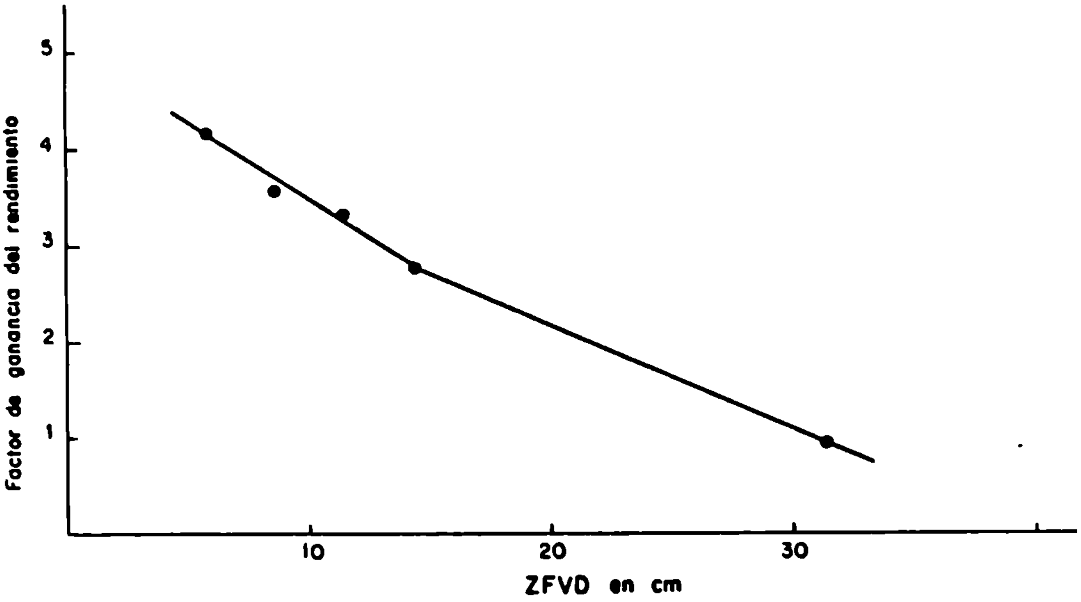


FIG. 4 - GAIN FACTORS WITH MOVABLE COUNTING EFFICIENCY IN FUNCTION OF THE 2FVD
DETECTOR-PACKAGE DISTANCE : 10.8 cm

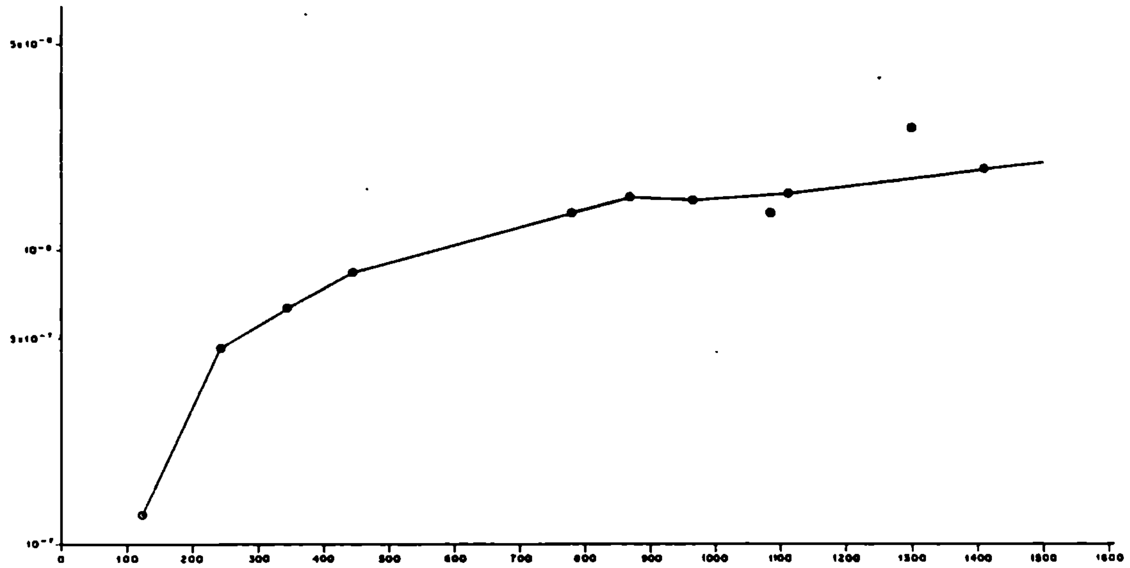


FIG. 5 – CARTRIDGE FILTERS GEOMETRY EFFICIENCY CURVE
COLLIMATION : 5.0 cm

EXPERIMENTAL STUDY ON THE DECTECTION OF FREE FLUIDS AND GASES IN WASTE PACKAGES BY ACOUSTIC METHODS

Contractor: Battelle-Institut e.V., Frankfurt am Main, Federal Republic of Germany

Contract No: FI1W-0227-D(AM)

Duration of contract: July 1989 to July 1990

Period covered: July 1989 to December 1989

Project leader: J. Eisenblätter

A. OBJECTIVES AND SCOPE

The aim of the work is to study the possibilities and limitations of various non-destructive testing (NDT) methods to check for unwanted substances in complete packages filled with radioactive waste. In detail, the following properties are to be determined from outside:
- free water at the surface of the waste,
- the matrix level, and
- the internal gas pressure.

The methods to be tested and improved are mainly acoustic and ultrasonic methods. In addition, for the measurement of the pressure inside waste packages a compensation method will be applied. Main objects of investigation are full-size 200 litre drums of 1.5 mm wall thickness (rolling hoop and rolling channel drums).

B. WORK PROGRAMME

B1: Preparation of samples. Preparation of small laboratory test bodies and 200 l drums.
B2: Free water detection using
- acoustic impedance measurement
- evaluation of swash sound (acoustic spectrometry)
- measurement of Lamb wave attenuation

B3: Determination of the matrix level using
- acoustic impedance measurement on vertical line scans
- location of friction points by means of acoustic emission

B4: Measurement of the internal gas pressure using
- compensation of pressure by an internal force applied to the drum cover
- analysis of the resonance frequencies of the cover

B5: Evaluation of the results and reporting.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Because of delays in the contract settlement, the work could not be started before August 1989. Besides sample preparation (task B1) the work has concentrated so far on task B4 of the programme: measurement of the internal gas pressure by analying the resonance frequencies of the cover and by the compensation method. Some preliminary results were obtained on acoustic impedance measurements for matrix level determination (task B3).

Progress and results

B 1: **Sample preparation.** Eight 200-1 rolling hoop drums and two rolling channel drums were obtained from the producer. Three rolling hoop drums were filled with concrete to different level (about 60 %, 75 % and 90 %).

B 3: **Matrix level determination using acoustic impedance measurement (AIM).** A small hammer is electromagnetically excited so that it periodically strikes the steel sheet. The reaction of the hammer is determined by means of a piezoelectric vibration sensor applied to the hammer. The excitation system and the sensor are integrated in a probe head which is manually passed along the structure. The evaluation unit combines signal level, signal width and possibly splitting to give an indication. This indication permits detection of defects under the steel sheet, such as major air or water inclusions. So far first investigations have shown that a difference, mainly in the signal width, exists between the sensor signals in the concrete zone and in the air space.

B 4: **Measurement of the internal gas pressure by analysis of the resonance frequencies.** Striking the drum cover (like beating a drum) generates vibrations whose frequencies increase with internal pressure. The rolling hoop drums to be investigated were placed on a rubber mat. The drum covers were excited by means of a pendulous ball-bearing ball 30 mm in diameter. The sound was detected by airborne-sound and contact microphones, and the signals were stored on transient recorders. The spectral content of the signal was evaluated using a computer PDP11-24 with array processor. Initial investigations have shown that the informative value of airborne acoustic signals is markedly higher than that of structure-brone acoustic signals, which show a strong dependence on excitation site and microphone position.

To determine the frequency increase with increasing internal pressure, the pressure was raised and lowered in steps. A set of frequency spectra for pressure cycles up to 0.3 bar, 0.6 bar and 0.9 bar maximum pressure is plotted in Fig. 1. The plot indicates that an accuracy of pressure measurement of about 0.1 bar appears feasible.

Internal pressure measurement using the compensation method. The deflection of the cover is compensated by applying counterpressure via a plate loaded by a hydraulic cylinder. Fig. 2 shows schematically the device that has been built. The point of compensation is verified by the displacement measurement in the centre of the cover and further outward; the internal pressure can then be determined by the necessary force. In the practical performance of the investigations, the internal pressure can be adjusted via a lateral compressed-air inlet. Initial measurements indicated a proportionality between internal pressure and compensation force. To determine in how far the effect of a permanent deformation can be separated needs closer evaluation of the displacement-force curves recorded during compensation.

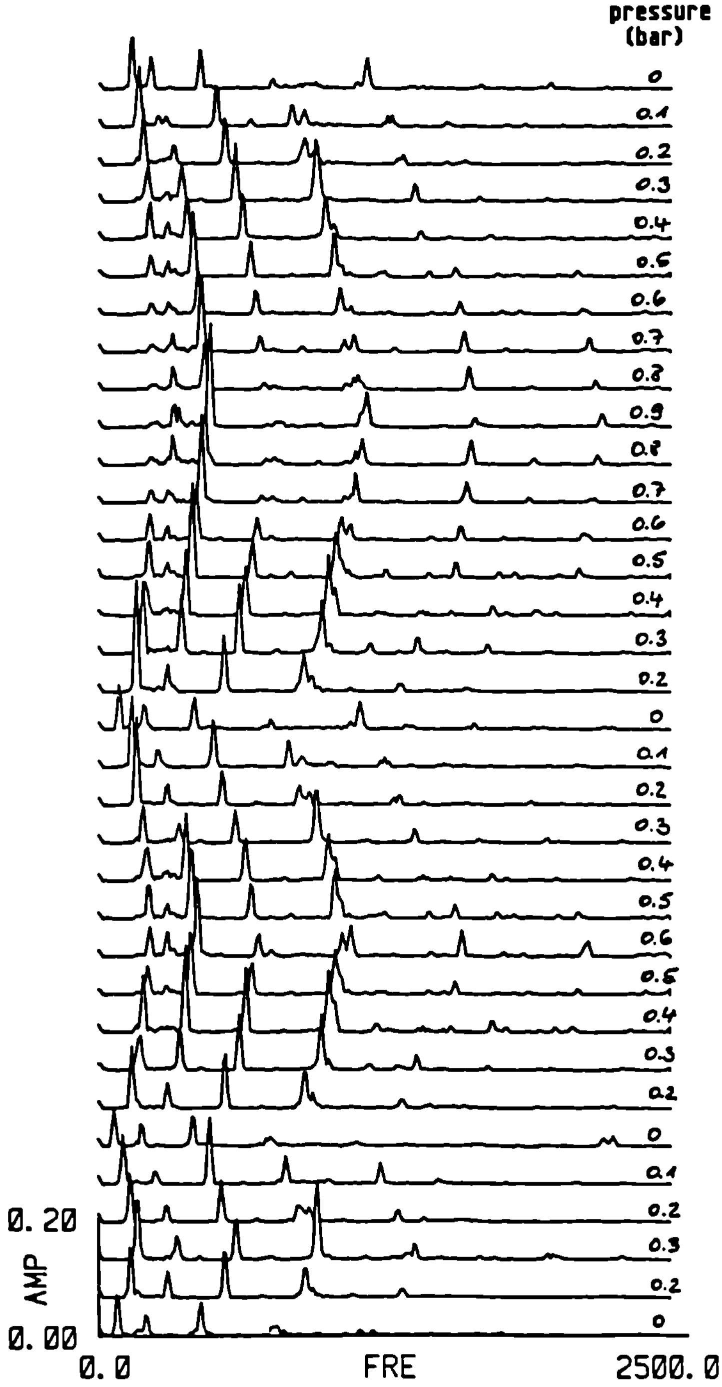


Fig.1: Frequency spectra of airborne sound of membrane vibrations during three cycles up to different peak pressures

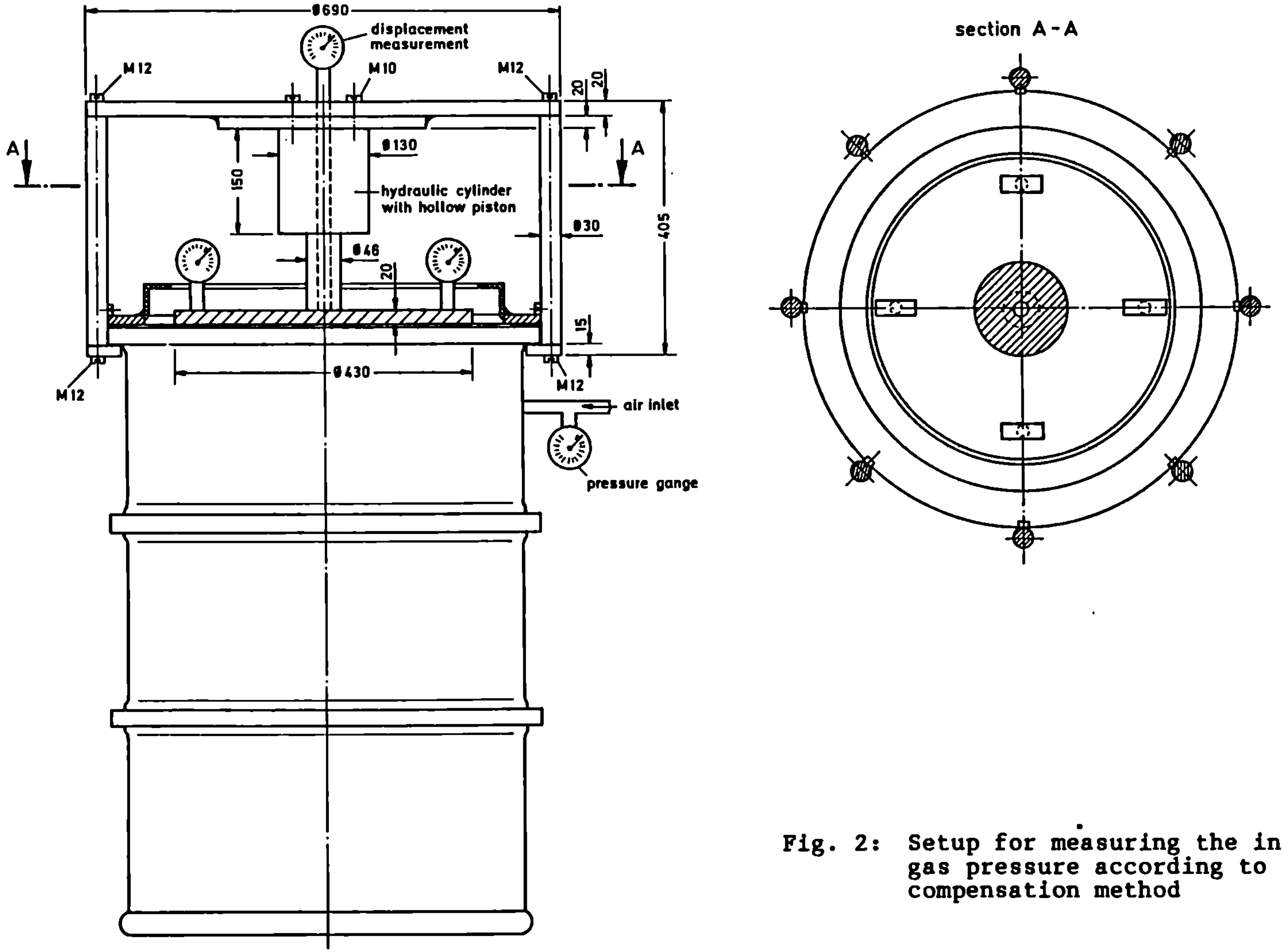


Fig. 2: Setup for measuring the internal gas pressure according to the compensation method

ACOUSTIC MONITORING TECHNIQUES FOR CORROSION DEGRADATION IN CEMENTED WASTE CANISTERS

Contractor:	Harwell Laboratory, Didcot, Oxon, UK
Contract No:	FI 1W.0229.UK(H)
Duration of Contract:	November 1988 - March 1990
Period Covered:	January 1989 - December 1989
Project Leader	C C Naish

A. OBJECTIVES AND SCOPE

There is a requirement on radioactive waste producers to ensure the integrity of the cemented wasteforms that they produce. Presently available corrosion monitoring and NDT techniques are not readily applicable to waste canisters. A technique that offers promise in monitoring the corrosion-induced degradation of cemented wasteforms from outside of the drum is acoustic emission. This programme aims to investigate the feasibility of using acoustic emission monitoring as a quantifiable measure of corrosion-induced degradation and develop prototype equipment for monitoring a number of canisters simultaneously.

B. WORK PROGRAMME

The programme will measure acoustic emissions from a typical cemented wasteform eg Magnox, steel or aluminium in a 3:1 Blast Furnace Slag (BFS)/Ordinary Portland Cement (OPC) grout and compare the results with corrosion rates measured by electrochemical techniques and, in the case of Magnox and aluminium, hydrogen gas evolution. The acoustic emission technique has the potential to distinguish "critical" corrosion, ie the corrosion that stresses the cement matrix from corrosion occurring into voids in the cement matrix whereas other techniques indicate the total amount of corrosion, including that into voids, which will carry no threat to wasteform integrity. It is hoped therefore that acoustic emission will prove to be a sensitive monitor of degradation processes which threaten the monolithic nature of a cemented waste form.

2.1 Sample Preparation and Curing

Laboratory scale samples will be prepared, cured and conditioned to simulate cemented metal wastestreams. These will be cast as cylinders with loadings of typical metal eg Magnox. The samples for electrochemical tests will require metal coupons to allow an electrical connection to be made. The cement grout used will be 3:1 BFS/OPC. If necessary corrosion will be induced and accelerated by additions of chloride in the grout mix.

2.2 Measurement of Corrosion Rates

The acoustic emissions, electrochemical corrosion rate and hydrogen gas evolution rates will be recorded with time either on the same samples or on identical duplicates. This will allow a comparison of the rates of degradation indicated by the two recognised techniques compared with the acoustic measurements. This data combined with destructive examination of the samples post-test should allow calibration of the acoustic signals with other measures of corrosion rate. The electrochemical corrosion rate will be measured using ac impedance or the coulostatic pulse technique to obtain the minimum perturbation of the corroding system. The hydrogen gas will be collected over water and its volume measured.

2.3 Critical Versus Non-Critical Corrosion

To determine the sensitivity of the acoustic measurement to corrosion that stresses the cement compared to corrosion that occurs into voids samples will be prepared that are identical in all respects apart from the degree of cement voidage they contain. In this way it is hoped to demonstrate that acoustic signals are a sensitive gauge of the corrosion which threatens the integrity of the wasteform.

2.4 Portable Measuring and Recording Equipment

Parallel to the above tasks the presently available equipment and microcomputer recording equipment will be further developed to make it adaptable to use in a waste drum store.

2.5 Tests on Full Size Waste Packages

The effects of signal attenuation by the wasteform and the optimum number of acoustic transducers for a standard 200 or 500 litre waste canister will be investigated. This would involve measurements being made on such a standard package prepared at the UKAEA's pilot cementation plant at Winfrith.

C. PROGRESS

State of Advancement

A range of samples of 1 or 2 litre size have been cast using 3:1 BFS:OPC grout in steel canisters with additions of magnox or aluminium. These have been monitored for gas evolution and electrochemical corrosion rate. Rugged electronic equipment has been constructed to allow the monitoring of up to 64 transducers by one microcomputer. The effects of attenuation of the various components of the acoustic signals by the cement grout has been measured. Present experiments are continuing in this area along with the preparation and monitoring of a full size (200 litre) waste package containing aluminium metal waste simulate.

Progress and Results

Electronic equipment has been designed, constructed and used to monitor acoustic emissions from cemented samples. The equipment has been designed to allow the long term remote monitoring of the random and relatively rare acoustic bursts which are characteristic of ageing cemented metal waste corrosion and shrinkage. The system employs a "look-at-me" amplifier (LAMA) which continuously samples the acoustic signal from a transducer but only records to the parent microcomputer if a pre-set threshold is exceeded.

Samples have been prepared using candidate grout infill mixes (3:1 BFs:OPC) with simulated metal waste additions of aluminium and magnox. The hydrogen gas evolution from these samples, which is proportional to the rate of metal corrosion, has been compared to the number of acoustic emission events and the electrochemically measured corrosion rate, figures 1, 2 and 3 show data for aluminium in a 3:1 BFS:OPC grout. These data show that there is a good correlation between acoustic events and corrosion rate as measured by hydrogen gas and electrochemical methods.

The attenuation of the acoustic signal by the cement grout has been measured using a laser system to apply a known amount of energy to a range of grout sample thicknesses and monitoring the attenuation of the various acoustic waves (surface, bulk). This has been done for water saturated samples and is presently underway for "dry" samples (dry samples are equilibrated in a chamber with a relative humidity of less than 20%). The attenuation results are presented in figures 4 and 5. The data indicates that the surface waves have a velocity of 1.87 $\mathrm{mm.\mu s^{-1}}$ and are attenuated by e (2.718) over a distance of 27 mm. The bulk waves have a velocity of 3.73 $\mathrm{mm.\mu s^{-1}}$ and an attenuation of e in 18 mm. The complete event signal, the RMS-DC output measured by the computer as output data from the transducer/amplifier set-up is attenuated by e every 109 mm of grout. This latter figure would give a reduction in signal strength of an order of magnitude over a distance of 400 mm.

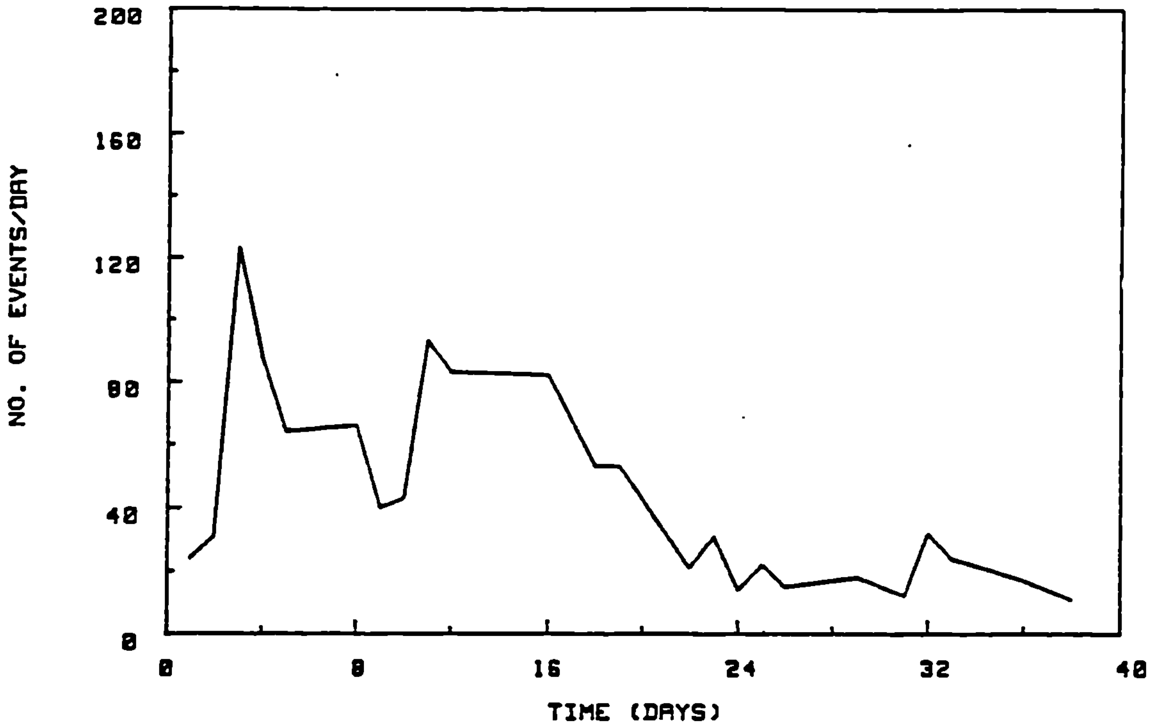


FIGURE 1 ALUMINIUM IN 3/1 BFS/OPC ACOUSTIC EVENTS

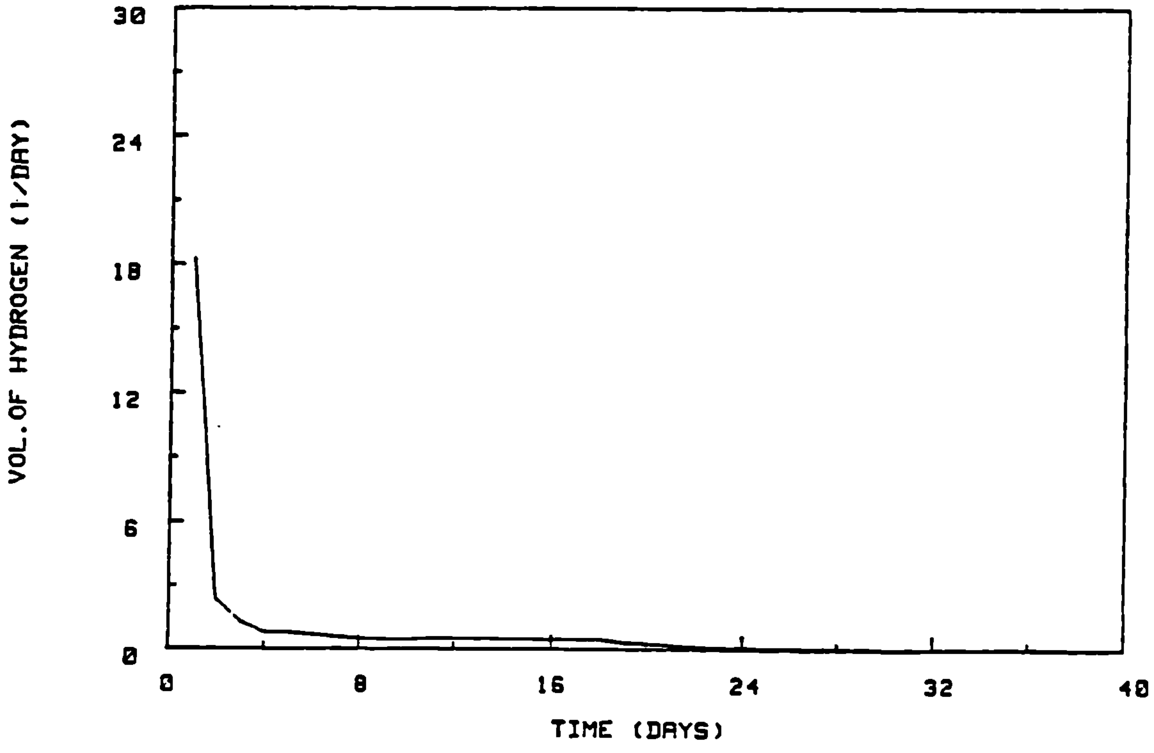


FIGURE 2 ALUMINIUM IN 3/1 BFS/OPC HYDROGEN GAS EVOLUTION

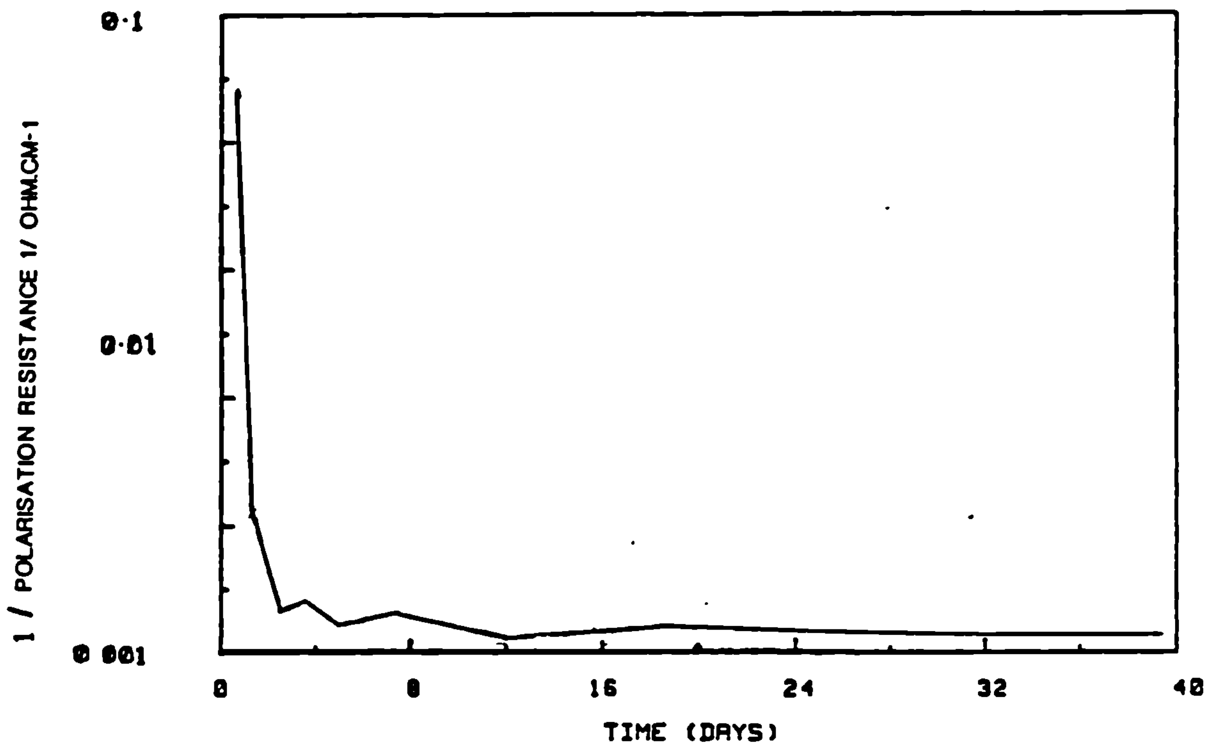


FIGURE 3 ALUMINIUM IN 3/1 BFS/OPC ELECTROCHEMICAL CORROSION RATE

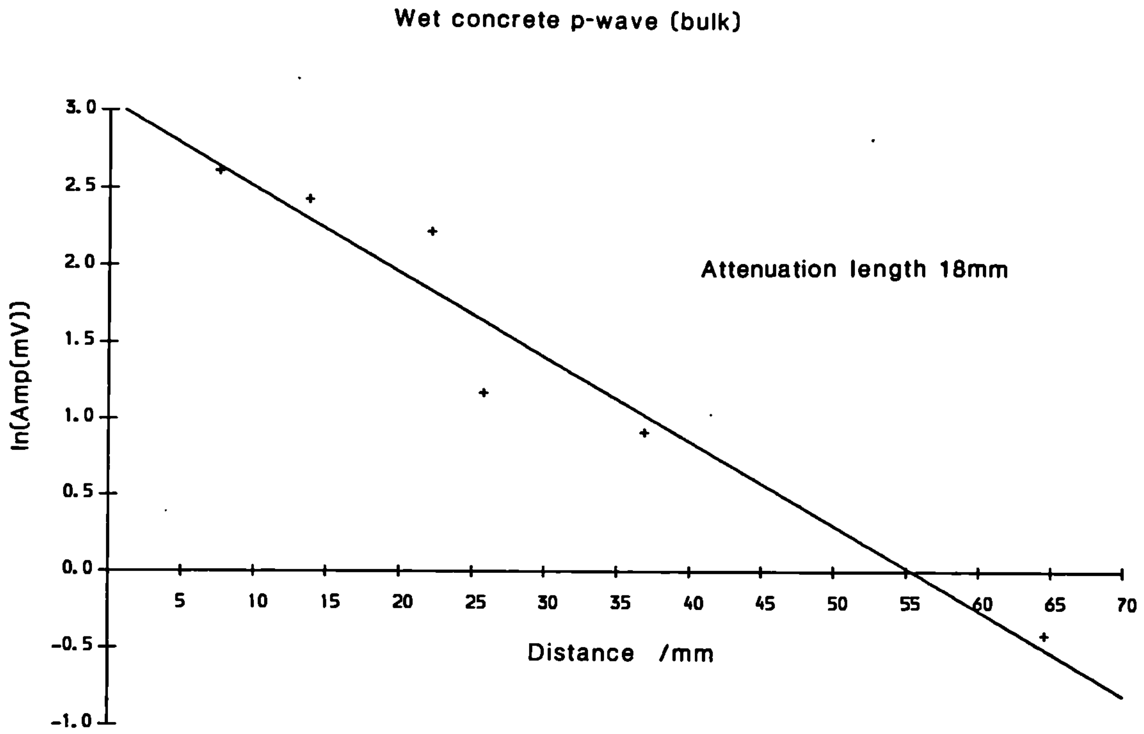


FIGURE 4 ATTENUATION OF BULK WAVE

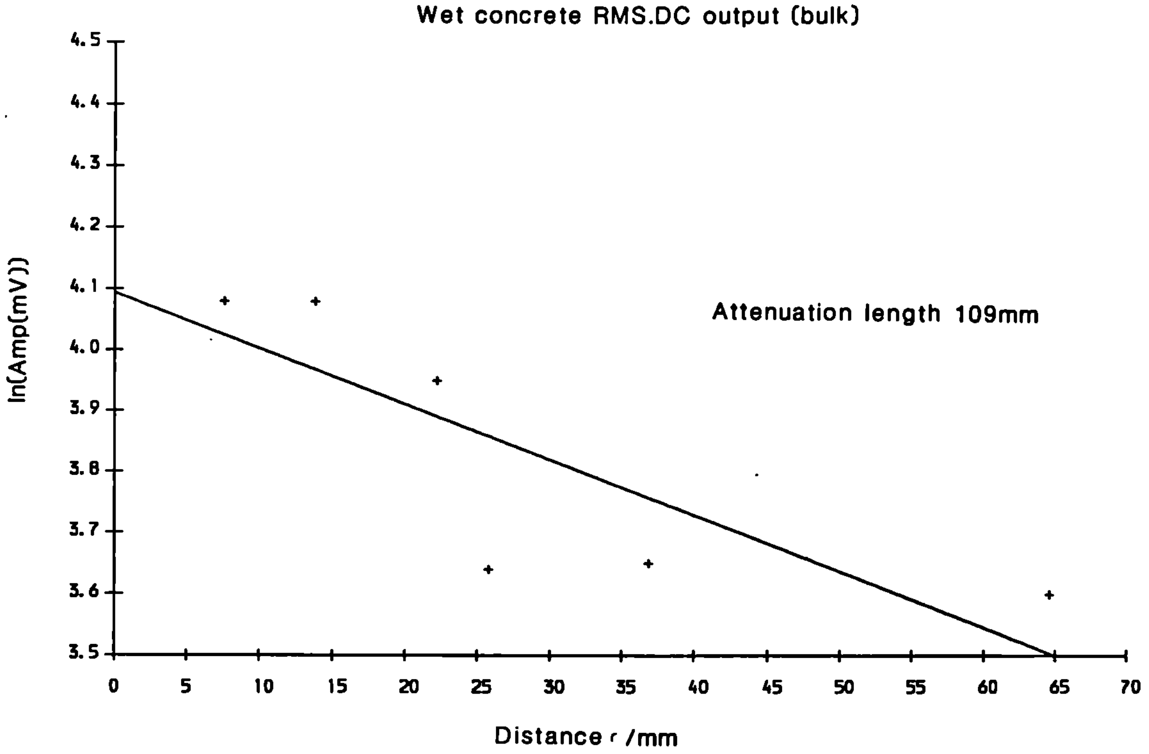


FIGURE 5 ATTENUATION OF BULK RMS.DC OUTPUT

SURVEY OF SOLID WASTE ARISINGS, NON-DESTRUCTIVE ASSAY SYSTEMS AND FEASIBILITY OF A MOBILE UNIT

Contractor: CEA Cadarache and AEA Dounreay
Contract No: FI 1W0248/F (CD) and FI 1W0249/UK (JR)
Duration: from 1 July 1989 to 31 May 1990
Period covered: 1 July 1989 to 31 December 1989
Project leaders: P Bernard, CEA Cadarache
W B Bremner, AEA Dounreay

A. OBJECTIVE AND SCOPE

A short research contract has been undertaken jointly be CEA and AEA to review the basic data related to non-destructive assay (NDA) techniques for application to solid waste arisings in CEC countries. They covered the following areas:-

(i) Review of current waste arisings and stocks;
(ii) Review waste disposal criteria used in the various facilities;
(iii) Performance of existing NDA systems including detection limit achievable under operational conditions;
(iv) Identify areas where NDA technology is inadequate;
(v) Consider the technical feasibility of mobile NDA unit and the potential application in the community.

B. WORK PROGRAMME

2 The waste arisings for facilities in France, UK, West Germany, Italy, Spain and Belgium, have been tabulated. Information is given on volumes, activity levels, density, matrix and conditioning.

2.1 The criteria for waste storage varies both within countries and from one country to another. There are also differences in the interpretation of the regulations such as maximum activity on individual waste items and the relationship to the averaged inventory for the whole facility.

2.2 The performance of the NDA systems where appropriate is given. In some cases more than one NDA approach is used either to improve the precision of measurement or to deal with variations in the waste matrix or density. The quality control procedures are also being investigated but are not fully evaluated at the present stage of the work.

C. PROGRESS OF WORK AND OBTAINED RESULTS STATE OF ADVANCEMENT

This intermediate report has provided most of the information which will be required for the next stage of the work. In particular due consideration can now be given to the use of mobile, variable geometry devices coupled with the use of data interpretation procedures using mathematical modelling. A detailed appraisal of these issues will be carried out for the final report.

Cases where there are clearly identified shortcomings in the NDA capability will be identified in the final report. However, there are some areas where such shortcomings are already apparent.

D. PROGRESS AND RESULTS

The conceptual design for a mobile NDA unit which could address many of the waste arisings listed in appendix 1 is currently well advanced. It is already clear that a variable geometry system will be required with the capability of applying passive neutron, active neutron (delayed neutron), active neutron (delayed gamma), differential die-away and passive gamma. It now needs to be established whether such a range of techniques could be included in one detector arrangement, or whether more detector arrangements will be required.

In order to calibrate the system both for varying sizes of containers and varying matrices within the containers it seems likely that mathematical modelling needs to be applied - this should lead to both an additional QA/QC procedure and to meeting varying detection limits for the waste stream

Appendix 1 gives detailed results for most of the relevant waste arisings in the Community. The criteria for storage or disposal of solid wastes has not yet been defined by all members states but in many categories there is a considerable degree of similarity.

GLOSSARY

A : Actinides
AEAT : AEA Technology
AGR : Advanced gas cooled reactor
AI : Amersham International
AP : Activation products
BNFL : British Nuclear Fuels PLC
FP : Fission products
g : Grams
HLW : High Level or Heat Generating Wastes
Wastes in which the temperature may rise significantly as a result of their radioactivity, so that this factor has to be taken into account in designing storage or disposal facilities.
hr : Hour
HRGS : High Resolution Gamma Spectrometry
ILW : Intermediate Level Waste
Wastes with radioactivity levels exceeding the upper boundaries for LLW, but which do not require heating to be taken into account in the design of storage or disposal facilities.
l : Litres
LLW : Low Level Waste
Wastes containing radioactive materials other than those acceptable for dustbin disposal, but not exceeding $4*10^9$ Bq/t alpha and/or $1.2*10^{10}$ Bq/t beta/gamma.
LRGS : Low Resolution Gamma Spectrometry.
LWR : Light Water Reactor
m : Meters
mg : Milli grams
mn : Minutes
mSv : Milli sieverts
NDA : Non-Destructive Analysis
NDS : National Disposal Service
NE : Nuclear Electric
NM : Not measured
PCM : Plutonium Contaminated Waste
PNCC : Passive Neutron Coincidence Counter
PNTC : Passive Neutron Total Counter
Pu : Plutonium
SN : Scottish Nuclear
Sv : sieverts
t : Tonnes
TBq : Tera becquerels
TLD : Thermo Luminescent Dosimeters
uSv : Micro sieverts

MAIN WASTE PRODUCING SITES (UNITED KINGDOM)

RESEARCH ORGANISATIONS

SITE	ORGANISATION
DOUNREAY	AEAT
WINDSCALE	AEAT
SPRINGFIELDS	AEAT
RISLEY	AEAT
CULHAM	AEAT
HARWELL	AEAT
WINFRITH	AEAT

NUCLEAR INDUSTRY

SITE	ORGANISATION
SELLAFIELD & CALDER HALL	BNFL
SPRINGFIELDS	BNFL
CAPENHURST	BNFL

UTILITIES

SITE	ORGANISATION
TORNESS	SN
HUNTERSTON	SN
HARTLEPOOL	NE
HEYSHAM	NE
WYLFA	NE
TRAWSFYNYDD	NE
SIZEWELL	NE
BERKELEY	NE
OLDBURY	NE
BRADWELL	NE
DUNGENESS	NE
HINKLEY POINT	NE

UNITED KINGDOM WASTE STREAMS

PCM

SITE	*WASTE STREAM DESCRIPTION*
SELLAFIELD	*Magnox PCM*
SELLAFIELD	*Magnox PCM crated*
SELLAFIELD	*PCM Thorp*
DOUNREAY	*PCM Combustible*
DOUNREAY	*PCM Non-combustible*
WINFRITH	*Low beta gamma activity PCM solids*
WINFRITH	*PCM in sea dump packages*
HARWELL	*Alpha ILW NDS Solids*
HARWELL	*Alpha ILW Fissile*
HARWELL	*Alpha ILW Fissile*
WINDSCALE	*Operational wastes fast reactor fuel development + PCM*

HEAD END WASTES

SELLAFIELD	*Magnox cladding and sludge*
SELLAFIELD	*Zircaloy hulls*
SELLAFIELD	*Leached stainless steel hulls*
SELLAFIELD	*Thorp cladding*
DOUNREAY	*High alpha beta gamma solid*
DOUNREAY	*Low alpha, high beta gamma solid*

COUNTRY	*UNITED KINGDOM*
SITE	*WINDSCALE*
DESCRIPTION	*Operational wastes fast reactor fuel development + PCM*

RADIOACTIVITY

Type	*ILW*
Alpha	*<0.07 TBq/m^3*
Beta/Gamma	*<0.0004 TBq/m^3*
Main radionuclides	*A*
Contact dose rate	*$<25\mu$ Sv/hr*

STOCKS/ARISINGS

To 1988	*45 m^3*
1989-1994(per year)	*60 m^3*

PACKAGING

Type	*Drum*
Volume	*220 l*
Density(Range)	*0.1-1 t/m^3*
" (Average)	*0.3 t/m^3*
Main support matrix	*Various*
Conditioned	*No*

PRESENT NDA MEASUREMENT

Method	*LRGS + PNCC*
Detection limit	*50 mg*
Measurement time	*1800 mn*
Geometry	*Well counter*
Anticipated future method	*PNCC + HRGS*

COMMENTS

Packages measured before drumming (gamma probe)
Segregated into combustible(40%), non-combustible (50%) and polythene (10%) before drumming.
LRGS is drum scanner.

COUNTRY	UNITED KINGDOM
SITE	HARWELL
DESCRIPTION	Alpha ILW fissile

RADIOACTIVITY

Type	ILW
Alpha	0.1 TBq/m^3
Beta/Gamma	0.005 TBq/m^3
Main radionuclides	A
Contact dose rate	1m Sv/hr

STOCKS/ARISINGS

To 1988	62.7 m^3
1989-1994	None

PACKAGING

Type	Drum
Volume	220 l
Density(Range)	0.2-0.4 t/m^3
" (Average)	0.3 t/m^3
Main support matrix	paper/plastic
Conditioned	concrete

PRESENT NDA MEASUREMENT

Method	None
Detection limit	mg
Measurement time	mn
Geometry	
Anticipated future method	HRGS + PNCC

COMMENTS	Wastes shredded and packaged for sea dumping.

COUNTRY	*UNITED KINGDOM*
SITE	*SELLAFIELD*
DESCRIPTION	*Thorp cladding*

RADIOACTIVITY

Type	*ILW*
Alpha	*0.8 TBq/m³*
Beta/Gamma	*700 TBq/m³*
Main radionuclides	*FP + AP*
Contact dose rate	*50 Sv/hr*

STOCKS/ARISINGS

To 1988	*0 m³*
1989-1994(per year)	*61 m³*

PACKAGING

Type	*Drum*
Volume	*220 l*
Density(Range)	*0.5-2 t/m³*
" (Average)	*1 t/m³*
Main support matrix	*Steel*
Conditioned	*No*

PRESENT NDA MEASUREMENT

Method	*None*
Detection limit	*mg*
Measurement time	*mn*
Geometry	
Anticipated future method	*PNCC + HRGS*

COMMENTS

NDA equipment under development
Proposal is to encapsulate in concrete matrix

COUNTRY	UNITED KINGDOM
SITE	SELLAFIELD
DESCRIPTION	Magnox cladding and sludge

RADIOACTIVITY

Type	ILW
Alpha	2 TBq/m^3
Beta/Gamma	600 TBq/m^3
Main radionuclides	FP+AP
Contact dose rate	20 Sv/hr

STOCKS/ARISINGS

To 1988	9206 m^3
1989-1994(per year)	588 m^3

PACKAGING

Type	None
Volume	See comments
Density(Range)	0.5-2 t/m^3
" (Average)	1 t/m^3
Main support matrix	Steel
Conditioned	No

PRESENT NDA MEASUREMENT

Method	None at present
Detection limit	mg
Measurement time	mn
Geometry	
Anticipated future method	PNCC

COMMENTS

Swarf in water filled compartments
When corrosion occurs sludge is form

COUNTRY	*UNITED KINGDOM*
SITE	*SELLAFIELD*
DESCRIPTION	*Zircaloy hulls*

RADIOACTIVITY

Type	*ILW*
Alpha	*0.7 TBq/m^3*
Beta/Gamma	*60 TBq/m^3*
Main radionuclides	*FP + AP*
Contact dose rate	*20 Sv/hr*

STOCKS/ARISINGS

To 1988	*30 m^3*
1989-1994(per year)	*None*

PACKAGING

Type	*None*
Volume	*see comments*
Density(Range)	*0.5-2 t/m^3*
" (Average)	*1 t/m^3*
Main support matrix	*Steel*
Conditioned	*No*

PRESENT NDA MEASUREMENT

Method	*None*
Detection limit	*mg*
Measurement time	*mn*
Geometry	
Anticipated future method	*PNCC*

COMMENTS

Zircaloy hulls in water filled compartment

COUNTRY	UNITED KINGDOM
SITE	SELLAFIELD
DESCRIPTION	Leached stainless steel hulls
RADIOACTIVITY	
Type	ILW
Alpha	1 TBq/m^3
Beta/Gamma	60 TBq/m^3
Main radionuclides	FP + AP
Contact dose rate	20 Sv/hr
STOCKS/ARISINGS	
To 1988	10 m^3
1989-1994(per year)	None
PACKAGING	
Type	None
Volume	see comments
Density(Range)	0.5-2 t/m^3
" (Average)	1 t/m^3
Main support matrix	Steel
Conditioned	No
PRESENT NDA MEASUREMENT	
Method	None
Detection limit	mg
Measurement time	mn
Geometry	
Anticipated future method	PNCC
COMMENTS	
	Steel hulls in water filled compartments

COUNTRY	*UNITED KINGDOM*
SITE	*SELLAFIELD*
DESCRIPTION	*Magnox PCM*

RADIOACTIVITY

Type	*ILW*
Alpha	*1 TBq/*m^3
Beta/Gamma	*20 TBq/*m^3
Main radionuclides	*FP + A*
Contact dose rate	*1m Sv/hr*

STOCKS/ARISINGS

To 1988	*5451* m^3
1989-1994(per year)	*819* m^3

PACKAGING

Type	*Drum*
Volume	*220 l*
Density(Range)	*0.5-2 t/*m^3
" (Average)	*1 t/*m^3
Main support matrix	*Various*
Conditioned	*No*

PRESENT NDA MEASUREMENT

Method	*LRGS + PNCC*
Detection limit	*50 mg*
Measurement time	*1800 mn*
Geometry	*Well Counter*
Anticipated future method	*HRGS + PNCC*

COMMENTS

Matrix is 30% paper, 50% plastic, 10% wood, 10% metal.
Material will eventually be segregated and repacked in 500l drums.
Individual packages checked by gamma probe before drumming.
Detection limit is for PNCC.
LRGS is drum scanner

COUNTRY	UNITED KINGDOM
SITE	SELLAFIELD
DESCRIPTION	PCM Thorp

RADIOACTIVITY

Type	ILW
Alpha	0.07 TBq/m^3
Beta/Gamma	20 TBq/m^3
Main radionuclides	FP + A
Contact dose rate	1m Sv/hr

STOCKS/ARISINGS

To 1988	0 m^3
1989-1994(per year)	8 m^3

PACKAGING

Type	Drum
Volume	220 l
Density(Range)	0.3-1.5 t/m^3
" (Average)	0.5 t/m^3
Main support matrix	Various
Conditioned	No

PRESENT NDA MEASUREMENT

Method	None
Detection limit	mg
Measurement time	mn
Geometry	
Anticipated future method	PNCC + HRGS

COMMENTS

NDA equipment under development.
Packages measured at source using PNTC.
Packages sorted into hard and soft waste at source.

COUNTRY	*UNITED KINGDOM*
SITE	*DOUNREAY*
DESCRIPTION	*High alpha beta gamma solid*
RADIOACTIVITY	
Type	*ILW*
Alpha	*1 TBq/m^3*
Beta/Gamma	*<20 TBq/m^3*
Main radionuclides	*FP + A*
Contact dose rate	*50 Sv/hr*
STOCKS/ARISINGS	
To 1988	*70 m^3*
1989-1994(per year)	*3 m^3*
PACKAGING	
Type	*Drum*
Volume	*220 l*
Density(Range)	*1 t/m^3*
" (Average)	*1 t/m^3*
Main support matrix	*Steel*
Conditioned	*No*
PRESENT NDA MEASUREMENT	
Method	*PNCC + Active neutron (Cf source)*
Detection limit	*2000 mg*
Measurement time	*30 mn*
Geometry	*Well counter*
Anticipated future method	*As present*
COMMENTS	
	Measured in shielded facility

COUNTRY	UNITED KINGDOM
SITE	DOUNREAY
DESCRIPTION	Low alpha, high beta gamma solid

RADIOACTIVITY

Type	ILW
Alpha	0.007 TBq/m^3
Beta/Gamma	20 TBq/m^3
Main radionuclides	FP + AP
Contact dose rate	50 Sv/hr

STOCKS/ARISINGS

To 1988	760 m^3
1989-1994(per year)	18 m^3

PACKAGING

Type	Drum
Volume	20 l
Density(Range)	1 t/m^3
" (Average)	1 t/m^3
Main support matrix	Steel
Conditioned	No

PRESENT NDA MEASUREMENT

Method	PNCC + Active neutron (Cf source)
Detection limit	15 mg
Measurement time	30 mn
Geometry	Well counter
Anticipated future method	As present

COMMENTS

Also some 220l drums

COUNTRY	UNITED KINGDOM
SITE	SELLAFIELD
DESCRIPTION	Magnox PCM crated

RADIOACTIVITY

Type	ILW
Alpha	NM TBq/m^3
Beta/Gamma	NM TBq/m^3
Main radionuclides	A
Contact dose rate	1m Sv/hr

STOCKS/ARISINGS

To 1988	1146 m^3
1989-1994(per year)	71 m^3

PACKAGING

Type	Crate
Volume	<5000 l
Density(Range)	0.1 t/m^3
" (Average)	0.1 t/m^3
Main support matrix	Air
Conditioned	No

PRESENT NDA MEASUREMENT

Method	None
Detection limit	mg
Measurement time	mn
Geometry	
Anticipated future method	PNCC

COMMENTS

No crate monitor at present, in development
Redundant gloveboxes etc, checked for criticallity using TLD's or total neutron counting.
(Gamma techniques used for position of activity)

COUNTRY	*UNITED KINGDOM*
SITE	*HARWELL*
DESCRIPTION	*Alpha ILW Fissile*
RADIOACTIVITY	
Type	*ILW*
Alpha	*3 TBq/m^3*
Beta/Gamma	*0.01 TBq/m^3*
Main radionuclides	*A*
Contact dose rate	*1m Sv/hr*
STOCKS/ARISINGS	
To 1988	*104.5 m^3*
1989-1994(per year)	*44 m^3*
PACKAGING	
Type	*Drum*
Volume	*220 l*
Density(Range)	*0.15-1.5 t/m^3*
" (Average)	*0.3 t/m^3*
Main support matrix	*Various*
Conditioned	*No*
PRESENT NDA MEASUREMENT	
Method	*HRGS + PNCC*
Detection limit	*1000 mg*
Measurement time	*10 mn*
Geometry	*Rectangular*
Anticipated future method	*As present*
COMMENTS	*Support matrix is mainly plastic (80%) and metals with some drums containing concrete (5%). Detection limit is for PNCC, for HRGS detection limit is 2000mg in 60mn.*

COUNTRY	UNITED KINGDOM
SITE	DOUNREAY
DESCRIPTION	PCM Combustible

RADIOACTIVITY

Type	ILW
Alpha	0.07 TBq/m^3
Beta/Gamma	<0.0004 TBq/m^3
Main radionuclides	A
Contact dose rate	<750µ Sv/hr

STOCKS/ARISINGS

To 1988	49.5 m^3
1989-1994(per year)	9.1 m^3

PACKAGING

Type	Drum
Volume	220 l
Density(Range)	0.2 -0.4 t/m^3
" (Average)	0.3 t/m^3
Main support matrix	Paper
Conditioned	No

PRESENT NDA MEASUREMENT

Method	PNCC
Detection limit	10 mg
Measurement time	30 mn
Geometry	Well Counter
Anticipated future method	As present

COMMENTS

Items also previously measured by HRGS

COUNTRY	UNITED KINGDOM
SITE	HARWELL
DESCRIPTION	Alpha ILW NDS Solids

RADIOACTIVITY

Type	ILW
Alpha	0.2 TBq/m^3
Beta/Gamma	0.04 TBq/m^3
Main radionuclides	FP + AP
Contact dose rate	1m Sv/hr

STOCKS/ARISINGS

To 1988	49.1 m^3
1989-1994(per year)	12 m^3

PACKAGING

Type	Drum (where possible)
Volume	220 l
Density(Range)	0-12.5 t/m^3
" (Average)	1 t/m^3
Main support matrix	Various
Conditioned	No

PRESENT NDA MEASUREMENT

Method	None
Detection limit	mg
Measurement time	mn
Geometry	
Anticipated future method	HRGS + PNCC

COMMENTS	These wastes are in various sizes of container from a few mls to sources in lead flasks. Includes medical waste.

COUNTRY	UNITED KINGDOM
SITE	WINFRITH
DESCRIPTION	PCM in sea dump packages
RADIOACTIVITY	
Type	
Alpha	0.08 TBq/m^3
Beta/Gamma	3 TBq/m^3
Main radionuclides	A
Contact dose rate	1m Sv/hr
STOCKS/ARISINGS	
To 1988	23 m^3
1989-1994(per year)	None
PACKAGING	
Type	Drum
Volume	220 l
Density(Range)	0.2-0.4 t/m^3
" (Average)	0.3 t/m^3
Main support matrix	Plastics, rubber, paper, metal, etc.
Conditioned	Yes
PRESENT NDA MEASUREMENT	
Method	PNCC
Detection limit	100 mg
Measurement time	15 mn
Geometry	Well Counter
Anticipated future method	As present
COMMENTS	100 litre waste drums are encased with concrete in 220 litre drums. Density of drum is 1.16. Concrete cladding is 55% by volume.

COUNTRY	UNITED KINGDOM
SITE	WINFRITH
DESCRIPTION	Low beta gamma activity PCM solids
RADIOACTIVITY	
Type	ILW
Alpha	0.08 TBq/m^3
Beta/Gamma	3 TBq/m^3
Main radionuclides	A
Contact dose rate	1m Sv/hr
STOCKS/ARISINGS	
To 1988	45 m^3
1989-1994(per year)	14 m^3
PACKAGING	
Type	Drum
Volume	100 l
Density(Range)	0.4-1.0 t/m^3
" (Average)	0.7 t/m^3
Main support matrix	Various
Conditioned	No
PRESENT NDA MEASUREMENT	
Method	PNCC
Detection limit	100 mg
Measurement time	15 mn
Geometry	Well Counter
Anticipated future method	As present
COMMENTS	Beta/gamma activity is nearly all pure beta from 241Pu. With a 1 hour count detection limit is reduced to 10mg. Gamma checks done on some packages.

COUNTRY	*UNITED KINGDOM*
SITE	*DOUNREAY*
DESCRIPTION	*PCM Non-combustible*
RADIOACTIVITY	
Type	*ILW*
Alpha	*0.3 TBq/m^3*
Beta/Gamma	*<0.0004 TBq/m^3*
Main radionuclides	*A*
Contact dose rate	*<750µ Sv/hr*
STOCKS/ARISINGS	
To 1988	*67.1 m^3*
1989-1994(per year)	*28 m^3*
PACKAGING	
Type	*Drum*
Volume	*220 l*
Density(Range)	*0.3-0.7 t/m^3*
" (Average)	*0.5 t/m^3*
Main support matrix	*Rubber, plastic*
Conditioned	*No*
PRESENT NDA MEASUREMENT	
Method	*PNCC*
Detection limit	*10 mg*
Measurement time	*30 mn*
Geometry	*Well Counter*
Anticipated future method	*As present*
COMMENTS	*Items also previously measured by HRGS*

FRANCE : MAIN CENTERS

CEA = Atomic energy commission

Main centers : Saclay
Fontenay
Grenoble
Cadarache
IRDI
Pierrelatte

Cogema = fuel reprocessing facilities

Main centers : La Hague
Marcoule
Pierrelatte

Utilities = EDF = Electricity of France

COUNTRY	FRANCE	
SITE	COGEMA LA HAGUE	
DESCRIPTION	Wastes from reprocessing fuel process	
RADIOACTIVITY	ALPHA /	BETA GAMMA with ALPHA
Type	LLW, ILW	
Alpha	90 % < 70 mg Pu	
Bêta Gamma		50 % < 3.7 MBq/m3
Main radionuclides	Co, Cs, Am, Pu	
Contact dose rate	80 % < 2 mSv/h	
STOCKS / ARISINGS		
To 1988	no stocks for technological wastes	
1989-1994 (per year)	5,000 m3 (alpha = 5%)	
PACKAGING		
Type	metallic drums / metallic or cement boxes	
Volume (1)	120 1 / 1.7 m3 / 500 1	
Density / range (t/m3)	intermediate to heavy	
/ average (t/m3)		
Main support matrix		
Conditioned	no	
PRESENT NDA MEASUREMENT		
Method	50 % PNCC and 50 % PNTC , HRGS	
Detection limit (mg)	10 mg Pu 240	
Measurement time (mn)	20 mn	
Geometry		
ANTICIPATED FUTURE METHOD	Neutron Active techniques	
COMMENTS		

COUNTRY	FRANCE		
SITE	CEA GRENOBLE		
DESCRIPTION	miscellaneous (solid)		
RADIOACTIVITY	ALPHA BETA GAMMA	/	BETA GAMMA
Type	LLW and ILW		
Alpha	0.1 MBq to 1 MBq/m3		
Beta Gamma			30 to 200 MBq/m3
Main radionuclides	Co,Pu, Am ...		
Contact dose rate	< 2 mSv/h		
STOCKS / ARISINGS			
To 1988			
1989-1994 (per year)	182 m3	/	60 m3
PACKAGING			
Type	metallic drums, boxes and hulls		
Volume (1)	100 and 200 1 , 5 m3 and 2 m3		
Density / range (t/m3)	0.1 to 1		
/ average (t/m3)	0.3		
Main support matrix	PVC (and, if embedded, concrete)		
Conditioned	yes		
PRESENT NDA MEASUREMENT			
Method	radiochemical measurements		
Detection limit (mg)			
Measurement time (mn)			
Geometry			
ANTICIPATED FUTURE METHOD	HRGS (June 1990)		
COMMENTS			

COUNTRY	FRANCE
SITE	CEA SACLAY
DESCRIPTION	

RADIOACTIVITY	ALPHA BETA GAMMA	
Type	LLW	ILW, HLW
Alpha	< 1.5 GBq/m3	
Beta Gamma	< 3.7 Bq/m3	
Main radionuclides		max.=350 g Pu 239(drums) max.=500 g U 235 "
Contact dose rate		< 2 Sv

STOCKS / ARISINGS

To 1988	450 m3	
1989-1994 (per year)	420 m3 (ALPHA=5%)	450 m3

PACKAGING

Type	drums	metallic boxes	drums
Volume (1)	100 and 200 1	5 and 10 m3	60 1
Density / range (t/m3)			
/ average (t/m3)	70 % = 0.2	0.8	70 % = 0.2
Main support matrix			
Conditioned	no	no	

PRESENT NDA MEASUREMENT

Method	HRGS, PTNC
Detection limit (mg)	- , 0.8 GBq / m3 alpha
Measurement time (mn)	
Geometry	

ANTICIPATED FUTURE METHOD

COMMENTS

COUNTRY	FRANCE
SITE	CEA FONTENAY
DESCRIPTION	
RADIOACTIVITY	ALPHA BETA GAMMA
Type	LLW and ILW
Alpha	75 % < 3.7 MBq/t
Beta Gamma	from 3.7 (LLW) to more than 37 MBq/t
Main radionuclides	Pu, Am, Cm, Co, Cs ...
Contact dose rate	75 % < 0.05 mSv/h, 25 % < 2 mSv/h
STOCKS / ARISINGS	
To 1988	2,000 m3 alpha (8701 cement drums)
1989-1994 (per year)	800 m3 (500 bêta gamma, 300 alpha) + 15 m3 very irradiant
PACKAGING	
Type	drums, metallic boxes
Volume (l)	200 l, 50 l
Density / range (t/m3)	0.2 to 1
/ average (t/m3)	0.25
Main support matrix	80 % PVC, except for Prolix (resin)
Conditioned	no except stocks
PRESENT NDA MEASUREMENT	
Method	portable dosimeter and estimation by mean of reference spectra .
Detection limit (mg)	
Measurement time (mn)	
Geometry	
ANTICIPATED FUTURE METHOD	PNTC and ANC, HRGS by the end of 1991
COMMENTS	

COUNTRY	FRANCE
SITE	CEA IRDI (Monts d'Arrée)
DESCRIPTION	
RADIOACTIVITY	
Type	BETA GAMMA
Alpha	
Beta Gamma	6 MBq / t (0.2 MCi/t)
Main radionuclides	
Contact dose rate	< 2 mSv/h
STOCKS / ARISINGS	
To 1988	
1989-1994 (per year)	100 m3
PACKAGING	
Type	drums and metallic boxes
Volume (1)	200 1 5 and 10 m3
Density / range (t/m3)	
/ average (t/m3)	0.5
Main support matrix	
Conditioned	
PRESENT NDA MEASUREMENT	
Method	LRGS
Detection limit (mg)	
Measurement time (mn)	
Geometry	
ANTICIPATED FUTURE METHOD	
COMMENTS	

COUNTRY	FRANCE
SITE	CEA UDIN
DESCRIPTION	
RADIOACTIVITY	ALPHA BETA GAMMA
Type	LLW
Alpha	
Beta Gamma	NC
Main radionuclides	
Contact dose rate	< 2 mSv/h
STOCKS / ARISINGS	
To 1988	350 m3
1989-1994 (per year)	after 1992 : 450 m3 (dismantling operation)

PACKAGING		
Type	drums	metallic boxes
Volume (1)	100 and 200 l , 5 m3	
Density / range (t/m3)	NC	
/ average (t/m3)		
Main support matrix		
Conditioned		

PRESENT NDA MEASUREMENT	
Method	Gamma total, PNTC
Detection limit (mg)	NC
Measurement time (mn)	
Geometry	
ANTICIPATED FUTURE METHOD	
COMMENTS	

COUNTRY	FRANCE		
SITE	CEA CADARACHE		
DESCRIPTION	Technological wastes		
RADIOACTIVITY	ALPHA	BETA GAMMA	ALPHA BETA GAMMA
Type	ILW	LLW	ILW
Alpha			
Beta Gamma			
Main radionuclides			
Contact dose rate	< 2mSv/h	< 2mSv/h	< 0.2 Sv/h
STOCKS / ARISINGS			
To 1988			
1989-1994 (per year)	300 m3	500 m3	15 m3
PACKAGING			
Type	metallic drums		
Volume (l)	100 l	100 l	50 l
Density / range (t/m3)			
/ average (t/m3)	0.25	0.25	0.8
		(package = 2)	
Main support matrix			
Conditioned	yes / cement-bitumen after compaction (for BetaGamma, hydraulic after 90)		
PRESENT NDA MEASUREMENT			
Method	HRGS	HRGS	HRGS
Detection limit (mg)	10 mg Pu, light density, low contact dose rate.		
Measurement time (mn)	20 mn		
Geometry			
ANTICIPATED FUTURE METHOD	neutron interrogation method (generator) and HRGS for 1990-1991		
COMMENTS			

COUNTRY	SPAIN
SITE	GLOBAL
DESCRIPTION	HETEROGENEOUS SOLID WASTES
RADIOACTIVITY	BETA GAMMA
Type	LLW
Alpha	
Beta Gamma	< 37 GBq/t (1 Ci/t)
Main radionuclides	Cs 137, Co 60
Contact dose rate	< 2 mSv / h
STOCKS / ARISINGS	
To 1988	2,000 m3 (from 1968)
1989-1994 (per year)	300 m3
PACKAGING	
Type	metallic drums
Volume (l)	200 l
Density / range (t/m3)	various
/ average (t/m3)	0.5 t/m3
Main support matrix	various (wastes are precompacted)
Conditioned	no
PRESENT NDA MEASUREMENT	
Method	numerical evaluation based on dose rate
Detection limit (mg)	
Measurement time (mn)	
Geometry	
ANTICIPATED FUTURE METHOD	non defined
COMMENTS	

COUNTRY	SPAIN
SITE	GLOBAL
DESCRIPTION	HOMOGENEOUS SOLIDIFIED WASTES Sludges, spent resins, concentrates
RADIOACTIVITY	BETA GAMMA
Type	LLW and ILW
Alpha	
Beta Gamma	NC
Main radionuclides	Co 60, Cs 137
Contact dose rate	max. 50 mSv/h
STOCKS / ARISINGS	
To 1988	10,000 m3
1989-1994 (per year)	2,000 m3
PACKAGING	
Type	metallic drums
Volume (l)	200 l
Density / range (t/m3)	
/ average (t/m3)	2 t/m3
Main support matrix	
Conditioned	
PRESENT NDA MEASUREMENT	
Method	HRGS
Detection limit (mg)	
Measurement time (mn)	
Geometry	
ANTICIPATED FUTURE METHOD	non defined
COMMENTS	

COUNTRY	ITALY
SITE	ENEL
DESCRIPTION	utilities
RADIOACTIVITY	BETA GAMMA
Type	LLW, ILW
Alpha	
Beta Gamma	NC
Main radionuclides	Co, Cs
Contact dose rate	NC
STOCKS / ARISINGS	
To 1988	4,000 m3
1989-1994 (per year)	800 m3
PACKAGING	
Type	NC
Volume (1)	
Density / range (t/m3)	0.2 - 1
/ average (t/m3)	
Main support matrix	
Conditioned	
PRESENT NDA MEASUREMENT	NONE
Method	
Detection limit (mg)	
Measurement time (mn)	
Geometry	
ANTICIPATED FUTURE METHOD	

COMMENTS

(ENEL data have to ne completed soon)

COUNTRY ITALY

SITE EUREX (ENEA)

DESCRIPTION technological wastes

RADIOACTIVITY	ALPHA	BETA GAMMA	ALPHA BETA GAMMA	
Type	LLW	LLW	LLW	
Alpha				
Beta Gamma	NC	NC	NC	
Main radionuclides				
Contact dose rate				
STOCKS / ARISINGS				
To 1988	500 m3(*)	700 m3		
1989-1994 (per year)		20 m3	30 m3	
PACKAGING				
Type	drums	drums and boxes	drums	
Volume (l)	220 l	220 l	220 l	
Density / range (t/m3)	0.1 - 2	0.1 - 2	0.1 - 2	
/ average (t/m3)	60 % = 0.2	id.	id.	
Main support matrix	PVC	PVC	PVC	Metal
Conditioned	no	no	no	no

PRESENT NDA MEASUREMENT NONE

Method

Detection limit (mg)

Measurement time (mn)

Geometry

ANTICIPATED FUTURE METHOD NONE

COMMENTS 3000 m3 alpha beta gamma (LLW, ILW) from dismantling operations are anticipated .

(*) 2,000 drums,,not measured yet

COUNTRY	ITALY
SITE	ITREC (ENEA)
DESCRIPTION	technological wastes
RADIOACTIVITY	BETA GAMMA
Type	LLW
Alpha	
Beta Gamma	150 MBq / m3
Main radionuclides	Co, Cs
Contact dose rate	NC
STOCKS / ARISINGS	
To 1988	1600 m3 (cement embedding matrix)
1989-1994 (per year)	50 m3
PACKAGING	
Type	drums
Volume (l)	220 and 380 l
Density / range (t/m3)	0.1 - 1
/ average (t/m3)	0.2
Main support matrix	PVC
Conditioned	no (except stock)
PRESENT NDA MEASUREMENT	NONE
Method	
Detection limit (mg)	
Measurement time (mn)	
Geometry	
ANTICIPATED FUTURE METHOD	NONE
COMMENTS	
	1500 m3 from a dismantling campaign

COUNTRY	ITALY		
SITE	CASACCIA (ENEA)		
DESCRIPTION	gloves, filters, papers		
RADIOACTIVITY	ALPHA		ALPHA BETA GAMMA
Type	LLW,	ILW	LLW
Alpha	200 mg Pu/m3 ,	>100g Pu	NC
Beta Gamma			
Main radionuclides	Co, Cs, Pu, U, Am		
Contact dose rate	< 2 mSv/h		
STOCKS / ARISINGS			
To 1988	416 m3		150 m3 (*)
1989-1994 (per year)	10 m3		included in NUCLECO figures
PACKAGING			
Type	drums,	boxes (Pu>100g)	NC
Volume (l)	220 l	150 l	
Density / range (t/m3)	0.1 - 1		0.5 - 1.5
/ average (t/m3)	0.2	0.2	0.2
Main support matrix	papers and gloves		
Conditioned			
PRESENT NDA MEASUREMENT			
Method	HRGS		
Detection limit (mg)	20 mg Pu 240		
Measurement time (mn)	20 mn		
Geometry			
ANTICIPATED FUTURE METHOD	PNCC and PNTC		

COMMENTS

(*) unknown

Future trend = increasing of alpha contaminated wastes with the dismantling of 50 gloves boxes .

COUNTRY	ITALY
SITE	NUCLECO (CASACCIA + nuclear industries + hospitals)
DESCRIPTION	technological wastes
RADIOACTIVITY	BETA GAMMA

Type	LLW
Alpha	
Beta Gamma	NC
Main radionuclides	Co, Cs
Contact dose rate	< 0.05 mSv/h

STOCKS / ARISINGS

To 1988	3,000 m3
1989-1994 (per year)	600 m3

PACKAGING

Type	drums
Volume (l)	220 l
Density / range (t/m3)	0.1 - 2
/ average (t/m3)	50 % = 0.2
Main support matrix	paper and PVC
Conditioned	

PRESENT NDA MEASUREMENT	HRGS

Method	
Detection limit (mg)	20 mg Pu 240
Measurement time (mn)	20 mn
Geometry	

ANTICIPATED FUTURE METHOD	NONE

COMMENTS

COUNTRY	GERMANY -
SITE	GLOBAL
DESCRIPTION	technological wases
RADIOACTIVITY	BETA GAMMA and ALPHA BETA GAMMA
Type	
Alpha	5 Bq / g
Beta Gamma	5 KBq / g
Main radionuclides	
Contact dose rate	
STOCKS / ARISINGS (*)	DETAIL GIVEN PAGE HEREAFTER
To 1988	11,725m3 unconditionned + 40,701 conditionned
1989-1994 (per year)	6960 m3
PACKAGING	
Type	drums and a few castiron containers
Volume (1)	200 1 (90 %), 400 1 and some 1001 for reprocessing
Density / range (t/m3)	1 - 2
/ average (t/m3)	
Main support matrix	cement
Conditioned	embedded for the stock
PRESENT NDA MEASUREMENT	
Method	Bêta and gamma spectrometry, computer tomography, active neutron technic, chemical analyses
Detection limit (mg)	10 mg Pu 239
Measurement time (mn)	20 mn
Geometry	
ANTICIPATED FUTURE METHOD	Alpha analysis by means of X / Gamma detection
COMMENTS	new tendancy = treatment by evaporation and compression of the ashes (liquid wastes = cemented products by evaporation) GERMANY RULES = 10 g Pu 239 BY 2201 drum ARE ACCEPTED .

(*) DETAIL OF THE STOCKS AND THE ARISINGS (M3)

	unconditioned	conditioned	
	stock 31-12-88	stock 31-12-88	arisings 1989
UTILITIES (alpha bêta gamma)	6,841	12,875	3,232
NUCLEAR CENTERS (" " ")	1,581	16,337	2,544
NUCLEAR INDUSTRY	984	1,476	288
REPROCESSING (alpha)	165	8,341	800
MEDICAL	1,998	1,589	90
MILITARY	165	83	8
TOTAL	11,725	40,701	6,962

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