Commission of the European Communities

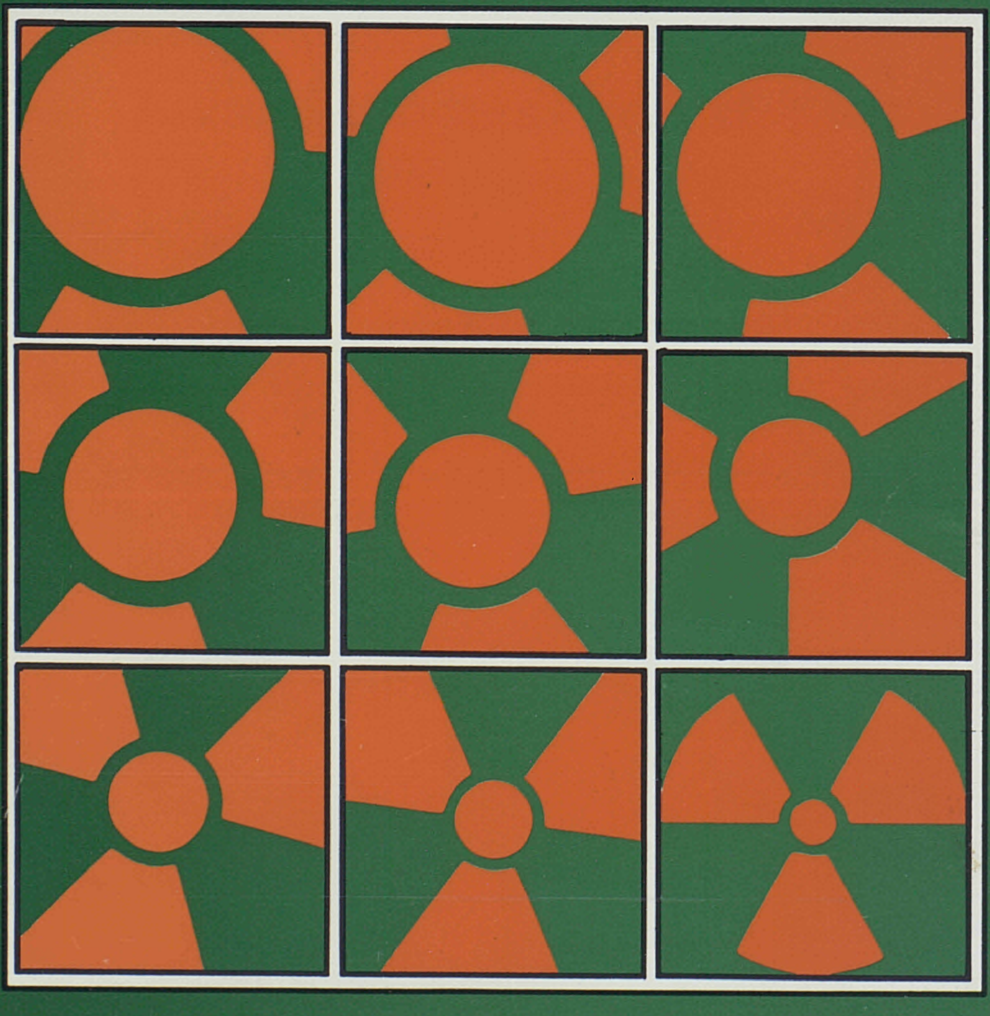
nuclear science and technology

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

Shared cost action

Annual progress report 1988

Volume 1



Report

EUR 12141 EN/1

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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 Commission's responsibility mainly through shared-cost contracts with competent public organisations and private firms within the Member States. At the end of 1988 over 200 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 page 461, 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 1988, is the third of this type, the previous being published under no EUR 11089, for the year 1986 and EUR 11482 covering the year 1987. 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 24-28, 1990 in Luxembourg.

S. ORLOWSKI
Head, Nuclear Fuel Cycle Division

1) O.J. No. L83, March 25, 1985, page 20

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VOLUME 1

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.

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

Contractor : S.C.K./C.E.N., Mol, Belgium
Contract No. : FI1W-0123
Duration of contract : November 1987 - February 1990
Period covered : January 1988 - December 1988
Project Leader : L. Geens

A. OBJECTIVES AND SCOPE

This study makes 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 will be based on economical and radiological criteria.

A management route is defined as each assembly of co-ordinated actions by which the management of hulls and caps, from their production to their disposal, is implemented. Usually, these actions comprise treatment, conditioning, packaging, interim storage, transport and disposal operations.

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

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

B. WORK PROGRAMME

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

2.2. Drawing-up of the following basic management routes :
No. 1 : hulls compaction/conditioning/packaging/interim storage;
No. 2 : hulls decontamination/cementation/packaging/interim storage.

2.3. Sensivity studies to study the impact of some important parameters on :
- waste product characteristics and arisings;
- the total volume of the treatment/conditioning facility buildings.

2.4. 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

After the reference scenario was defined, the basic data concerning amounts of cladding waste generated and characteristics of the hulls and caps, provided by the CEA, have been discussed and confirmed.

Due to the different characteristics of hulls and caps, the original idea of compacting them together, before conditioning, has been abandoned (Route No. 1). First, separate compaction was envisaged; later, compaction has only be retained for the hulls, while cementation has to be considered as conditioning method for the caps. The compaction process has already been demonstrated earlier /1/. The cementation process is based on the French process /2/3/. A flow sheet, comprising these two processes, has been drawn up. This results in the production of 277 canisters with compacted hulls (255 Mg, 55 m^3) and of 22 drums with cementated caps (80 Mg, 38 m^3). The influence of several parameters on the costs and radiological impact have been discussed. The most important parameters here are the size of the nuclear park, the size of the compaction press, and the compaction efficiency.

A second flow sheet has been drawn up which deals with the decontamination of the hulls and the cementation of both hulls and caps. The decontamination process used is the washing with cold HNO3 3N, which mainly results in 95 % alpha decontamination of the hulls /4/. The French cementation process, mentioned earlier, has been chosen. The combined process results in the production of 231 cemented drums (924 Mg, 395 m^3). The activities of the conditioned product are on the limit for acceptance for shallow land burial.

Progress and results

1. Discussion of data concerning amounts and characteristics of hulls and caps (2.1.)

A reference scenario has been defined in order to determine the amounts of hulls and caps produced. This reference scenario assumes a 20 GWe nuclear park of standard PWR's, which corresponds to a reprocessing capacity of 600 MTHM per year. The characteristics of the cladding waste produced is based on standard PWR fuel which 3.5 % enrichment and a burn-up of 33 GWd/MTHM. Reprocessing and conditioning are foreseen 3 years after reactor discharge.

The corresponding annual cladding waste production and its characteristics are summarized in Table I.

2. Drawing-up of basic management routes (2.2.)

Two basic management routes have been drawn up :

- Route No. 1 : hulls compaction/conditioning/packaging/interim storage;
- Route No. 2 : hulls decontamination/cementation/packaging/interim storage.

The original idea of compacting hulls and caps together was abandoned due to the different characteristics, especially the alpha activities. Since no experimental data were available concerning the press compaction of caps, it was decided to split up Route No. 1 in hulls compaction and caps cementation. A flow diagram of this route is given in Figure 1. The compaction process has been developed by S.C.K./C.E.N.

/1/. The cementation process is the process proposed by C.E.A. /2/3/. Application of both processes results in the production of the following amounts of conditioned waste :

- 277 canisters with compacted hulls, i.e. 255 Mg or 55.4 m^3, with an alpha activity of 217 MBq/kg and a beta-gamma activity of 628 GBq/kg;
- 22 drums with cemented caps, i.e. 80 Mg or 38.1 m^3.

Since the cemented caps do not contain alpha emitters and their beta-gamma activity is not too high, shallow land burial remains possible as final disposal.

The major steps of Route No. 2 are decontamination of the hulls and cementation of hulls and caps according to the French process. The aim of the decontamination is to lower the alpha content of the hulls to such an extent that shallow land burial will be allowed for final disposal. A flow diagram of Route No. 2 is given in Figure 2. The decontamination process retained consists of washing with cold $HNO3$ 3N, which results in a 95 % alpha decontamination /4/. This value is on the limit to be allowed for shallow land burial. Application of decontamination/cementation results in the production of 231 drums of cemented hulls and caps, i.e. 395 m^3 or 924 Mg.

3. Sensivity studies (2.3.)

The influence of a number of parameters on the characteristics and arisings of the conditioned waste product and on the total volume of the treatment and conditioning facility buildings has been studied. For Route No. 1, the following specific parameters are of importance :

- the size of the compaction press;
- the compaction efficiency.

For Route No. 2, the decontamination performance is the most important parameter in view of final disposal. Of course, for both routes, the size of the nuclear park is the most relevant parameter.

REFERENCES

/1/ P. DE REGGE
EUR-10824

/2/ C.E.A.
Joint study on management routes for LWRS hulls and ends
FI1W-0131-F
Cementation description.

/3/ C.E.A.
Joint study on management routes for LWRS ulls and ends
FI1W-0131-F
Process materials.

/4/ "COCQUENSTOCK"
EUR-10923

Table I : Annual cladding waste arisings

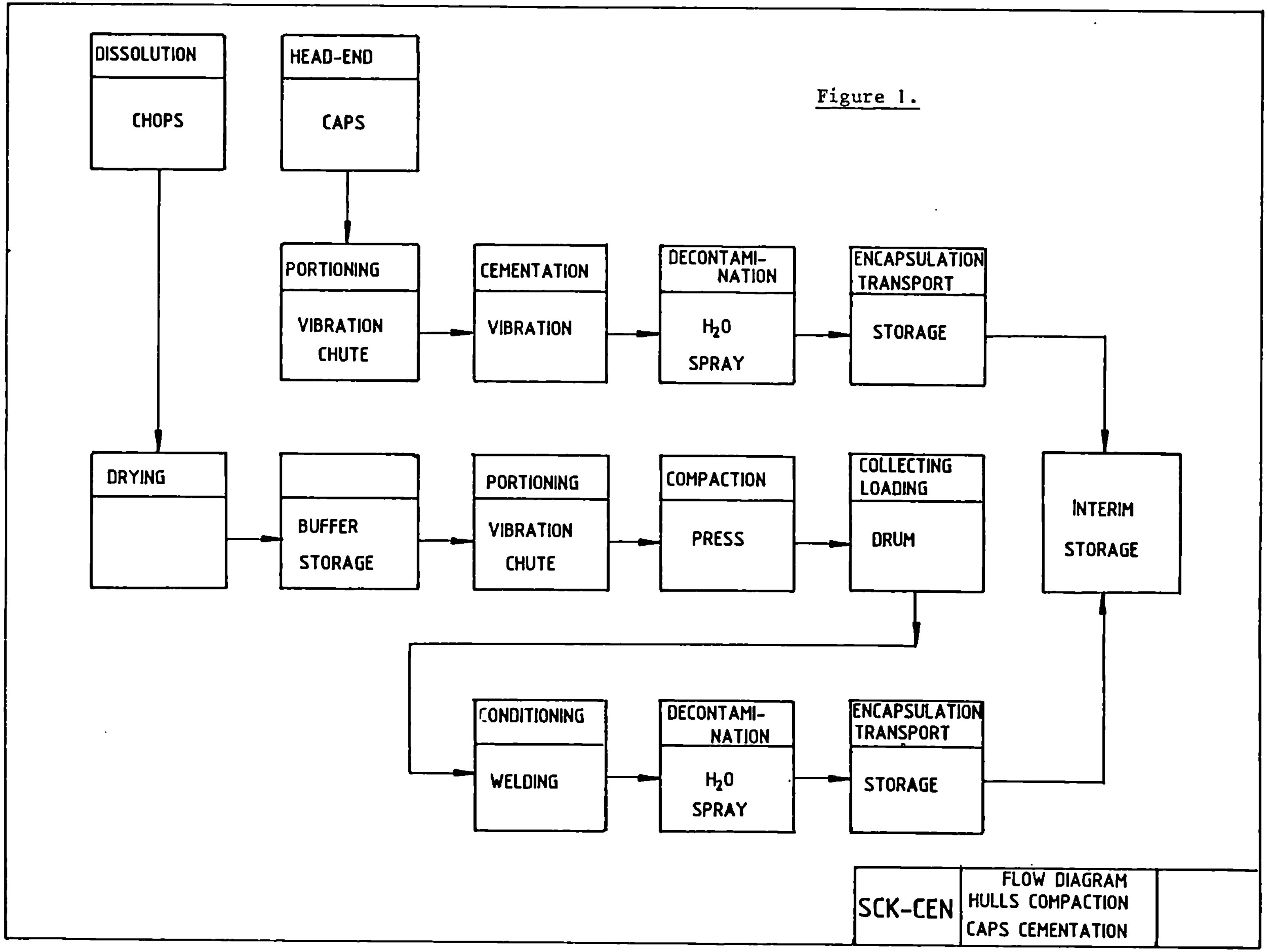
Scenario :

- 20 GWe Nuclear power
- 1000 MWe PWR units
- 600 THM/a reprocessing plant
- Fuel burn-up = 33.000 MWd/MTHM
- Fuel cooling time : 3 years.

Data :

		hulls	caps	TOTAL
mass	kg/a	171360	18060	189420
	%	90.5	9.5	100
density	kg/m^3	1000	1000	
volume	m^3/a	171.4	18.1	189.4
	%	90.5	9.5	100
activity				
- alpha	GBq/MTHM	100	--	100
- beta-gamma	TBq/MTHM	266.4	41.1	307.5
- total	TBq/MTHM	266.5	41.1	307.6
	%	86.6	13.4	100
Thermal power	W/MTHM	39.6	5.4	45

Figure 1.


DISSOLUTION
CHOPS
HEAD-END
CAPS
PORTIONING
VIBRATION CHUTE
CEMENTATION
VIBRATION
DECONTAMI-NATION
H_2O SPRAY
ENCAPSULATION TRANSPORT
STORAGE
DRYING
BUFFER STORAGE
PORTIONING
VIBRATION CHUTE
COMPACTION
PRESS
COLLECTING LOADING
DRUM
INTERIM STORAGE
CONDITIONING
WELDING
DECONTAMI-NATION
H_2O SPRAY
ENCAPSULATION TRANSPORT
STORAGE
SCK-CEN
FLOW DIAGRAM
HULLS COMPACTION
CAPS CEMENTATION

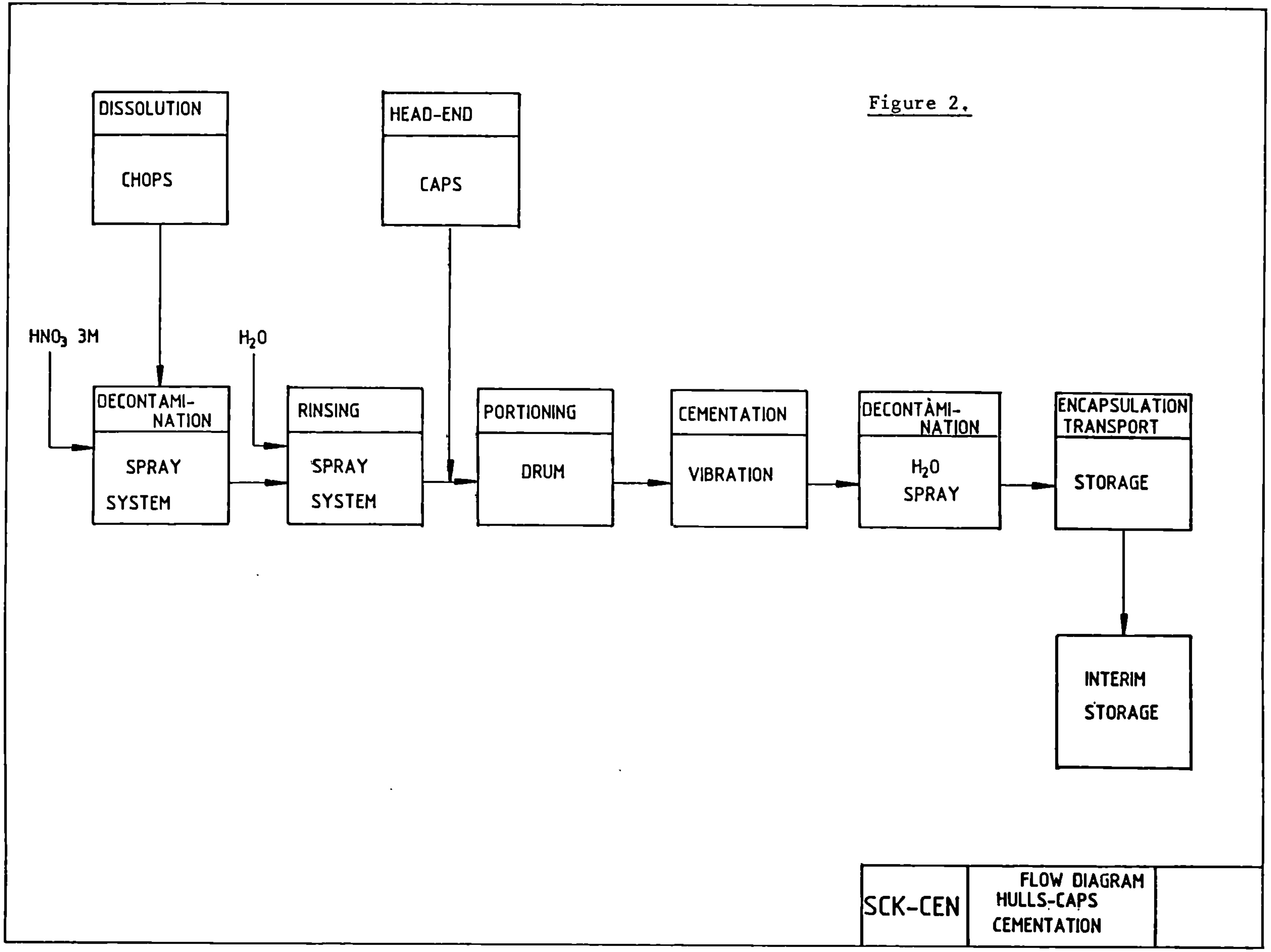


Figure 2.

DISSOLUTION
CHOPS
HEAD-END
CAPS
HNO3 3M
H2O
DECONTAMINATION
SPRAY SYSTEM
RINSING
SPRAY SYSTEM
PORTIONING
DRUM
CEMENTATION
VIBRATION
DECONTÀMINATION
H2O SPRAY
ENCAPSULATION TRANSPORT
STORAGE
INTERIM STORAGE
SCK-CEN
FLOW DIAGRAM HULLS-CAPS CEMENTATION

ASSESSMENT OF MANAGEMENT ALTERNATIVES FOR REACTOR WASTES

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

CONTRAT N° : FI 1W-0124

DURATION OF CONTRACT : November 1987 - January 1990

PERIOD COVERED : November 1987 - December 1988

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 ont 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 reactor 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.

State of advancement :

Point 1 : After several meetings with the French and German representatives, an agreement was found concerning the primary waste inventories for liquids, gas and solids as well for the design values which have to be taken into account in the design of the treatment equipment, as for the real values which must be taken into account in the activity balances.

Point 2 : Concerning the discharge limits, a trade-off was agreed upon between all the representatives, for the fixation of two limits for each radionuclide category.

With respect to the transport regulations it was agreed upon the Commission's suggestion to draw up the basic management routes following the current national practices.

Point 3 : The description of management route followed in Belgium for the gaseous wastes is completed.

The general description of the management route for the liquid waste giving the activity balance is completed.

The corresponding Technical description giving more detailed explanations on flow sheet and equipement will be soon available.

The same documents related to solid waste are also in preparation.

Point 6 : BELGATOM has already supplied TASK/KAH with the data related to the equipment cost of the off-gas treatment ;
of the ventilation air treatment ;
of the liquid effluents treatment ;
of the solid waste treatment.

With respect to operating costs, data are already supplied for the gaseous and liquid waste. The corresponding document for solid waste is in preparation.

Point 7 and 8 : The study begins in February 1989.

Progress and results :

Point 1 : The primary waste inventory for liquid waste of PWR's is based on the basic assumptions of a load follow and a maximum value of 0.1 % of cracked fuel elements and are given in Table I.

The primary waste inventory for gaseous waste is given in Table II, and in the concern for casiness, the same radionuclide composition was applied to ventilation gases as this for off-gases.

The primary waste inventory for solid waste is quoted in Table III ; a distinction was made between the most and least active fractions of primary resins as well as for the primary filters. The low levels solid waste is subdivised in four categories to enable its further processing by means of several variants.

Point 2 : The adoption of two discharge limits for each radionuclide category given in Table IV, corresponds to the following objectives : the design values are discharge limits which should necessarily be met by the treatment and conditioning facilities whereas the objectives values are the goals to be reached during normal operation of the treatment chains.

Point 3 : The descriptions of the basic management routes used in Belgium for gaseous, liquid and solid wastes form the subject of two kinds of documents : firstly the so-called General Descriptions where are described the basic flow sheets of each treatment chain including mass and activity balances and secondly the so-called Technical Descriptions where are given the detailed flow sheets of all processes and the specific equipment characteristics including instrumentation and control allowing the equipment cost evaluation. Informations is also supplied on applicable regulations.

The Technical Description of the gaseous waste treatment is splitted into off-gas treatment and ventilation air treatment due to the specificity of each waste stream.

Point 6 : To allow the cost evaluation, two kinds of documents are also elaborated, one for the equipment costs, another for the operating cost and this related to the four waste streams : off-gases ; ventilation air ; liquid effluents and solid waste.

The solid waste is therefore a particular case as far as the localisation of the treatment unit is concerned : I.E.R., filter cartridges, evaporators concentrates and flocculates are treated in the on-site installations, while the so-called technological waste are treated in a central treatment unit together with other solid waste coming from other waste sources than nuclear power plants. This situation imply a different way for evaluation for the corresponding operating costs.

TABLE I : PRIMARY WASTE INVENTORY FOR LIQUIDS (PWR's)

Waste origin	Design Value	Real Value
Primary circuit effluents	$3{,}7.10^{12}$ Bq/m^3 (with gas) $3{,}7.10^{11}$ Bq/m^3 (without gas) 24.000 m^3/a	$3{,}7.10^{10}$ Bq/m^3 (out of gas) 10.000 m^3/a
Secondary drain waste	$3{,}7.10^{10}$ Bq/m^3 (peak value)* $3{,}7.10^{9}$ Bq/m^3 (on average) 4.000 m^3/a	$3{,}7.10^{8}$ Bq/m^3 2.500 m^3/a
Laundry waste	$3{,}7.10^{6}$ Bq/m^3 4.000 m^3/a	$3{,}7.10^{6}$ Bq/m^3 (peak value) $3{,}7.10^{5}$ Bq/m^3 (on average) 4.000 m^3/a
Decontamination operations	$3{,}7.10^{9}$ Bq/m^3 500 m^3/a	$3{,}7.10^{8}$ Bq/m^3 10 m^3/a
Chemicals	$3{,}7.10^{8}$ Bq/m^3 1.500 m^3/a	$3{,}7.10^{7}$ Bq/m^3 1.500 m^3/a
Building waste	$3{,}7.10^{7}$ Bq/m^3 6.000 m^3/a	$3{,}7.10^{7}$ Bq/m^3 3.000 m^3/a

TABLE II : PRIMARY WASTE INVENTORY FOR GAS (PWR's)

Waste origin	Design Value	Real Value
Chem. & Volume Control system + Primary circuit degasing	10.000 Nm^3/a $7{,}4.10^{12}$ Bq/Nm^3	6.000 Nm^3/a $< 2{,}4.10^{12}$ Bq/Nm^3
Ventilation	150.000 Nm^3/h $3{,}7.10^{5}$ Bq/Nm^3	150.000 Nm^3/h $18{,}5.10^{3}$ Bq/Nm^3

TABLE III : PRIMARY WASTE INVENTORY FOR SOLIDS (PWR's)

Waste origin	Design Value	Real Value
Primary resins		
highly active	1.3 m^3/a 25,9.10^{12} Bq/m^3	1.3 m^3/a 18,5.10^{12} Bq/m^3
low active	2.6 m^3/a 3,7.10^{12} Bq/m^3	2.6 m^3/a 1,85.10^{12} Bq/m^3
Primary filters		
RCV	15 filt/a 3,7.10^{12} Bq/filt.	10 filt/a 1,85.10^{12} Bq/filt
PTR	25 filt/a 7,4.10^{10} Bq/filt.	20 filt:a 3,7.10^{10} Bq/filt
Core components	1 m^3/a 37.10^{12} Bq/m^3	1 m^3/a 37.10^{12} Bq/m^3
Normal equipment combustible + compactable*	260 m^3/a 3,7.10^8 Bq/m^3	260 m^3/a 3,7.10^8 Bq/m^3
Normal equipment non combustible + compactable	100 m^3/a 3,7.10^8 Bq/m^3	100 m^3/a 3,7.10^8 Bq/m^3
Normal equipment combustible + non compactable	20 m^3/a 3,7.10^8 Bq/m^3	20 m^3/a 3,7.10^8 Bq/m^3
Normal equipment non comb. + non compact.	20 m^3/a 7,4.10^9 Bq/m^3	20 m^3/a 7,4.10^9 Bq/m^3

* Density before compaction : 0.15.

TABLE IV : DISCHARGE LIMITS RELATED TO ONE PWR UNIT (900 MWe)

Waste origin	Objective Value	Design Value
Liquid effluents		
. Total (β,γ) (H-3 excluded)	$7{,}4.10^{10}$ Bq/a	$3{,}33.10^{11}$ Bq/a
. H-3	$2{,}8.10^{13}$ Bq/a	$3{,}5.10^{13}$ Bq/a
Airborne effluents		
. Noble gases	$7{,}4.10^{13}$ Bq/a	$7{,}4.10^{14}$ Bq/a
. Halogens	$7{,}4.10^{8}$ Bq/a	$1{,}11.10^{10}$ Bq/a
. Aerosols	$7{,}4.10^{8}$ Bq/a	$1{,}85.10^{10}$ Bq/a
. Tritium	$3{,}7.10^{12}$ Bq/a	$7{,}4.10^{12}$ Bq/a

COST EVALUATION OF ALTERNATIVE MANAGEMENT SCHEMES FOR LWR WASTE

Contractors : TASK Ricerca & Sviluppo S.r.l. - Kraftanlagen AG
Contract N° : FI1W-0125
Duration of Contract: from 01.10.87 to 31.01.90
Period Covered : from 01.01.88 to 31.12.88
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.

During the second phase of the work, TASK R&S and KAH will 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 are performing the cost evaluation of five 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 due to the delays encountered in the programmes of the other partners of the joint strategy study, responsible for the engineering of the management routes. As a result, the cost assessment procedure has only partially been applied to one LWR route, whose engineering and process aspects have been elaborated by GNS-Framatome.

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 as illustrated in Figure 1. 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 must be defined in collaboration with the other participating organisations. On the basis of these data, the transport costs in 1988 by either rail or road 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 has partially been applied to the management route based on the German practice for PWR's (route LWR1-PWR). The costing is based on the process information provided by GNS-Framatome, with the exception of the off gas treatment, for which the data of Belgatom have been utilised. The preliminary results are given in Tables I and 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. They 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)).

Figure 1 - Elements considered for the evaluation of the plant cost.

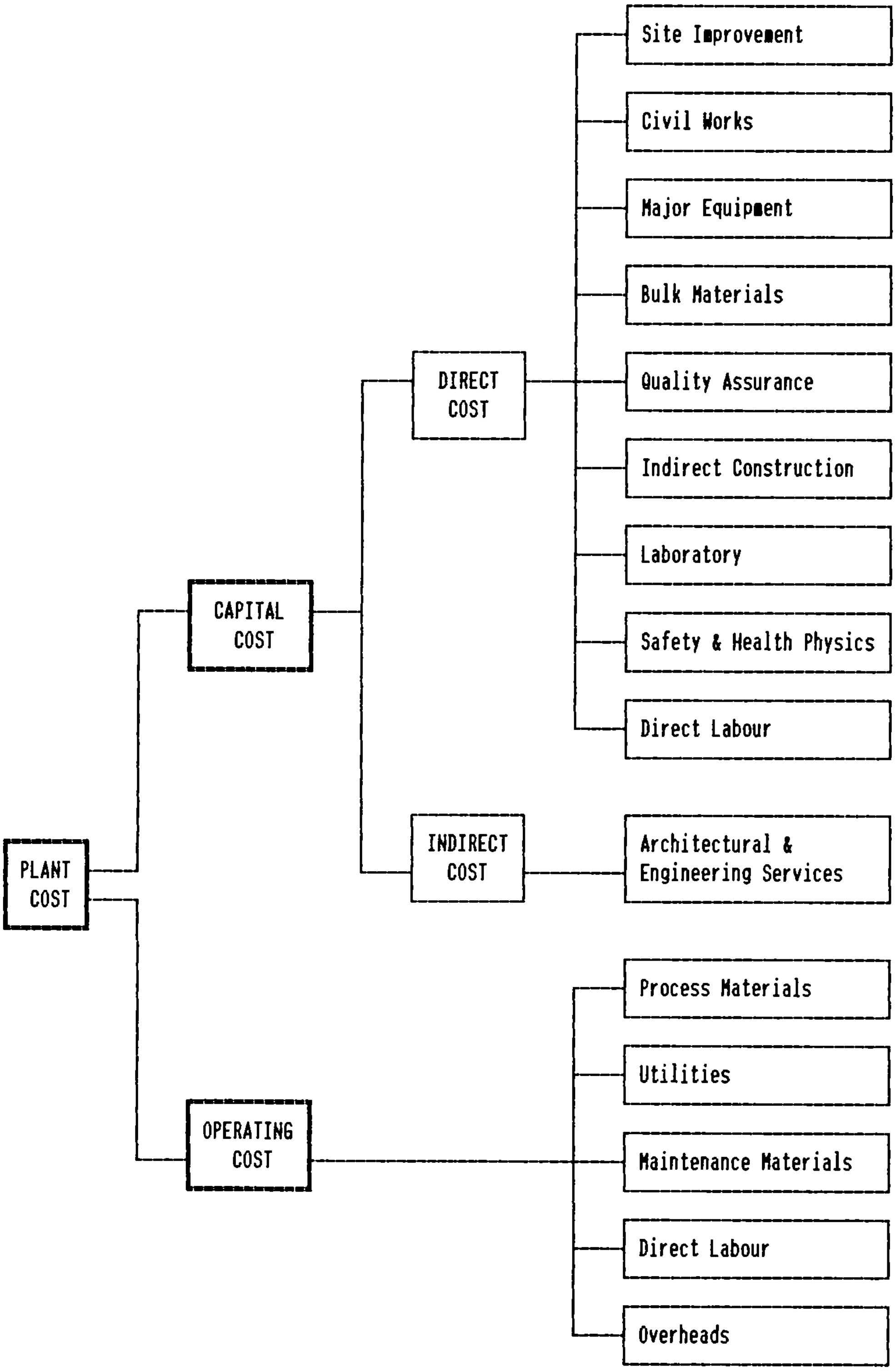


Table I – Material cost of the Major Equipment for the different unit operations and Base Value of route LWR1-PWR (20 GW(e)). All the figures are quoted for 1988.

UNIT OPERATION	TOTAL COST (MECU$_{88}$)
Coolant degassing system	9.603
Off gas treatment	31.361
Radioactive waste water treatment	47.139
Radioactive concentrate treatment (exclusive mobile unit*)	3.664
BASE VALUE	91.767

* In Germany, the mobile conditioning unit is rented.

Table II - Capital cost for route LWR1-PWR (20 GW(e)). The capital cost is defined as the combined costs for material and labour of each cost element.

COST ELEMENT	CAPITAL COST (MECU$_{88}$)
SITE IMPROVEMENT	10.850
CIVIL WORKS	69.911
UNIT OPERATIONS *	
Coolant degassing system	24.968
Off gas treatment	81.539
R.A. waste water treatment	122.562
R.A. concentrate treatment (excl. mobile unit)	9.527
QUALITY ASSURANCE	36.707
INDIRECT CONSTRUCTION	16.059
LABORATORY	2.294
SAFETY & HEALTH PHYSICS	6.883
ARCHITECTURAL & ENGINEERING SERVICES	4.480
TOTAL	385.780

* The capital cost of each unit operation includes the material cost of the Major Equipment and Bulk Materials and the labour cost for their installation.

COST EVALUATION OF ALTERNATIVE MANAGEMENT SCHEMES FOR ZIRCALOY HULLS

Contractors : TASK Ricerca & Sviluppo S.r.l. - Kraftanlagen AG
Contract N° : FI1W-0126
Duration of Contract: from 01.10.87 to 31.01.90
Period Covered : from 01.01.88 to 31.12.88
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 hulls and caps 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.

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.

During the second phase of the work, TASK R&S and KAH will scale 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 are performing the cost evaluation of five management options for Zircaloy hulls. 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 due to the delays encountered in the programmes of the other partners of the joint strategy study, responsible for the engineering of the management routes. As a result, the cost assessment procedure has only been applied to one Zircaloy hulls route, whose engineering and process aspects have been elaborated by NUKEM GmbH.

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 as illustrated in Figure 1. 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 must be defined in collaboration with the other participating organisations. On the basis of these data, the transport costs in 1988 by either rail or road 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 assessment procedure has been applied to the management route developed by NUKEM, namely hull compaction/cementation/packaging/ interim storage (route ZH2). The preliminary results are shown in Tables I and 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. They 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)).

Figure 1 - Elements considered for the evaluation of the plant cost.

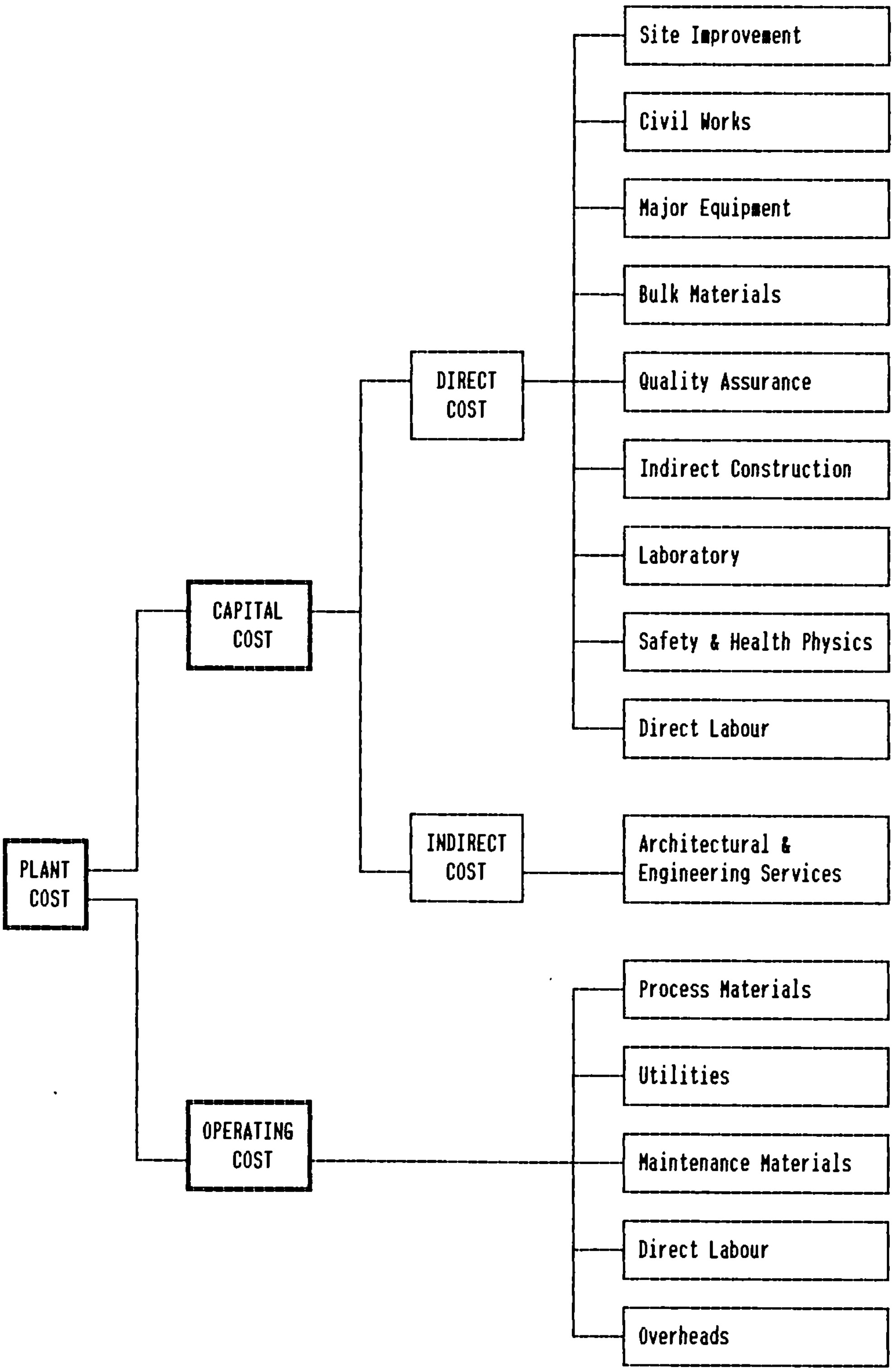


Table I - Material cost of the Major Equipment for the different unit operations and Base Value of route ZH2. All the figures are quoted for 1988.

UNIT OPERATION	TOTAL COST (MECU$_{88}$)
Waste delivery	0.675
Compaction & cementation	2.090
Cement preparation	0.049
Packaging (incl. decontamination)	0.745
Interim storage (5 years capacity)	4.239
BASE VALUE	7.798

Table II – Capital and annual operating costs for route ZH2. The capital cost is defined as the combined costs for material and labour of each cost element.

COST ELEMENT	CAPITAL COST (MECU$_{88}$)	OPERATING COST (MECU$_{88}$/a)
SITE IMPROVEMENT	0.975	---
CIVIL WORKS	4.336	---
UNIT OPERATIONS §		
Waste delivery	1.114	0.051
Compaction & cementation	3.448	0.277
Cement preparation	0.081	0.058
Packaging	1.229	0.081
Interim storage (5 years)	6.995	0.287
QUALITY ASSURANCE	1.950	---
INDIRECT CONSTRUCTION	1.560	---
LABORATORY	---	---
SAFETY & HEALTH PHYSICS	1.560	0.084
ARCHITECTURAL & ENGINEERING SERVICES	4.533	---
LABOUR ASSOCIATED WITH PLANT OPERATION *	---	0.084
OVERHEADS	---	0.112
TOTAL	27.781	1.034

§ The capital cost of each unit operation includes the material cost of the Major Equipment and Bulk Materials and the labour cost for their installation. The annual operating cost represents the cost for Process Materials, Utilities and Maintenance Materials and the labour cost for the operators directly involved in the mentioned unit operations.

* The labour associated with plant operation represents the labour cost for shift leaders, maintenance crew and transport registrars.

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

Contractor: Initec S.A., Madrid, Spain
Contract N°: FI1W-0127
Working Period: December 1987 - May 1989
Period Covered: January 1988 - December 1988
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 will focus 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:

- To 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 will be taken into account: ground water migration of radioactive elements, surface water releases and atmospheric releases. Three different stages will be considered in the life of the installation: operation of the facility, institutional control phase and free use of the land after termination of the license. Different scenarios will be assumed for each of the different stages, including normal operation scenarios as well as accidental scenarios.
- To determine the radiological burden to the facility operators.
- Cost assessment related to the disposal of LWR waste products in below ground vaults, including capital and operating costs.

B. Work Programme

2.2. Waste acceptance criteria will be established in terms of specific activity limits, matrix types, leaching rates, mechanical properties, drum sizes etc. so as to accomplish protection goals for the public.

2.3. Drawing up of storage facility layout and description of the operations to be carried out (sorting of the waste products, waste conditioning provisions, general layout etc. ...) as detailed as needed for the cost and radiological impact assessment.

2.5. The impact of the package type (retrievable or not) on the volumes of waste to be disposed of will be assessed, as well as the impact of varying both the volumes and categories of LWR wastes.

2.6. A cost assessment related to disposal of LWR waste products in below ground vaults will be carried out, including a relationship between disposal cost and quantities of various categories of waste products, and scaling cost for variations of the nuclear park size.

2.7. The occupational exposure (annual individual dose and collective dose) will be determined for normal and abnormal disposal operations, for the latter case expressed as probability of occurrence, for each working place and 30 years of operation.

2.8. The radiological impact to the public will be assessed and individual and collective doses will be calculated. The disposal site environment will be defined as well as pathways and scenarios considered.

C. Progress of Work and Obtained Results

1. Introduction

Determination of waste acceptance criteria for below ground vaults required the performance of short and long-term radiological impact calculations to identify limiting values of beta-gamma emitters, since limiting values of alpha emitters are established in Spanish regulations. Beta-gamme activity limits identified correspond to USA 10CFR61 regulations. Disposal site capacity is based on an average waste production rate of 200 m^3/reactor, which results in a total volume of wastes of 120,000 m^3.

Regarding conceptual design of the disposal centre, buildings and equipment provided are essentially similar to shallow land disposal facilities. Main differences identified concern the disposal area site preparation works, both prior to constructing the disposal vaults (drainage layers, see attached figure 1) and final preparation of the site (earth movements, compactation and drainage layers).

Costs related to civil works in the disposal area (site preparation, earth movements, construction and final preparation of the site) appear to be significantly higher than those associated to shallow land burial and the main contributors to total cost (± 90%).

Assessment of the radiological impact to individual members of the public was performed taking into consideration transuranics and long-lived isotopes to identified in waste streams provided by processists, due to their very low or untraceable concentrations. A theoretical concentration was estimated in order to figure out a theoretical long-term impact when these isotopes become dominant.

2. Progress and Results

2.1. Waste acceptance criteria

Radiological waste acceptance criteria have been developed, based on a distribution of 75% PWR and 25% BWR reactor wastes. The base spectrum adopted corresponds to reference /1/ and was normalised to radioactivity concentration limits of 10CFR61, except for alpha emitters which correspond to ENRESA limits.

A radiological impact assessment was performed to verify that such limits, both in concentration and in total activity, do not exceed dose limits. Various scenarios were considered:

a) normal evolution scenario: calculation of doses received by an individual through the inhalation of resuspended activity from soil contaminated by irrigation, and through the ingestion of contaminated drinking water and foodstuff, assuming the infiltration of rain water through the site cover, which lixiviates waste packages and reaches the underlying aquifer, which in turn discharges into a river;

b) intruder excavating a well downstream in the site boundary: calculation of doses due the ingestion of contaminated drinking water and foodstuff and inhalation of resuspended soil contaminated by irrigation;

c) intruder constructing a home: calculation of doses due to external exposure, the ingestion of contaminated foodstuff and the inhalation of suspended particles.

Resulting doses are presented in attached table 1. As can be seen, maximum normal evolution doses are below 0.04 mSv/y, i.e. well within ICRP limits. For intrusion scenarios, maximum doses found are in the order of 4 mSv/y, which is also within applicable ICRP limits for this case (5 mSv/y). Non-radiological acceptance criteria were taken from Spanish requirements.

2.2. Drawing up of management routes

Facility conceptual design for below-ground vaults focused on the following items:

a) general site description and site preparation requirements, where main relevant requirements for the site have been put forward, mainly the water table level (5 meters below excavation level), aquifer permeability (10^{-2} cm/s), homogeneous and isotopic media, the permeability of layer above aquifer (10^{-7} cm/s) and the slope of the layer (5%);
b) disposal area description, including vault characteristics and operation, volume of wastes to be disposed of etc. ...;
c) general description of the facility, including general design data, design criteria, storage procedures and facility organisation;
d) description of buildings and equipment housed in each building.

Reference /2/ contains detailed information on this item.

2.3. Cost assessment

Cost assessment was itemised as follows:

	Cost (pts x 1,000)
- site preparation including acquisition costs, permits, engineering, preparation works, vault construction and site reclamation	21,722,400
(lowering water table if necessary)	22,322,400
- buildings and general systems	2,288,000
- Total cost	23,010,400
(lowering water table if necessary)	24,010,400

Operation costs need further development.

According to TASK/KAH comments, cost assessment will be revised taking into account different itemisations.

2.4. Radiological impact to individual members of the public

Radiological impact to individual members of the public will be performed assuming only normal evolution scenarios as described in paragraph 2.1.. Impact to intruder is not considered relevant, except for waste acceptance criteria. Nevertheless, in order to obtain long-term radiological impact, the spectrum to be used should include long-lived isotopes. These long-lived isotopes have not been provided by process designers, since they are only present as traces in fresh waste spectrum, and they can be estimated through calculations. INITEC proposes using a spectrum of long-lived isotopes based on reference /1/ data.

References

/1/ Nureg CR-1759, Data Base for Radioactive Waste Management, 1981.
/2/ INITEC, Below-Ground Vaults, Facility conceptual Design and Cost Estimation, Nov. 1988.

TABLE I RESUME OF CALCULATED EFFECTIVE DOSES
(SV/A)

(MAXIMUM VALUES)

CASE A: NORMAL EVOLUTION (RIVER)

		PATHWAY			
POP. GROUP	DRINK WATER	INHALAT	ING.TERR.FOOD	ING.ACUAT.	TOT
ADULTS	4.19(-8)	8.42(-11)	1.06(-5)	5.03(-7)	1.12(-5)
CHILDREN	4.89(-8)	3.56(-11)	2.00(-5)	2.41(-7)	2.03(-5)
INFANTS	5.87(-8)	8.32(-12)	3.47(-5)	0.	3.48(-5)

CASE B: INTRUDER WITH WELL

		PATHWAY		
POP. GROUP	DRINK. WATER	INHALATION	INGESTION	TOTAL
ADULTS	5.22(-4)	4.25(-7)	1.62(-3)	2.14(-3)
CHILDREN	6.79(-4)	1.82(-7)	3.50(-3)	4.18(-3)
INFANTS	6.10(-4)	4.22(-8)	2.85(-3)	3.46(-3)

CASE C: INTRUDER WITH EXCAVATION

		PATHWAY		
POP. GROUP	EXTERNAL EXP.	INHALATION	INGESTION	TOTAL
ADULTS	4.06(-5)	6.57(-5)	1.83(-3)	1.93(-3)
CHILDREN	2.03(-5)	2.69(-5)	3.64(-3)	3.68(-3)
INFANTS	7.40(-6)	5.81(-6)	1.83(-3)	1.84(-3)

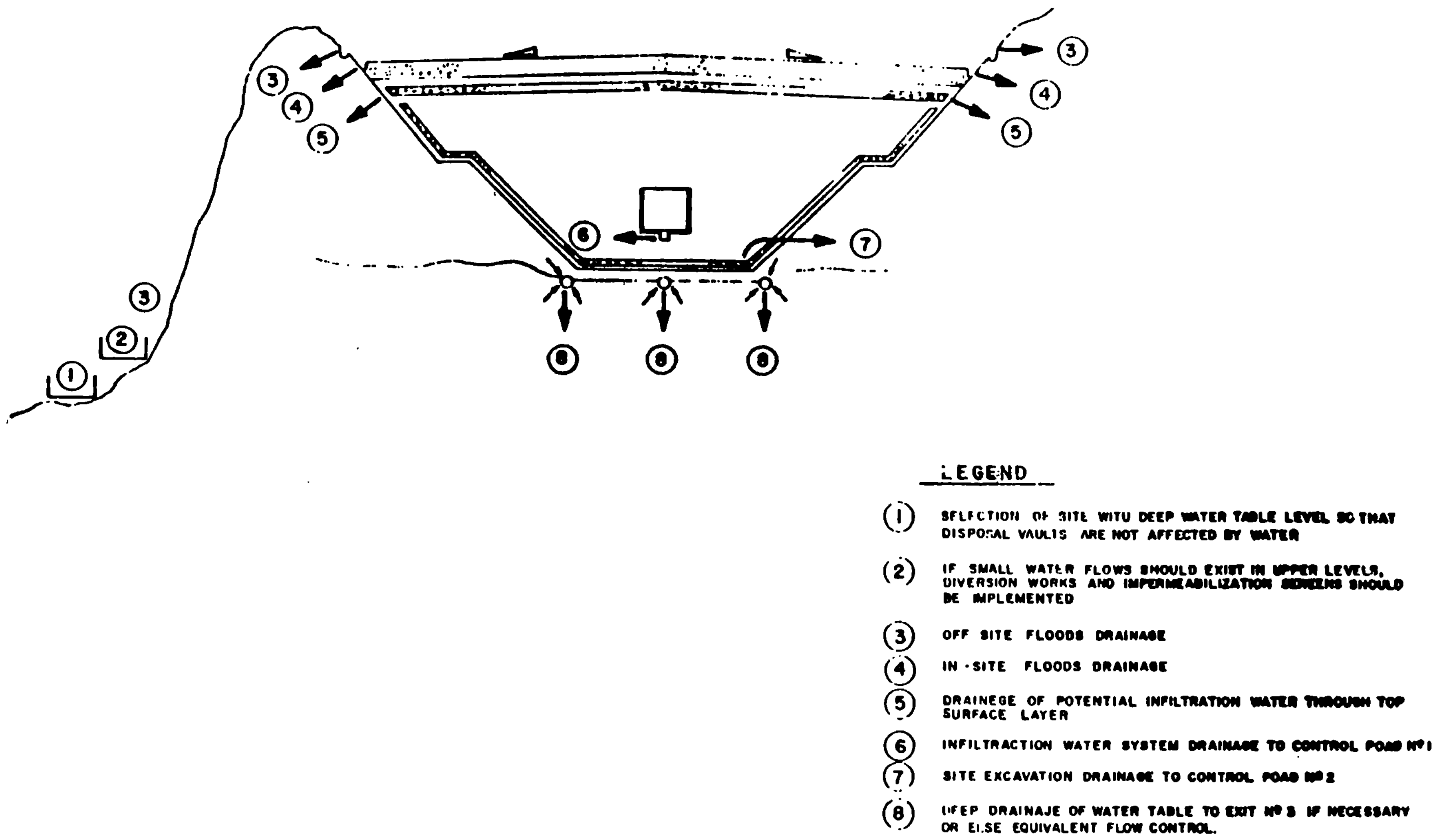


Figure 1. Drainage procedure diagramme.

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-0128-00
Duration of contract : 1 August 1987 - 31 December 1989
Period covered : 1 January 1988 - 31 December 1988
Project leader : S.F. Mobbs

A. OBJECTIVES AND SCOPE

Mehods 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

A research fellow, Dr P T Allen, has been appointed at the University of Surrey.

Stages 2.1 and 2.2 of the project have been carried out, that is, a set of components for which weighting factors are needed has been identified. (This does not rule out the identification of further components in the course of contact with respondents.)

In respect of stage 2.3, it has been assessed as unlikely that past waste management decisions and/or previous attitude surveys would provide sufficient information for our purposes. Therefore, it has been decided to develop a methodology for deriving weighting factors, focusing around the use of specially designed questionnaires for survey purposes. The background technical information for the questionnaire has been collected and this will be used to design the questionnaire early in 1989. The results of a number of pilot surveys will then be analysed to derive the weighting factors.

Progress and results

2.1, 2.2 Identification of components for which weighting factors are to be devised

Radiological protection is concerned not just with compliance with dose limits set by regulatory authorities, but with choosing the best option to minimise radiation exposures, taking into account economic costs and social costs. Such costs may include items which are hard to cost in monetary terms such as deterioration of the environment and hence a structured approach is necessary for the decision process. This study works at such an approach in the context of decisions on radioactive waste management options.

Different people will have different perceptions of the costs associated with the various management options for radioactive waste. Some people will rate the health effects to be of paramount importance whereas others will rate economic costs as equally important. These types of perception can be expressed in the form of numerical weighting factors which are then used in decision analysis to express difference preferences towards various consequences.

The factors to be weighted have been reviewed and a total of seven components have been identified. These are (i) attitudes to the various categories of health effects: fatal cancer, non fatal cancer and hereditary disease; (ii) the trade off of exposure to the public or to the workforce;
(iii) the relative acceptability of health effects occurring now or some time in the future by considering three time periods: within 100 years, between 100 and 1000 years in the future, and beyond 1000 years in the future; (iv) attitudes to the geographical spread of health effects by considering four geographical areas: local,

national, European Community and global; (v) the tradeoff between health effects and economic cost; (vi) attitudes to natural and artificial sources of radiation exposure; and (vii) attitudes to the different probabilities of developing cancer: these can be used to draw up a risk aversion curve.

2.3 Developing of a methodology

Four possible methods for establishing weighting factors have been considered. These are the analysis of past waste management decisions in the manner of revealed preference studies, the use of the results of previous attitude surveys, setting up a discussion group consisting of representatives of different sectors of society to argue the issues, and finally the use of a specially designed questionnaire to interview members of the public and representatives of interest groups. The last method was chosen as being that most appropriate for this work.

Considerable progress has been made on the design of the questionnaire. Two different approaches will be tried in a pilot study and the results will be used to determine the form of the final questionnaire. The first approach is the direct approach in which respondents are asked to score the different attributes and then these scores are built up into a valuation of a number of waste management options. The second approach is an indirect approach in which respondents are asked to score some specified waste management options and then multiple regression techniques are used to determine which attributes were important. In both cases it was felt that people would not be able to provide a meaningful response to questions unless they were placed into context. Therefore the fullest possible information would be provided in the form of background material, and in connection with each option.

In order to pursue the indirect approach it is necessary to present a range of options, chosen to provide attributes that are as different as possible. The options that remain open in the UK for many waste types are fairly limited and therefore it was decided to present people with two different cases, the options for reactor decommissioning wastes and the options for vitrified high level waste. These waste types were chosen because they either already exist or they will exist as a result of past electricity generation and hence the replies are less likely to be influenced by the individuals perception of the future of nuclear power. Indicative costs and radiological impacts were calculated for six options for Magnox and AGR decommissioning wastes: seadumping, shallow land burial, deep geological burial inland, deep geological burial under the sea but accessed from land, disposal in an offshore borehole and storage for 100 years or more. For vitrified high level wastes the costs and radiological impacts were calculated for a different six options: deep geological burial inland, deep geological burial under the sea but accessed from land, disposal in an offshore borehole, disposal in the deep ocean floor using penetrators, disposal into a hole drilled into the deep ocean floor, and storage for 300 years or more. These results will be used to formulate analogues for use in the questionnaire.

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 - December 1989
Period covered : January 1988 - December 1988
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 has been completed and work on items B.2, B.4 and B.5 has started. The radiological impacts of operational liquid discharges and shallow land burial of low level wastes on the public have been calculated. The radionuclide inventory for spent fuel has been derived and compared with that produced by CEA under another contract associated with this project. The waste inventories will be produced as soon as the few outstanding differences between these two inventories have been resolved. Work on B.3 and B.6 will start in mid 1989.

Progress and results

B.1 Agreement of study assumptions

The quantity of fuel to be considered, the times at which reprocessing and vitrification take place and the storage period for the vitrified high level waste were agreed in the previous reporting period. It was agreed that NRPB would calculate the radiological impact of disposal or release of unit activity of a series of radionuclides in a form that could be used by the CODDAR code being developed by CAP Scientific under an associated contract. The components of radiological impact that will be calculated will be risks to individuals and collective doses to local, national, European and global populations as a function of time. A list of the most important radionuclides which should be included in the assessment of each disposal option has been agreed.

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

BNFL has compiled the radionuclide inventory for spent fuel using the FISPIN code. This was compared with the inventory produced by CEA using the APOLLO-EVOGENE code under a contract associated with this project since it was important to maintain consistency. A number of differences were noted between the inventories and although the majority of these differences concerned radionuclides that would not be expected to give significant radiological impacts there were a few that were expected to be more important and hence these were looked into further. The few remaining discrepancies will be resolved as soon as possible. It will then be straightforward to produce the waste inventories. Flow diagrams describing the reprocessing process and the origin of the various waste streams have been provided by BNFL.

B.4 Assessment of operational radiological impact

NRPB has calculated the radiological impact of unit discharges to the marine environment during reprocessing operations. A total of 15 radionuclides were studied (see Table I) and the results were obtained for releases from the reprocessing plant at Sellafield and from the reprocessing plant at Cap de La Hague. The assessment was performed using the regional marine model MARIN1 developed for the CEC MARINA project and the associated database of seafood catches for the different ocean compartments. In both cases the releases were assumed to continue for 30 years. Peak individual doses and risks were calculated using the generic critical group habits adopted by NRPB for biosphere calculations/1/ so that the same assumptions were used for the two sites. Integrated collective doses were calculated for the following times: 30, 50, 60, 100, 1000, 10^4 and 10^8 years and the results were presented for the four different populations. These collective doses were calculated from the seafood catch data provided for each country in the MARINA database. The peak individual doses for unit releases from the two sites were practically the same for all radionuclides except ^{60}Co and ^{95}Zr. The dominant pathway for these two radionuclides is external exposure from contaminated sediments and hence the predicted dose is dependent upon the local sedimentation rate which differs for the two sites.

The integrated collective does from unit releases from the two sites also differed, sometimes by more than an order of magnitude, and this results from the different sizes of seafood catch that occur close to the two sites.

B.5 Assessment of post disposal radiological impact

NRPB has calculated the radiological impact of disposal of unit activity of low level waste to a shallow land burial trench at Drigg. A total of 14 radionuclides were studied, see Table I. The results were obtained by using the geosphere model GEOS and the biosphere model BIOS and the database was taken from a recent NRPB assessment of the Drigg site /2/. Peak individual doses and risks were calculated for the following 3 different pathways: leaching of the waste and migration of radionuclides through the groundwater leading to release to the Irish sea, leaching of waste and migration of radionuclides through the groundwater leading to release to a local stream, and intrusion into the site by drilling an exploratory borehole, by site occupancy or by abstracting water from a well. Other pathways has been found to give lower risks /2/. Integrated collective doses were calculated for the two leaching and migration pathways and were presented for six integration periods (50, 100, 1000, 10^4, 10^6 and 10^8 years) and the four different populations. The results were then summed over the different pathways in proportion to the probability of each pathway to give values of the total radiological impact. The peak individual doses and risks for the majority of the radionuclides were dominated by the first migration pathway (release to the Irish Sea). The exceptions were ^{137}Cs, ^{238}Pu, ^{239}Pu and ^{241}Am and the doses and risks for these four radionuclides were dominated by the pathway describing water abstraction from a well. The integrated collective doses at all times and for all four populations were dominated by the first migration pathway (release to the Irish Sea).

References

/1/ 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).

/2/ SMITH G M, FEARN, H S, SMITH K R, DAVIS J P, AND KLOS RA, Assessment of the radiological impact of disposal of solid radioactive waste at Drigg. NRPB-M148, Chilton (1988).

Table I

Radionuclides studied

a) Operational releases (Sellafield and Cap de La Hague sites)

^{14}C ^{60}Co ^{90}Sr ^{95}Zr ^{99}Tc ^{106}Ru ^{125}Sb ^{129}I
^{134}Cs ^{137}Cs ^{237}Np ^{238}Pu ^{239}Pu ^{241}Pu ^{241}Am

b) Shallow land burial (Drigg site)

^{14}C ^{60}Co ^{108m}Ag ^{126}Sn ^{129}I ^{137}Cs ^{226}Ra ^{232}Th
^{234}U ^{235}U ^{238}U ^{237}Np ^{238}Pu ^{239}Pu ^{240}Pu ^{241}Am

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 N° : FI1W - 0130
Duration of contract : from January 1988 to April 1990
Period covered : January 1988 to December 1988
Project Leaders: K. Janberg, 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 analysis 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 OBTAINED

Work Status

Tasks 2.2.,"Definition of typical primary waste inventories resulting from normal operation of PWR's and BWR's" and 2.3., "Definition of discharge limits, waste acceptance criteria and transport regulations" have been completed.

A slight slippage has occured in the schedule for task 2.4. " Drawing up of basic management schemes " concerning BWR's. Work has started on PWR's with the agreement of the project management in order that the downstream final disposal, economic and radiological impact analysis can be started as soon as possible. This will enable a start to be made on the mathematical models straight away. The assessment of the German management scheme for PWR's is practically finished.

The BWR management scheme will be carried out along the same lines, once the data already supplied have been analysed.

The information required for cost evaluation has already been communicated and a cost calculation first draft for the German PWR waste management scheme has been made.

Progress and results

For the assessment of German practice in waste management, both of the following assumptions have been made :

-the capacity of German power plants is approximately 1200 MWe. For the purposes of the study, a 900 MWe reactor has been chosen and the values must be adapted as a consequence,

-the operating values are taken for plants that have been in operation for several years (Biblis for instance in the case of PWR's) while the waste treatment system design corresponds to more recent plants.

2.2. Definition of typical primary waste inventories resulting from normal operation of pwr's and bwr's

The working group has decided to use the same primary waste inventories to draw up national management schemes in order to make the next part of the study, more consistent. The difference between these study inventories and the national ones will be taken into account as part of parametric studies.

For inventory purposes, the waste have been divided into :

- gaseous,
- liquid,
- solid.

These inventories are shown in tabular form with the waste broken down into streams and quantities corresponding roughly to those existing in France for PWR's and in the F.R.G. for BWR's, because of greater national experience in these areas. The real values are operating values and the design values will be used to size treament units. As far as the radionuclide composition of effluents is concerned, the given values are theoretical because they are likely to vary greatly for the plant according to type, age, operation, point in operating cycle and time of measurement (the composition depends on the half life of isotopes). For the study, it seems more appropriate to deal with the longer half-life isotopes and in the case of liquid waste to limit oneself to those isotopes which are the most radioactive.

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

The same discharge limits have been adopted for each national scheme. Two kinds of limits have been defined for each radionuclide category: design and objective values. The design value is a discharge limit which must be met by the treatment and conditioning facilities, whereas the objective value is the target to be reached during normal operation but is without any binding constraint.

Since the national waste transport regulations are quite different, the basic management schemes will first be drawn up with the current national practice. The impact of adopting the same IAEA recommendations will be examined as part of the parametric study. For the F.R.G, these recommendations are already in application. Nevertheless, they are going to be amended because of recent changes.

The acceptance criteria for the Konrad German iron-mine have been presented with the different requirements for the waste forms and packagings.

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

Data have been supplied about German waste management schemes for PWR's and BWR's : description of each treatment system, flow diagrams, equipment characteristics and costs.

These data have been processed and flow sheets have been made to outline the PWR management scheme.

The treatment systems are as follows :

- gaseous effluents : ventilation and off-gas system,
- liquid effluents : primary coolant treatment system and liquid waste treatment system,
- solid waste : technological waste treatment system and waste from liquid processing treatment systems (sludge, concentrate, resins).

The flow sheets have been evaluated with the waste inventories defined for the study (with real values).

Preliminary values have been given for the amounts of conditioned waste release. They will be used in the final disposal site sizing.

2.6. Costing of the basic management route as well as the variants evolved from sensitivity studies

Data needed for PWR and BWR cost evaluation have been given :

- equipment cost,
- building capacity,
- operating time, workers'salaries.

The same device for off-gas treatment should be applied for all management schemes. For the purposes of cost evaluation, the Belgian treatment system will be used. A preliminary cost evaluation (PWR's)has already been carried out for the German management scheme.

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 N° : FI 1 W - 0131

Duration of contract : september 1987 - december 1989

Period covered : november 1987 - november 1988

Project leader : C. SOMBRET

A/ OBJECTIVES AND SCOPE.

The objective of the 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 :

- Route n° 1 : Hulls and caps cementation/packaging/interim storage (Reference industrial route of the La Hague reprocessing plant).
- Route n° 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 options.
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 take in charge wholly tasks 3, 4, 5 and 8 partly task 9 for two basic management routes based on direct hulls cementation for the first one and on melting for the second one.

C/ PROGRESS OF WORK AND OBTAINED RESULTS.

STATE OF ADVANCEMENT.

The reference scenario was defined jointly by the working group. The basic specifications of the hulls and end caps were reported in october 1987 for a 900 MW 17 x 17 PWR reference fuel with a burnup of 33000 MWd.t^{-1} (20 GWe nuclear park).

The reference conditioning process (cementation) was described in documents referenced DIP/SEIP/88.443.54 and DIP/SEIP/86.443.124. The entire process (operation, equipment, layout, etc) is based on the data and concepts used for the UP3 reprocessing plant at La Hague, adapted to an annual throughput capacity of 600 metric tons.

The alternative hull melting process was described in document DIP/SEIP/88.443.126. The off-gas treatment process must be defined, particularly with regard to tritium trapping. The process flowsheet for end caps and structural components is now being developed.

1/ Basic data.

The date primarily concern the mass throughput, radioactive characteristics and thermal power for fuel reprocessed after 3 years.

2/ Description of cementing process.

In the La Hague UP3 plant design the hull and-cap conditioning unit is part of the fuel dissolution facility. Hulls and end-pieces are placed in the waste drum while the cement grout is prepared in a nonradioactive zone. The unit includes a single gravity-feed cementing line, with the conditioning steps on one level and the cement grout preparation above.

The principal process steps include :

. Introduction of the empty drum and inspection of the lid mechanism.
. Filling the drum with hulls, end caps and structural elements.
. Residual fissile material measurement.
. Cement grouting.
. Decontamination of the drum outer surfaces.

The drums are allowed to stand while the cement sets, and then transferred to an interim storage unit (with a capacity equivalent to the producction of 1 year) pending final storage. The heat released from the waste drums is removed by a ventilation system.

The annual production in a 600 t/year plant would be 231 UP3 waste drums representing a total volume of 404 m^3 and weighing 924 metric tons.

3/ Description of melting process.

The alternative process investigated by the CEA involves melting the hulls and end-pieces. The hulls would be skull-melted in a cold crucible, while the "end-pieces" (i.e. subassembly, end caps and grids) would be separated from the hulls in the dissolution facility and melted in a conventional crucible.

3.1./ Hulls.

The hulls would first be placed in a drum and dried in a hot argon stream before interim storage in a buffer hopper. Hulls would be fed to the molten bath by a metering system and continuously melted under inert argon atmosphere with mineral salt additives in batches corresponding to one ingot. The ingot would be continuously drawn from the melt, and the mineral salts would be separately recovered for conditioning in a waste drum.

Melting the hulls would release occluded gas from the cladding scraps, requiring specific off-gas treatment, notably for tritium.

The ingots would be placed and mechanically secured in groups of three in containers with dimensions similar to those of a standard R7T7 waste canister. After decontamination of the exterior surfaces, the container would be transferred to the onsite interim storage facility, with a capacity equivalent to a full year of production.

The annual production would correspond to 903 ingots, filling 301 containers representing a total volume of 58 m^3 and weighing 198 metric tons.

3.2./ End-pieces.

(Research in progress).

The work corresponding to tasks 5, 8 and 9 will be conducted during 1989.

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 : F1 - 1W - 0132
Duration of the contract : September 1987 - December 1989
Period covered : January 1988 - December 1988
Project Leaders : B. de WAVRECHIN, C. JAOUEN

A - OBJECTIVE AND SCOPE

The objective is to contribute to the implementation of a joint study on management options for LWR waste 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 LLR wastes from their production to their disposal is implemented. 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 respectively EDF and INYPSA who cooperate with SGN as contractors. More specifically, the contribution of INYPSA applies to the study of the BWR waste management options based on the Spanish experience.

B - WORK PROGRAMME

2.2. Definition of typical primary waste inventories resulting from normal operation of 900 MWe PWR and BWR in France and Spain.

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

2.4. Drawing up of the two basic management routes according to the French and Spanish practices considering a 20 GWe nuclear park (80% PWR and 20% BWR) and grouping reactors by four units.

2.5. Sensitivity studies to determine the impact of treatment and conditioning parameters on waste product characteristics and quantities, and the cost of major components.

2.6. Assessment of the occupational exposure.

2.7. Assessment of the radiological impact to the public from the radionuclide contents of each main effluent generated in the two basic management routes and the variants.

C - PROGRESS OF WORK AND OBTAINED RESULTS

Sate of advancement

During the reference year 1988, the following tasks were completed :

a - Definition of discharge limits and transport regulations,
b - Definition of typical primary waste inventories resulting from normal operations of PWRs and BWRs,
c - Drawing-up of basic management routes taking into account treatment and conditioning variants,
d - Costing elements of the basic management routes.

Progress and results

2.2. DEFINITION OF TYPICAL PRIMARY INVENTORY

Typical primary inventories were established during the second progress meeting, held on February 12, 1988 in Brussels. They serve as a common basis to draw up management routes for PWR and BWR wastes according the different national practices.
In the Spanish COFRENTES NPP, the use of a freon facility for the dry cleaning of clothes and a discriminating unit for "hot" and "cold" used clothes lead to an annual inventory for laundry wastes equal to 1/5th of the european inventory stated value i.e. 1000 m^3/y instead of 5000 m^3/y.

2.3. DEFINITION OF DISCHARGE LIMITS, WASTE ACCEPTANCE CRITERIA AND TRANSPORT REGULATIONS

The comparison between discharge limits and real discharges shows that current discharge of liquid and airborne effluents represent only a few percent of the limits. So it has seemed more relevant to take into consideration averaged current discharge as objective value for the drawing-up of management routes.
In order to determine the waste treatment installations, it has been considered as appropriate to define large annual limits for the design assessment, allowing the description of the management routes adapted to the various national practices. Objective values being the target to be reached during normal operation.

The possible effects of setting additional discharge limits for alpha emitters on management routes, will be investigated later on in the sensitivity studies. This will require to evaluate the alpha emitters content in primary effluents and the counting of their activity.
The replacement of the current practices in France in matter of transport regulations by the IAEA recommandations should require still little time. So during the first progress meeting, held on 24 November 1987 in Brussels, the working group agreed upon the Commission's suggestion to draw up first the basic management routes on the basic of current national practices in matter of transport and then, in the frame of the sensitivity studies, to evaluate the impact of adopting the same IAEA recommandations.

2.4. DRAWING-UP OF BASIC MANAGEMENT ROUTES

Waste treatment systems were described using process diagrams and data given by EDF (PWR) and INYPSA (BWR). As for the Spanish reference management route, the COFRENTES NPP has been chosen as it is the only 975 MWe BWR currently in operation in Spain. COFRENTES NPP was designed by GENERAL ELECTRIC with a "zero liquid release" type liquid waste treatment system under normal operating conditions. This is made possible through an efficient treatment process using a lot of recycle.

EDF treatment systems varies according to the waste activity levels. The main features of these systems includes :

- The boron recycle system (TEP) separates the non-contaminated reactor coolant effluents into boric acid solution and reactor grade water, both to be reused as make-up to the reactor coolant system (REA), thus limiting the amount of effluents to be discharged to the environment.
- The liquid waste treatment system (TEU) incorporates four functions : storage, demineralization, evaporation and filtration. Purified waste is released from the plant after monitoring. Should release conditions not to be met (too high radioactive level of the waste), they can be recycled for reprocessing.
- The gazeous waste treatment system (TEG) reduces effluents activity level before control to the plant stack and release to the atmosphere.
- The spent ion exchange resins are backwashed in the demineralizers (RCV, PTR, TEU, TEP), then flushed out using the demineralized water distribution system (SED). After which, they are transferred to the storage tanks where they are stored under water. They are then embedded in concrete using mobile treatment.
- The filters are embedded in liquid concrete into concrete containers.
- The concentrates are stored in a stainless steel tank. A mechanical mixer provides good homogeneity of concentrates before drumming. A metering pot located under the tank is used to dose concentrates in the concrete containers. Concentrates are mixed with concrete in concrete containers by means of a disposable mixer.
- Dry active wastes (Anything likely to have been in contact with radioactive substances : tools, vinyl bags, rags, clothes... and that cannot be decontaminated or washed), are put into metal drums because of their very low activity.

  The compactable ones are first precompacted in order to divide their volume by 3.

As an exemple the annual production of waste containers for solid wastes and for one 900 MWe PWR unit represents 340 m^3/y with an activity of 8,960 Curies.

In addition, cost elements have been provided to the working group, such as : characteristics of the major equipment used as based value for the cost determination procedure, estimated volume of the treatment systems building, for the assessment of the civil work costs, general information provided by EDF for the French experience, to serve as a basis of comparison operation cost assessment.

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

Contractor	:	Principia Mechanica Ltd
Contract No	:	FI1W/0133
Duration of Contract	:	September 1987 to March 1989
Period covered	:	January 1988 to December 1988
Project Leader	:	R S Laundy

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.

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 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.

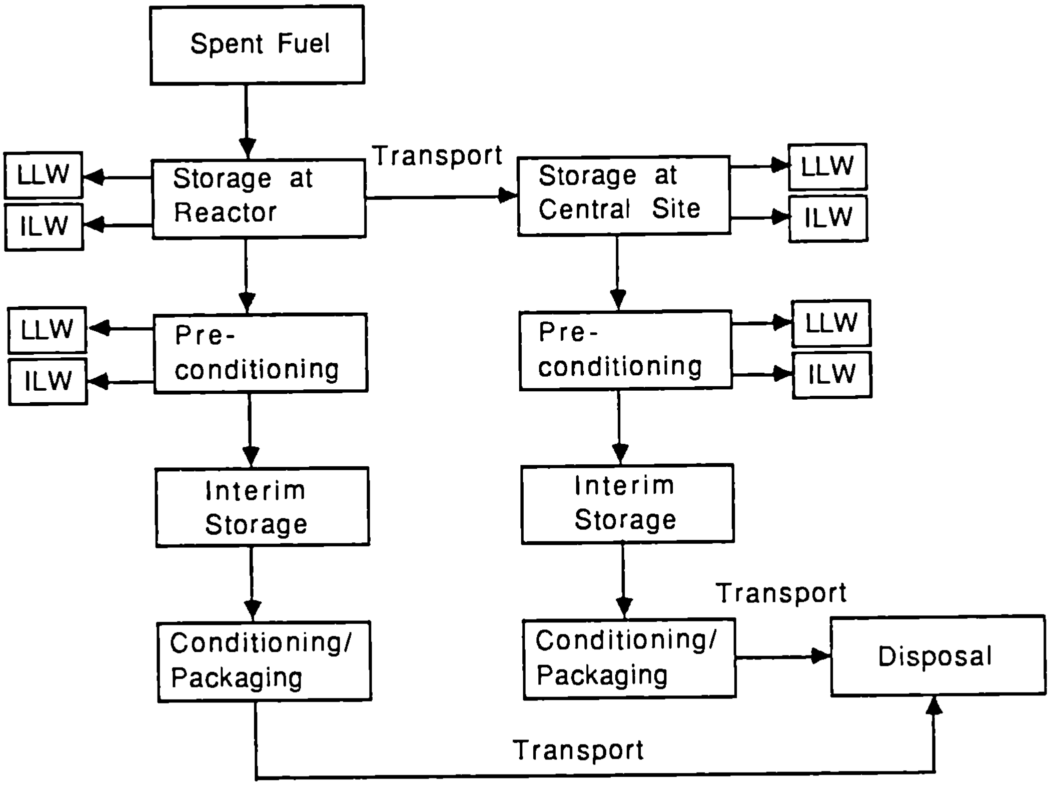


Figure 1 Schematic diagram of direct disposal options

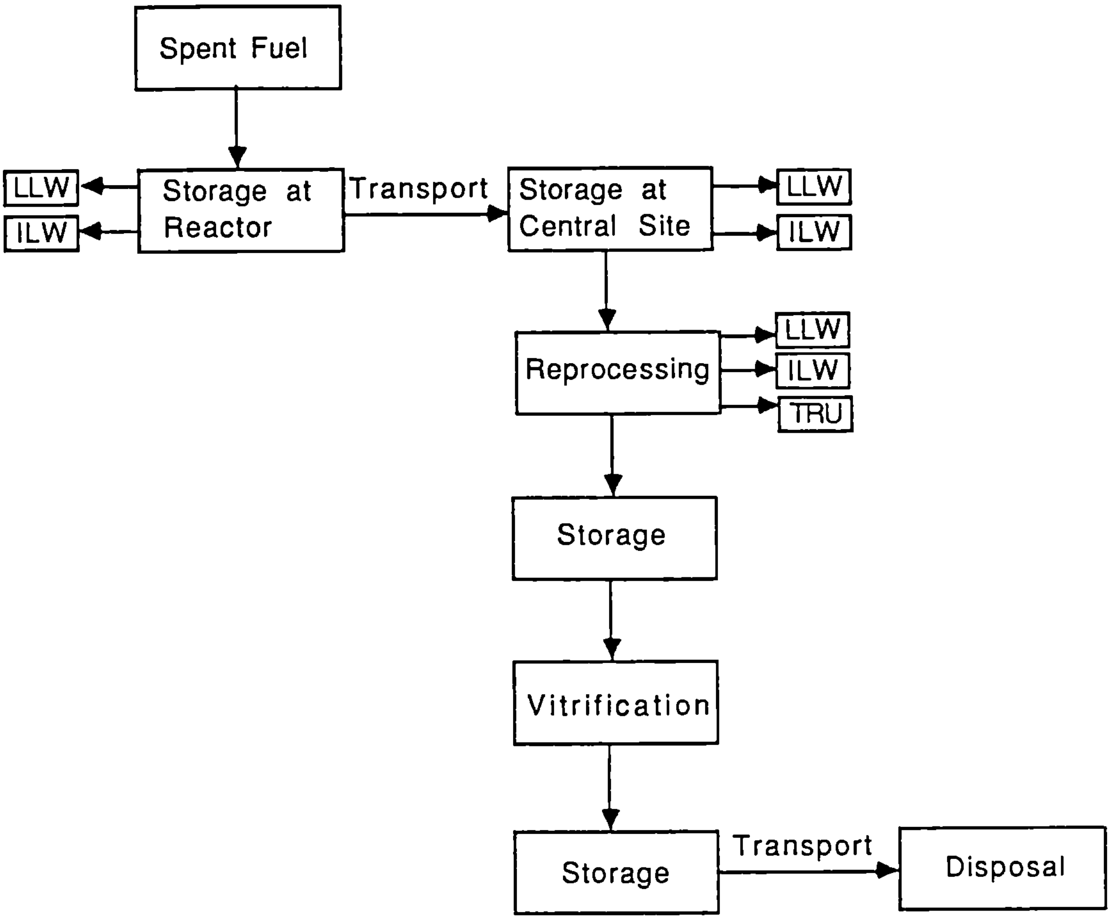


Figure 2 Schematic diagram of reprocessing options

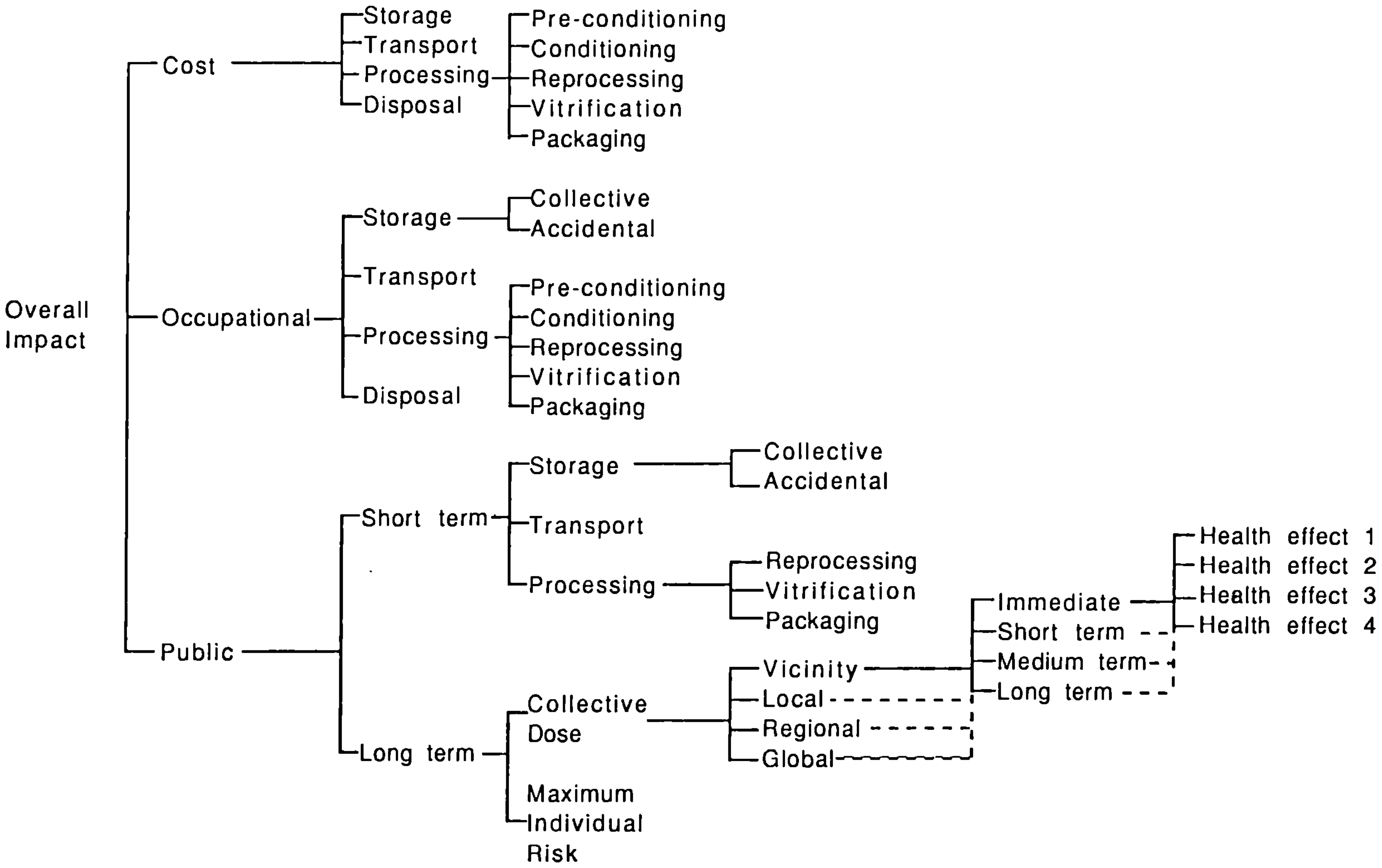


Figure 3 Multi-attribute hierarchy

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

Contractor: CEN Fontenay-aux-Roses, CEA, France
Contract N°: FI1W-0134
Working Period: September 1987 - December 1989
Period Covered: January 1988 - December 1988
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 of up to 50 years in a plant with 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 33,000 MWd/MTHM.

2.3. Extended storage: This part takes into account two successive steps: the first one is a 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 main scenarios, the conditioned waste arisings are classified in:
  - LLW for which the final storage is in shallow land burial;
  - MLW will be disposed of in geological formation;
  - HLW will be disposed of in geological formation after a cooling time from 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: Those 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 OF WORK AND OBTAINED RESULTS.

State of advancement.

Data base and waste inventory of reprocessing route have been established with quantity, type of packages and their activity.

Different kinds of intermediate storage have been studies for the delayed reprocessing route.

Studies on final disposal and transport have been well improved. The sensitivity studies have led to get the variation of waste inventory.

Progress and results.

2.2 Data base and waste inventory.

The activity of the reference spent fuel has been established as a function of time, time zero (t = 0) corresponding to 3 years of cooling time.

The waste inventory of immediate reprocessing (3 years cooling time) corresponds to a volume of 7 m^3/tHM of wastes with 0.15 m^3 for glass, 2 m^3 for alpha waste to be disposed in a deep repository and 5 m^3 of LLW to be stored in the Near Surface Disposal.

Except a part of Tritium which is included with hulls and caps, the fission gases and I, are evacuated in gases and liquid effluents.

The solution of fission products is concentrated and stored for one year before vitrification. The glasses are stored in air-cooled wells during several years before being disposed.

Hulls and caps are washed and rinsed out and cemented in a stainless steel container.

Sludges issued from the liquid effluent treatment station which carries out the decontamination of liquid effluents from the reprocessing plant are conditioned in bitumen. The organic residues issued from the distillation of organic effluents are mineralized and cemented in 200 l drum.

The technological wastes such as process and laboratory equipment and material no longer in working order, clothing worn by operating personnel, etc..., are stored and collected in metal drum, waste bins, mobile equipment evacuation enclosures or in vinyl sheathing.

The alpha emitter wastes are immobilized in a CAC (Cement/Asbestos Container) in which a concrete grout is injected.

The non alpha emitter wastes (alpha content $<$ 0,1 Ci/t) can be compacted before placing in a 200 l drum which is transfered in a CAC with injection of cement grout in the annular space.

Only 30 % of waste volume are to be stored in a deep geological disposal. That is glasses, hulls and caps, bitumen and part of technological wastes.

2.3 Extended storage.

In the management route of delayed reprocessing, an intermediate storage of spent fuel assembly is foreseen for a duration of 50 years.

A review of the alternate technologies for interim storage facility developped in France and abroad have been developped with their limits and applications.

Then, a selection has led to the three following concepts for a centralized storage :

Wet storage in pool with a dry unloading facility which offers advantages of :

- reduced waste production,
- fewer handling apparatus and reduced auxiliary equipment decontamination,
- higher automation of process.

SGN' vault concept with the main features :

- dry unloading,
- dry storage in suspended wells cooled by natural convection,
- modular storage enabling an increase in capacity.

Cask storage which ensures.

- receiving and monitoring of cask from the power plant,
- their storage,
- their preparation for their transfer to a repository or to a reprocessing plant.

To increase the storage capacities, the rod consolidation allows a packing ratio of 2:1 for the fuel and 10:1 for skeletons. For a reactor park of 20 GWe (22 PWRs) working during 30 years, the capacity of storage has to receive 38 940 spent fuel elements (approximately 18 000 tHM). But each module of storage has a 3 000 tHM capacity and the annual unloading capacity of the centralized storage installation (1298 spent fuel elements) has to be sized with a value of 66 casks per year for non consolidated or 44 casks per year for consolidated fuel element.

2.5 Final disposal.

For a throughout during 30 years of a reprocessing plant of 600 t/a, the volume of waste to be store in a near surface disposal correspond to 90.000 m³ and 30.000 m³ in a geological disposal. The definition of the final disposal route has been sketched and led to a first configuration for these disposals.

2.6 Transport.

The transportation of waste packages has to satisfy the AIEA regulation (1985) and type B cask are required for vitrified wastes, cimented hulls and caps, bituminized sludges and other cimented alpha wastes.

In case of very low specific activity wastes which can be included in the classification CI2 (industrial type), packages are transported just as they are.

The shielding of type B cask is able to limit the irradiation lower than 10 mrem/h (gamma + neutron) at 1 m and 20 mrem/h at contact. That is much lower than the authorized values.

The loading of package are made in dry cellule by remote operations ; the tightness is checked after closure of the cask ; then the cask is handled by 4 trunnions.

The size and mass of casks are limited by the road and railway regulations and dimensions are following :

- in horizontal position : Lenght = 7 m ; diameter = 2,5 cm
  Mass = 110 t
- in vertical position : height = 2.8 ; diameter = 2.5 ;
  Mass = 40 t

A limitation is also imposed by the heat power of the package.

2.9 Sensitivity study.

Considering the reprocessing of different types of fuel such as high burn up or MOX fuel and also the delayed reprocessing spent fuel, the resulting wastes characteristics have been compared with the reprocessing wastes of standard spent fuel.

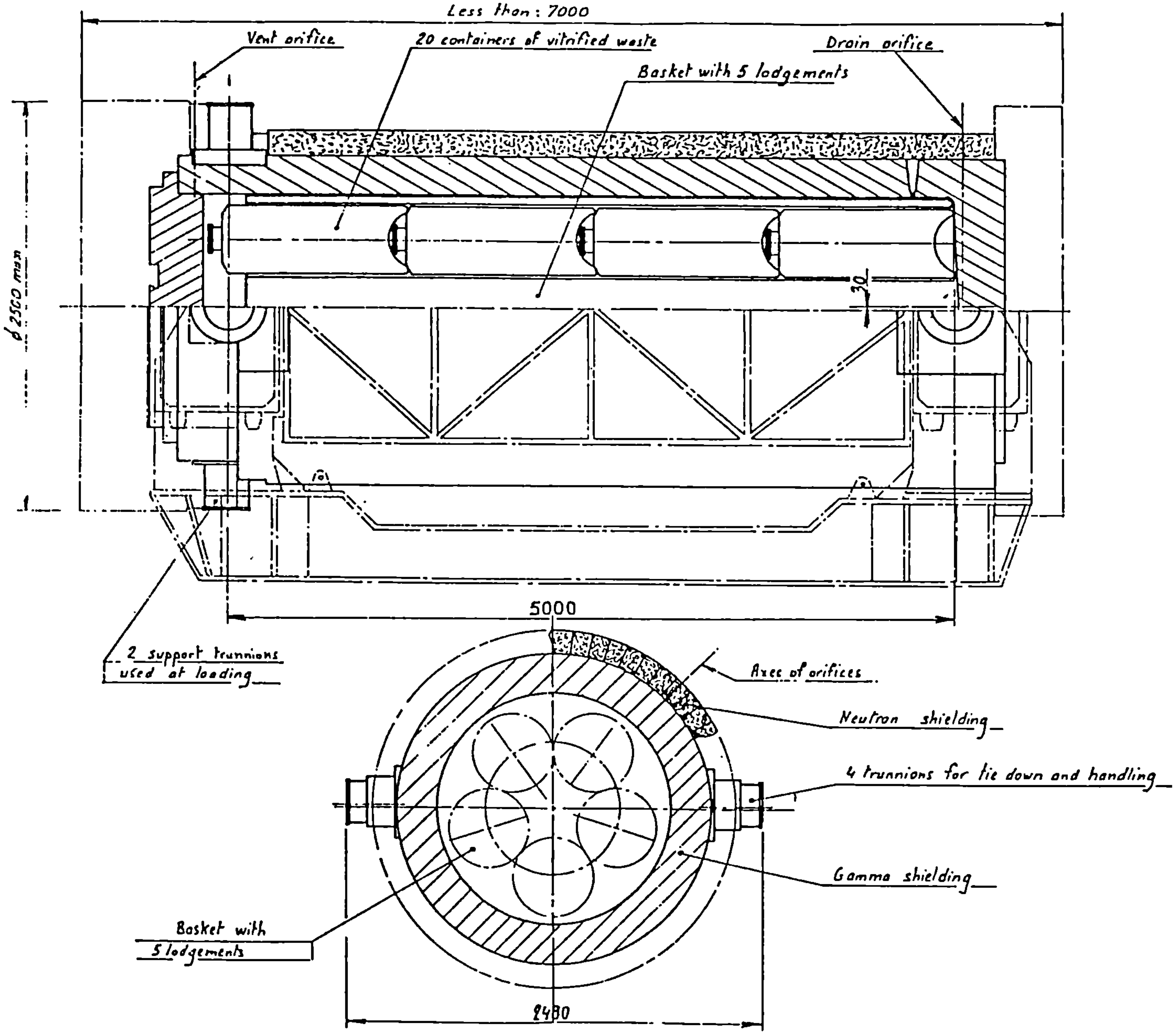
The comparison is based on a maximum value of heat power and fission product oxydes and actinide oxyde content for glasses, the activity for bituminized sludges. For hulls and caps, the quantity of hulls in one drum is constant, then only the activity of drums varies. It is the same for technological wastes.
Reported to the same quantity of energy, the volume of wastes for MOX and high turn up fuels are 22 and 23 l/GWh compared to 29 for a fuel at 33 GWd/t

	Package Number	Storage Volume	Near surface disposal	Deep geological disposal
Hulls and caps	300	525 m³		525 m³
Glasses	450	88 m³		88 m³
Ionic Exchanger	12	27 m³	27 m³	
Technological Wastes	3840	3127 m³	2914 m³	213 m³
Bitumen sludges	1788	423 m³		423 m³
Organic Effluent Treatment	309	68 m³	68 m³	
TOTAL		4258 m³ or 7.1 m³/t	3009 m³ (70,5 %)	1249 m³ (29,5 %)

Table 1 - Annual balance for 600 tHM/y

Type of spent fuel	33 GWd/t	45 GWd/t	MOX	Delayed reprocessing
Specific Volume of waste in l/GWh	29.5	22	23	29

TABLE 2 - Comparison of reprocessing wastes for various fuel



Sheet 1 - Packaging for vitrified residues
(long-term packaging)

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

Contractor: CEN Fontenay-aux-Roses, CEA, France
Contract N°: FI1W-0135
Working Period: September 1987 - December 1989
Period Covered: January 1988 - December 1988
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 each assembly of co-ordinated 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: Those 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

State of advancement

According to the time table of the contract the waste acceptance criteria have been performed.

The drawing up of basic management routes is performed with preliminary data.

The list of waste packages given by SGN for PWR and reprocessing waste packages have been taken as a reference to define the Near Surface Disposal.

The environmental impact has been calculated with the radionuclide disposed into the site (reactor wastes and the part. of reprocessing low level wastes).

Progress and Results.

2.2 Definition of waste acceptance criteria.

For this study, only the CSA (Centre de Stockage de l'Aube) disposal facility is considered. This reference disposal represents the approach of ANDRA in selecting the site on the geological and hydrogeological characteristics ; moreover, exploitation foreseen on this site will be rationalized with two types of disposal on a pad (platform) or "Tumulus" and in "Alveole" or "Monolith" according to the waste conditioning and its characteristics, the second one affording a supplementary containment with its reinforced concrete wall.

The criteria of waste acceptance will be very similar to those of the CSM disposal facility (Centre de Stockage de la Manche). These criteria are based on the activity level of the waste calculated at the end of 300 years of controlled period. The mean α activity has to be < 0.01 Ci/t with a maximum for any package of 0.1 Ci/t.

For $\beta\ \gamma$ activity, the limitation is given for each nuclide and depends wether the waste is conditioned or not. Only the $\beta\ \gamma$ nuclides with half live less than 30 years are considered.

Other requirements are imposed on the mechanical behaviour of the packages in order to warrant against fire, fall, weighting of superposed packages, and on the technical behaviour of the conditioning.

The waste producer has to respect a Quality Assurance programme.

2.3 Drawing up of basic management route.

According to the case, waste is stacked on a pad if the waste package offers, by itself, its intrinsic safety or in a "Alveole" if it is not the case but both types are based on a pad of same size. The loading is operated by a crane runway wich protects the workers against radiation. A removable shed shelters against the rain during the exploitation of the pad ; it is removed only when a tight layer covers all the stack. Thus the waste packages are unloaded and disposed without being wet by the rain.

The exploitation is foreseen for 30 years, and the disposal is under supervision during 300 years.

The wastes issued from PWR and non-alpha LLW issued from reprocessing plant have allowed to define the near surface disposal for basis hypothesis of a reactor park of 20 GWe.

To this near surface disposal are sent approximately 6000 m^3/year of wastes from reactors and 3000 m^3/year of reprocessing wastes. For 30 years of nuclear electricity production, that leads to 275 000 m^3 of wastes to be disposed.

2.7 Radiological Impact.

The study of radiological impact has been begun with the reprocessing waste only. It appears that in the reactor wastes there are no long lived radionuclides and that leads to a minor impact to the environment.

Hypothesis taken into account assumes a progressive degradation of the conditioning along the time with a sharp and total release at 300 years.

That explains the first peak of dose due mainly to ^{99}Tc, the second peak at 10^4 years by the release of ^{237}Np (or ^{79}Se for lower curve) and the third peak at 10^6 by the release of ^{93}Nb.

The 3 curves are calculated from 3 types of menus prepared with food (water drink, vegetables, fish, meat) produced near the disposal site.

The maximal dose is very low is all cases.

Fif. 1 - Alveole in exploitation

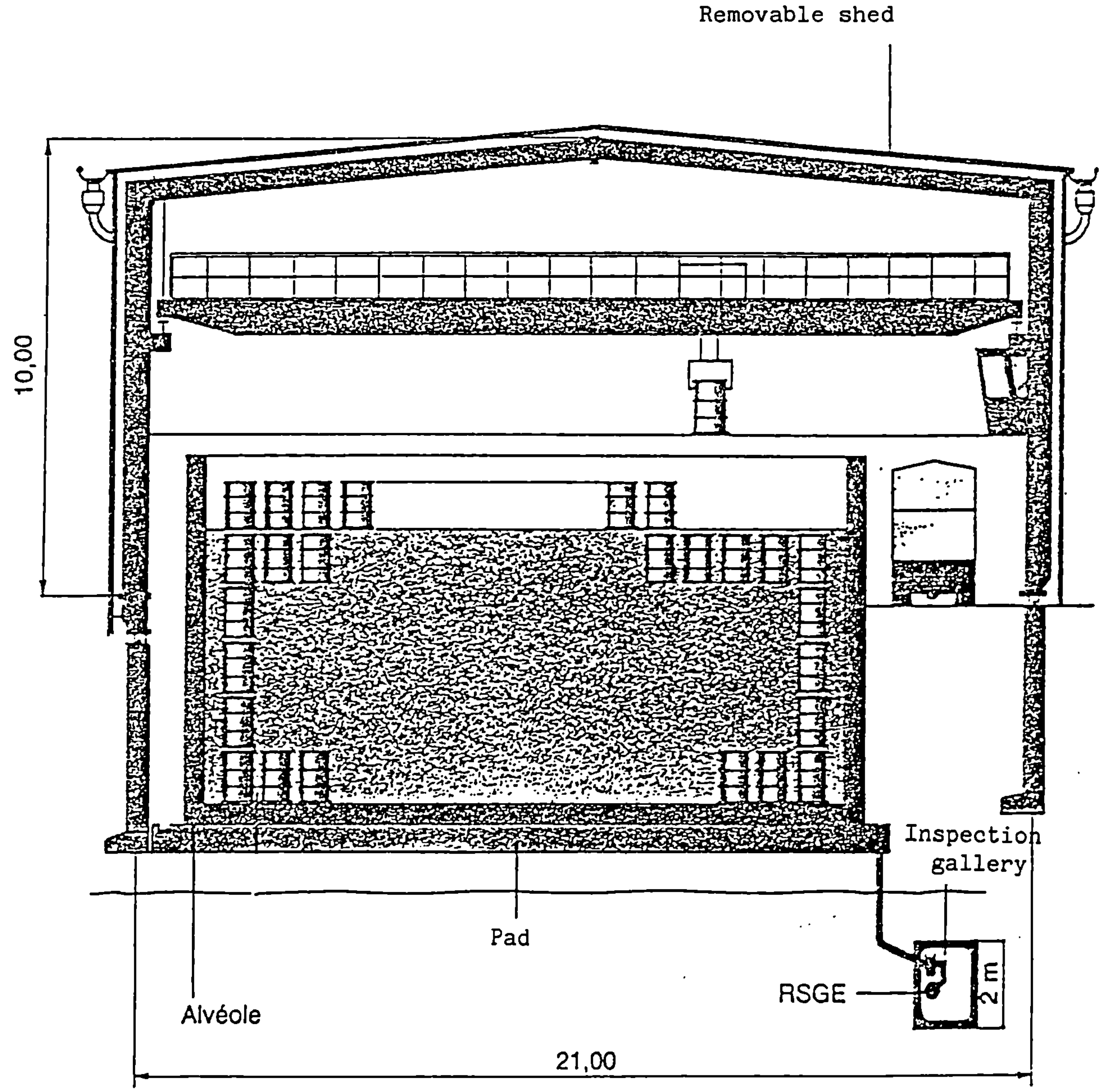


TABLE 1 : β NUCLIDES WITH A 1/2 LIVE < 30 YEARS

Nuclides	Non immobilized waste MBq/kg (Ci/t)		Conditioned waste MBq/kg (Ci/t)	
3 H	7,4	(0,2)	7,4 E1	(2)
60 Co	3,7	(0,1)	4,8 E4	(1300)
90 Sr	3,7	(0,1)	7,4 E2	(20)
137 Cs	3,7	(0,1)	4,8 E3	(130)
54 Mn	37	(1)	7 E5	(1,9 E4)
55 Fe	37	(1)	3 E6	(8,1 E4)
57 Co	37	(1)	2 E6	(5,4 E4)
65 Zn	10	(0,3)	1 E5	(2,7 E3)
93m Nb	37	(1)	3 E5	(8,1 E3)
110m Ag	20	(0,5)	2 E5	(5,4 E3)
106 Ru	9	(0,25)	8,8 E4	(2,4 E3)
125 Sb	37	(1)	8,1 E5	(2,2 E4)
134 Cs	3,7	(0,1)	3 E4	(8,1 E2)
137 Cs	3,7	(0,1)	4,8 E3	(1,3 E2)
144 Ce	9	(0,25)	8,8 E4	(2,4 E3)
152 Eu	30	(0,8)	3 E4	(8,1 E2)
154 Eu	20	(0,5)	2 E4	(5,4 E2)

TABLE 2 - ALPHA RADIONUCLIDES

Radionuclides	Non immobilized waste MBq/kg	(Ci/t)	Conditioned waste MBq/kg	(Ci/t)
226 Ra	3,7 x E-2	(0,001)	3,7	(0,1)
232 Th	3,7 x E-2	(0,001)	1,1	(0,03)
TOTAL OF RADIONUCLIDES	1,9 x E-1	(0,005)	3,7	(0,1)

	Production by year		Production for 30 years	
	Volume	Activity	Volume	Activity
Reactor wastes	6 160 m^3	19 499 Ci	184 800 m^3	584 970 Ci/$\beta\gamma$
Reprocessing wastes	3 009 m^3	22 622 Ci/β 135 Ciα	90 270 m^3	678 660 Ci/$\beta\gamma$
TOTAL	9 169 m^3	42 121 Ci/$\beta\gamma$ 135 Ci α	275 070 m^3	1 263 630 Ci/$\beta\gamma$

Table 3 - Waste quantities for the Near Surface Disposal for a reactor parc of 20 GWe

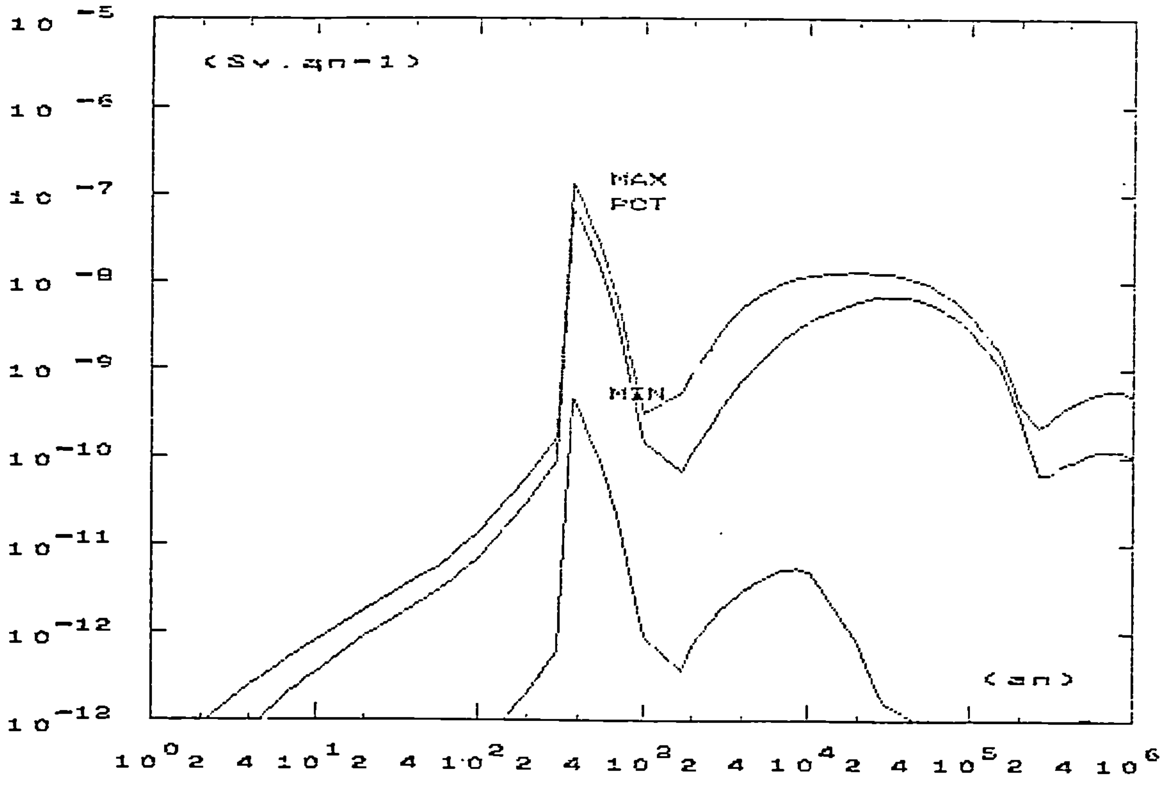


Figure 2 - Equivalent dose rate for 3 menus (realistic, potential and maximal)

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
Project leader: Armin-Dietmar Karpf

A. OBJECTIVES AND SCOPE

This study is 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 far future the latter should also be taken into account when assessing the future doses.

Since 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, valididation.

(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 OF WORK AND OBTAINED RESULTS

State of advancement

The evaluation of the doses of the natural background radiation is performed under the assumption that the population remains constant, that its geographic distribution at least averages out to a constant one and that the pathways remain more or less constant. Then the only time dependence which enters is that of the decay of the long-lived radionuclides. This justifies to use total collective doses only. They are derived from the annual individual doses by folding with the respective population and are then simply integrated.

In this evaluation all known sources and pathways of the general background radiation and all different situations of naturally arising long-lived radiating ores have been taken into account in a distinguishable way. Folded with an expected population it yields the corresponding local collective doses which are subsequently added up to the global collective dose.

The evaluation of the anthropogen doses necessitates additionally annual or life-time collective doses since the expected limited period of the nuclear fuel supply and its cycle introduces a strong time dependence which cannot be neglected.

This shows up mainly in two separated contributions, one from mining and milling wastes which have an immediate impact and one from the disposed waste in the repositories whose impact is delayed by tens to hundreds of thousand years.

Extrapolating the calculations to a total of some 200 repositories which will eventually be necessary to dispose of all the generated waste one finds activities e.g. in the ocean waters which lie still many orders of magnitude below the natural background activities.

The combination of annual and total collective doses allow to draw conclusions about the different waste management paths which, however, has not yet been performed.

Progress and results

This study is aimed at evaluating the influence of present day human activities on future generations. It is one of the rare attempts world-wide to estimate on a large space and time scale the impacts of human activities in a certain field of activity by comparing them to the undisturbed situation.

Uranium is particularly well suited to perform such a task since its use is almost exclusively restricted to nuclear reactor fuel where it is, on the other hand, indispensable and unreplaceable. With the unprecedented growth of the human population investigations of this kind should be extended to more fields of human activities.

(i) Due to the complexity of the processes in nature investigations of this kind must always resort to a comparison to some natural or to some undisturbed state. This measure is given here by the natural background activity both via external and internal pathways and is taken to be constant in time as outlined above.

We consider both the background due to the long-lived uranium-238 and its descendants in their original environment, that due to other primordials and that due to renewable radionuclides in a distinguishable way. This yields three different measures, which can be used for reasons of comparison.

In the earth's crust uranium appears with an abundance of 2 to 4mg/kg. As erosion exposes it, oxydation transfers it into soluble form and water dissolves it, it accumulates in the oceans to about 3.5 ug/kg. Hence a total amount of 4 Pg is estimated to exist in the oceans with the concentration increasing slowly over the last billions of years. This amount represents, however, probably only 1‰ of the total uranium content in the earth's crust which is estimated to some Eg.

Apart from uranium-238 and its descendants in the 4n+2 decay chain other primordials to be considered as a distinguishable measure are Th-232 with its 4n-decay chain whose most prominant representative is Th-228, accumulated mainly in bones, potassium-40 which irradiates the whole body and rubidium-87.

The third measure derives from renewable radionuclides such as the short-lived H-3 and C-14 which accumulate in the vegetation, and cosmic rays.

There are many pathways to man for the indicated radionuclides all of which have to be considered since it is their combined effect which counts, the individual effects being too small.

Hence for uranium we take ground waters which dissolve in particular the descendant Radium-226. Together with the waters from precipitations this results in an average concentration of 3.7 to 37 and even of 200 mBq/l in the surface waters. Mineral waters may even contain concentrations up to 370-925 mBq/l of Ra-226. Similar pathways can be defined for Pb-210 and Po-210, two other important descendants.

The gaseous descendant Rn-222 is predominantly incorporated via the aerosols inhaled with the air. An important pathway is related to the radon emitted by the building material of houses and confined in their interior.

The distribution of uranium in the ground depends strongly on the geological and mineralogical situation. One pathway is building material, another is phosphate rock, the basis for the production of most of the fertilizers, which contains from 0.001 to 0.07% of U. The deposits of phosphate rock are estimated to between 75 and 130 Pg with a total uranium content of 10 Tg.

From these pathways one evaluates an annual collective dose of up to .25 MSv/a for the water pathway and of up to 14 MSv/a for the other pathways. For 10 Ma this yields 2.5 and 140 TSv of total doses.

As for the second measure, thorium-232 is widely spread in the earth, but appears excessively in monazite sands such as in India or Brazil. The concentration reaches up to 10% at certain places. In these monazite sands arise the highest external doses to mankind at all; in the Indian province of

Kerala, e.g., up to 10 mSv/a, in certain towns of Brazil even 80 mSv/a. The radiological impact of thorium and its descendants can therefore reach annual collective dose values of up to 1 MSv/a or of 10 TSv in total for 10 Ma.

The third measure bases predominantly on K-40 and C-14 which reach each cell of the human body by metabolic processes and are therefore equally distributed. The effect of cosmic rays, on the other hand, depends on the altitude above sea level since it is a function of the arriving cosmic particles. They effect the whole body equally.

K-40 and C-14 cause an annual collective dose of, respectively, .2 and .015 MSv/a, i.e. of 2 to .15 TSv total collective doses.

(ii) Turning now to the impacts of the fuel cycle, the total needs of uranium for power plants until the year 2000 are in the range of 1.5 Tg with an annual damand of about 120 Mg. The known recoverable resources in crustal formations are estimated between 10 and 20 Tg U which would allow a continued operation of the installed reactors for up to 170a.

Most of the uranium deposits contain uranium in an abundance of 0.001% to 0.1%, an increase of only 10 to 1000 times above the average abundance. It usually results from accumulations in former ocean sediments or in previous organic matter. To recover uranium from ore of the above concentration one clearly has to process 1 - 100 Tg ore for each Mg U. Hence big amounts of masses have to be shifted in the production of uranium.

The further fuel cycle comprises the following steps: mining, milling, enrichment, burn-up, reprocessing, conditioning and waste disposal. Each of these steps produces some typical waste which is contaminated and has to be disposed of.

- The waste rock after mining remains on site with residual activity
- 70% of the activity remains in the tailings after milling,
- 50% of the uranium 238 is discarded at enrichment,
- a part of the uranium is transformed into other radionuclides in the reactor,
- the remaining U is disposed of after several cycles of reprocessing.

Finally the whole uranium and its decay and fission products will have been distributed on or under the earth's surface. In these repositories the uranium is clearly much more mobile and can be removed much faster than from its original deposits. Usually there are water pathways by which the population will be exposed to these radioactive remainders.

In this way one evaluates e.g. a total collective dose of .066 TSv for the effects of the mill tailings which is small by comparison to the chosen measures.

The impacts of HLW repositories remain localised for a certain time but in the long run a considerable part of the world's population is effected. And although the individual doses are relatively small the wide spread and the long duration of the contamination causes a total collective dose of only .00001 TSv for 10 Ma if all repositories were in the sub-seabed. Other geological repositories may yield higher values depending on the situation.

(iii) As yet no comparisons of different waste management schemes have been performed, nor have any conclusions been drawn.

(iv) All time dependent annual collective doses from the various pathways of uranium in the fuel cycle have been evaluated individually. Since they all add up to the whole amount of used uranium a display by pathways has been developed for these investigations. The idea behind this representation is the dissection of the whole amount of used uranium and the subsequently created activity into the individual pathways where it appears in the course of time.

This kind of display can be comprehended immediately and intuitively and lends itself to an easy interpretation.

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

Contractor : NUKEM GmbH, Hanau/Alzenau, FRG
Contract No. : FI1W-0137
Duration of contract: August 1987 - August 1989
Period covered : January 1988 - December 1988
Project leaders : O. Mehling, H.J. 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 co-ordinated actions by which the management of hulls and caps from their production to their disposal is implemented. Usually, these actions comprise 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 it 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 to NUKEM to discuss the data provided by an other 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 route

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

According to the time table of the study, the activities had to cover items 2.3, 2.4, 2.5, 2.6, whereas item 2.2 was to be completed in 1987. Actually, the completion of item 2.2 was delayed by 3 months, thus affecting the time table in a way that item 2.4 has not been completed by December 1988 as planned. Concerning item 2.5, it is to be mentioned that it was finished and submitted on a preliminary stage, since more recent updatings of the basic cost data are expected in early 1989. For the benefit of the study, the contractor has recommended a redoing of this item in 1989. Because of the remaining 8 months for the rest of the work, the overall time schedule of this study is not endangered in any way. The initial delay of item 2.2 and the proposed updating of item 2.5 have caused or will cause some additional work and raise some difficulties with the budget available, however.

Progress and results

2.2 Hulls and caps characteristics and arisings
The information provided by the CEA working group was intensively discussed and after some completion finally agreed upon in April 1988.

2.3 Drawing-up of basic management routes
Two basic management routes (figures 1 and 2) were investigated:

- route 1: hulls and caps compaction, cementation, packaging, and iterim storage /1, 2, 3, 4, 5/,
- route 2: hulls and caps compaction, embedding in graphite, packaging, and interim storage /1, 4, 6, 7/.

After completion of this item in August 1988, the information on buildings, equipment, staff required and operational details etc. were transferred to the KAH-working group for cost assessment purposes.

2.4 Sensitivity studies
This item was begun on the basis of the material collected in item 2.3. Results are not yet available in a form appropriate for communication.

2.5 Cost evaluation
This item originally referred to the disposal costs at the Gorleben salt dome repository. However, the effort has been extended to an investigation of the disposal costs at the Konrad repository, since without that relation even a preliminary Gorleben disposal cost estimate had not been successful in any way. At this point it is to be mentioned with utmost gratitude, that only the substantial support of PTB has enabled the contractor to turn up with a quantified result /8, 9, 10/. Although it is preliminary and subject of an up-dating in early 1989, some data are compiled in table I.

2.6 Assessment of occupational exposure
This item covers the hulls and caps treatment and conditioning as well as the subsequent shipment to the repositories and the activities necessary at and inside the repositories. Results are not yet available.

List of publications

There are not any publications by the contractor on the subject of the study, so far.

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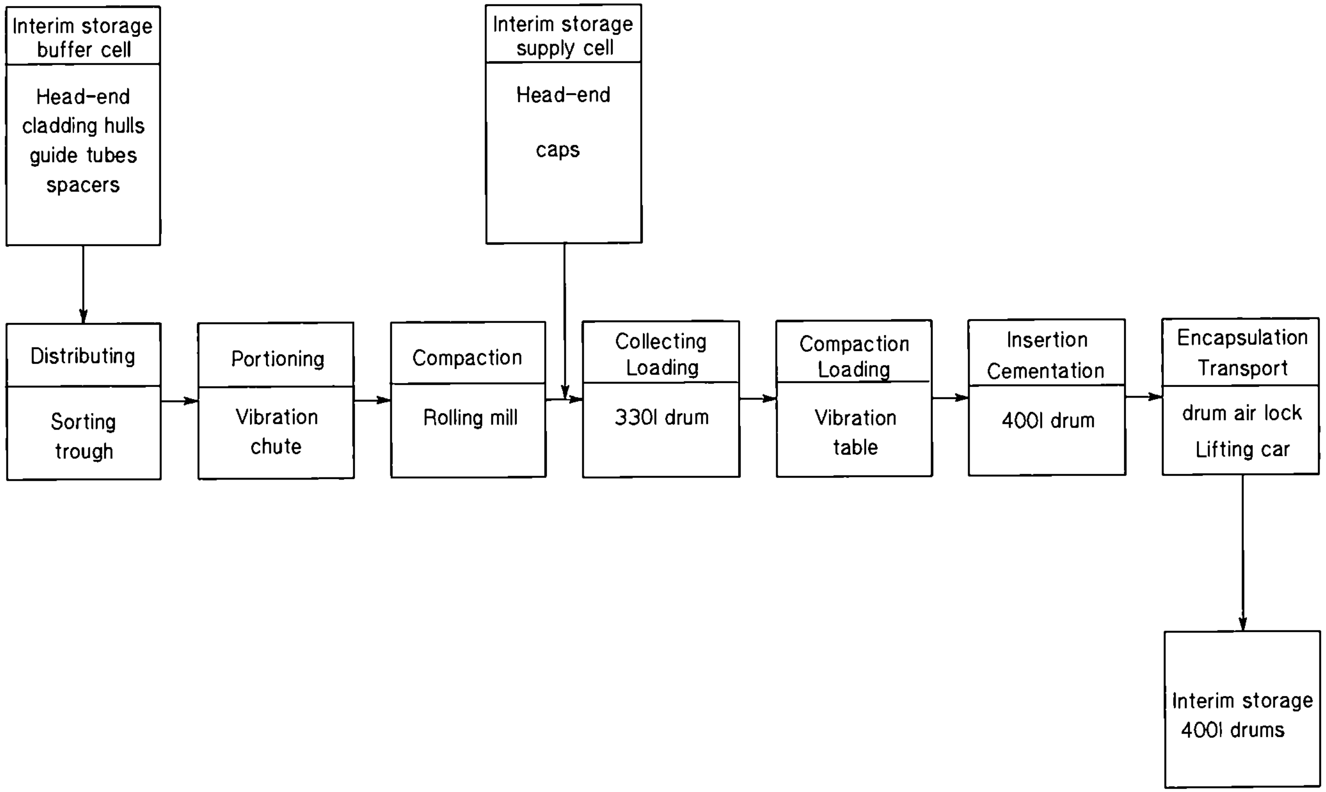
TABLE I: PRELIMINARY ASSESSMENT OF DISPOSAL COSTS (ECU/m^3)
BASED ON 1987 VALUES

Repository	Type of wastes heat generating	 not heat generating
Konrad	not permitted	2500 to 3000
Gorleben	16000 to 20000	2500 to 3000

Remarks:
a) Most of secondary wastes are qualified for Konrad disposal.
b) Caps waste may qualify for Konrad disposal after a 30 year cooling time; earlier only with a smaller Co-60 content.
c) Hulls waste do not qualify for Konrad within a reasonable cooling time (< 100 a).

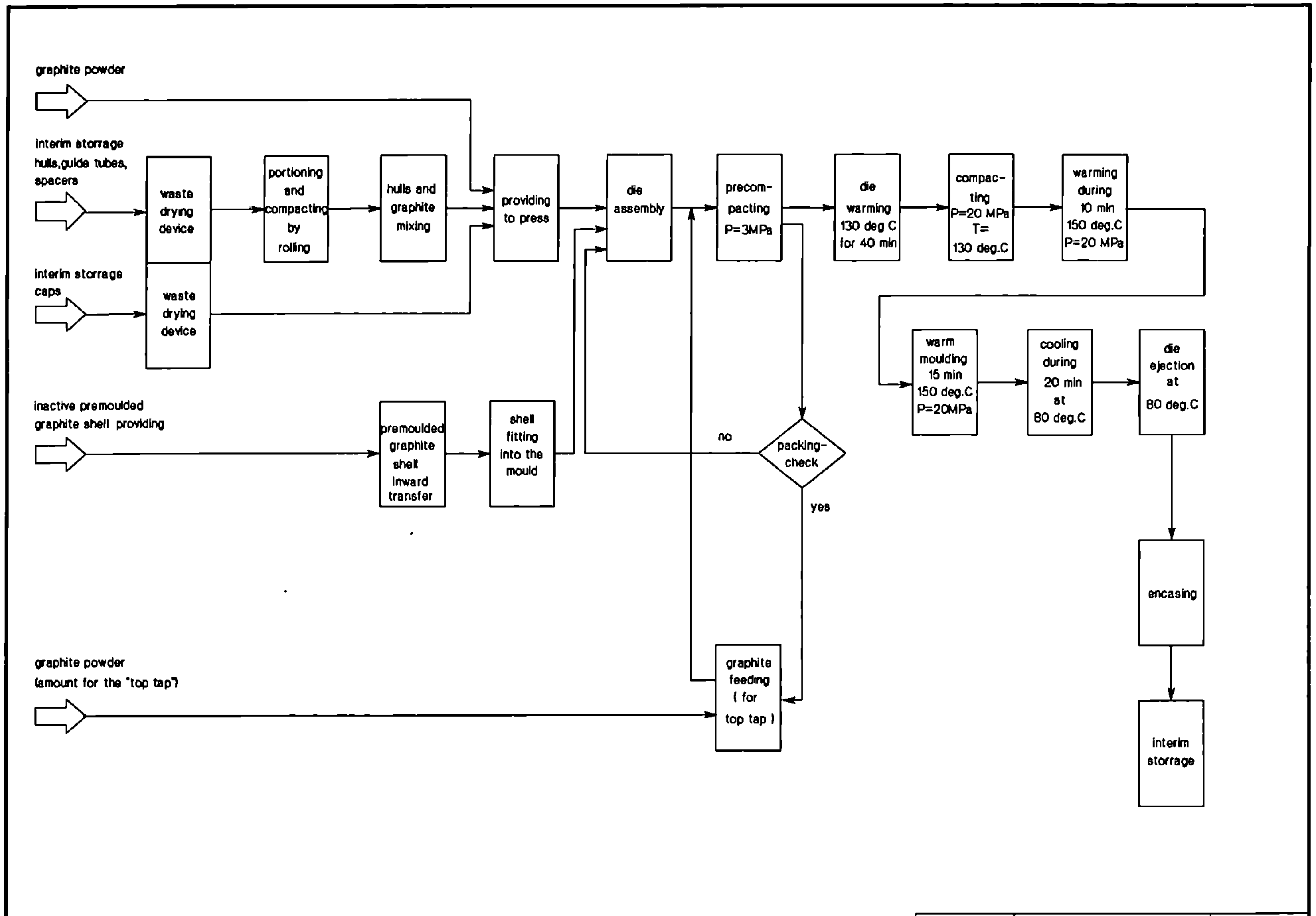


NUKEM

Flow diagram

Hulls compaction / cementation

Fig. 1



NUKEM

Flow diagram
Hulls compaction /
embedding in graphite

Fig. 2

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

Contractor : NUKEM GmbH, Hanau/Alzenau, FRG
Contract No. : FI1W-0138
Duration of contract: August 1987 - November 1989
Period covered : January 1988 - December 1988
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 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. 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

According to the time table of the study, the item 2.2 is to be completed in early 1989. Actually, this has been achieved by the end of 1988 except for finishing and adaptations eventually required after submission. Items 2.3 and 2.4 had to be begun in June 1988 and August 1988 respectively. For item 2.3 some results have been accomplished; open are here the investigations concerning accidents, risks, transportation, final disposal and costs. Item 2.4 has not reached a state yet, that results are available. Although the study has beneficially used prior work /1, 2, 3, 4/, quite a few subjects required more effort than estimated in advance. Moreover, the contractor has to provide an assessment of respository volumes required for HLW and conditioned spent fuel disposal in other than salt dome repositories. This is to be based upon information to be delivered by other working groups. No such material has been received so far.

Progress and results

Item 2.2

SPENT FUEL STORAGE AND PRECONDITIONING

a. Evaluation of basic data
   The basic data were provided by the CEA working group and checked for completeness and arranged according to the demands of this study by NUKEM. They comprise the data of the fuel elements, the radioactivity, fissile materials, heat output etc.
b. Storage phase prior to preconditioning
   A 4 year storage period after a 3 year storage time at reactor is sufficient for precooling required for pre-conditioning. Two types of dry storage have been considered: air cooled vault storage and cask storage.
c. Preconditioning process (3 options)
   An overview of the whole process is shown in figure 1.
   - Option 1: disassembling fuel elements, encasing fuel rods in dry storage containers, encasing end pieces and structural parts in dry storage containers of different type;
   - Option 2: use of the same type of dry storage containers for fuel rods and end/structural pieces;
   - Option 3: rod cutting and encasing rod pieces in canisters similar to those of the HLW-type which are also the final disposal containers; no further final conditioning required; end/structural pieces are treated as in option 1.
d. Interim storage phase after pre-conditioning
   In options 1 and 2, the fuel is stored for a period of 23 years prior to final conditioning. In option 3, a 3 year storage period is required prior to shipment to the repository. Final conditioning and pre-conditioning are the same step in this case. The type of storage is the air cooled vault like for the fuel storage. The details had to be arranged according to the different number of items, heat densities etc.

Item 2.3

CONDITIONING FOR FINAL DISPOSAL

Process flow and handling schemes have been established as well as the structures of the buildings, the compilations of equipment, staff and operational requirements like media etc. The waste arisings for final disposal (table I) and the staff exposures to be expected (table II) have been compiled.

Item 2.4
DISPOSAL OF LLW AND MLW
Any communication of results would be too early at this stage.

List of publications

There have been no publications by the contractor concerning the subject of the study.

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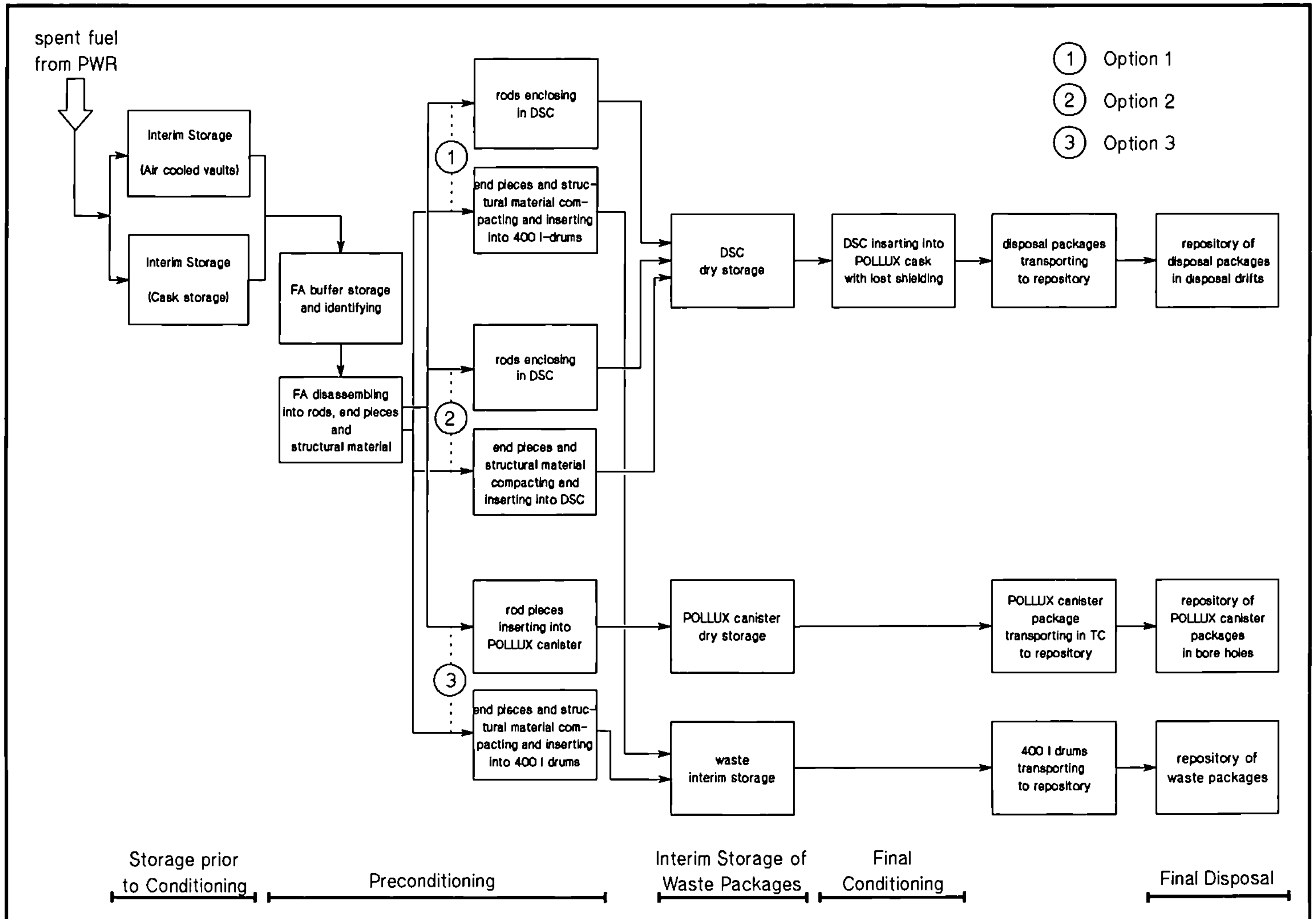
TABLE I: WASTE ARISINGS FROM SPENT FUEL CONDITIONING PER YEAR

Type	Options		
	1	2	3
secondary wastes			
MLW, solid, cemented 1)	35	35	35
MLW, liquid, cemented 1)	26	26	26
LLW, solid, cemented 1)	315	315	315
LLW, liquid, cemented 2)	66	66	66
Spent fuel FDC	130 3)	163 3)	2600 4)
End/structural parts	325 1)	-	325 1)

1) 400-1 drums in lost shielding
2) 400-1 drums
3) POLLUX containers
4) POLLUX canisters

TABLE II: STAFF EXPOSURES (mSv/a)

Time interval	staff	Options		
		1	2	3
0 to 23 years	233	700	700	-
23 to 30 years	250	900	900	-
30 to 50 years	88	360	360	-
0 to 33 years	250	-	-	860



PWR – Pressurised Water Reactor
FA – Fuel Assembly

DSC – Dry Storage Canister
TC – Transport Container

NUKEM	**Flow diagram** **Direct Disposal of Spent Fuels**	Fig. 1

TASK No 2

Improvement of radioactive waste treatment and conditioning technologies

TASK N. 2

IMPROVEMENT OF RADIOACTIVE WASTE TREATMENT AND CONDITIONING TECHNOLOGIES

Objective

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

1985-1989 programme

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

a) Waste from light water reactors

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

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

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

c) Optimization of waste management at source

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

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 : FI.1W.0006.UK(H)
Work Period: January 1988 - December 1988
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 treted 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 group - $(CH_3)_2(C_2H_4OH)N^+$.

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 from 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. The leach tests were undertaken as described in the International Standards Organisation (ISO) procedure(3).

Provisional results are given in Fig. 1 and show that 0.24% of the total ^{60}Co activity was leached from a cemented sample containing 36% by weight ion exchange resin. As expected samples containing less resin and therefore less ^{60}Co showed a reduction in activity leached.

REFERENCES

1. C. G. HOWARD, C. B. JOLLIFFE, D. J. LEE.
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.
Immobilisation in Cement of Ion Exchange Resins arising from the Purification of Reagents used for the Decontamination of Reactor Circuits. Fourth Semestrial Report, January - June 1988. AEEW - M 2536.

3. Long Term Testing of Solidified Radioactive Wasteforms, First Edition 1982. ISO 6961.

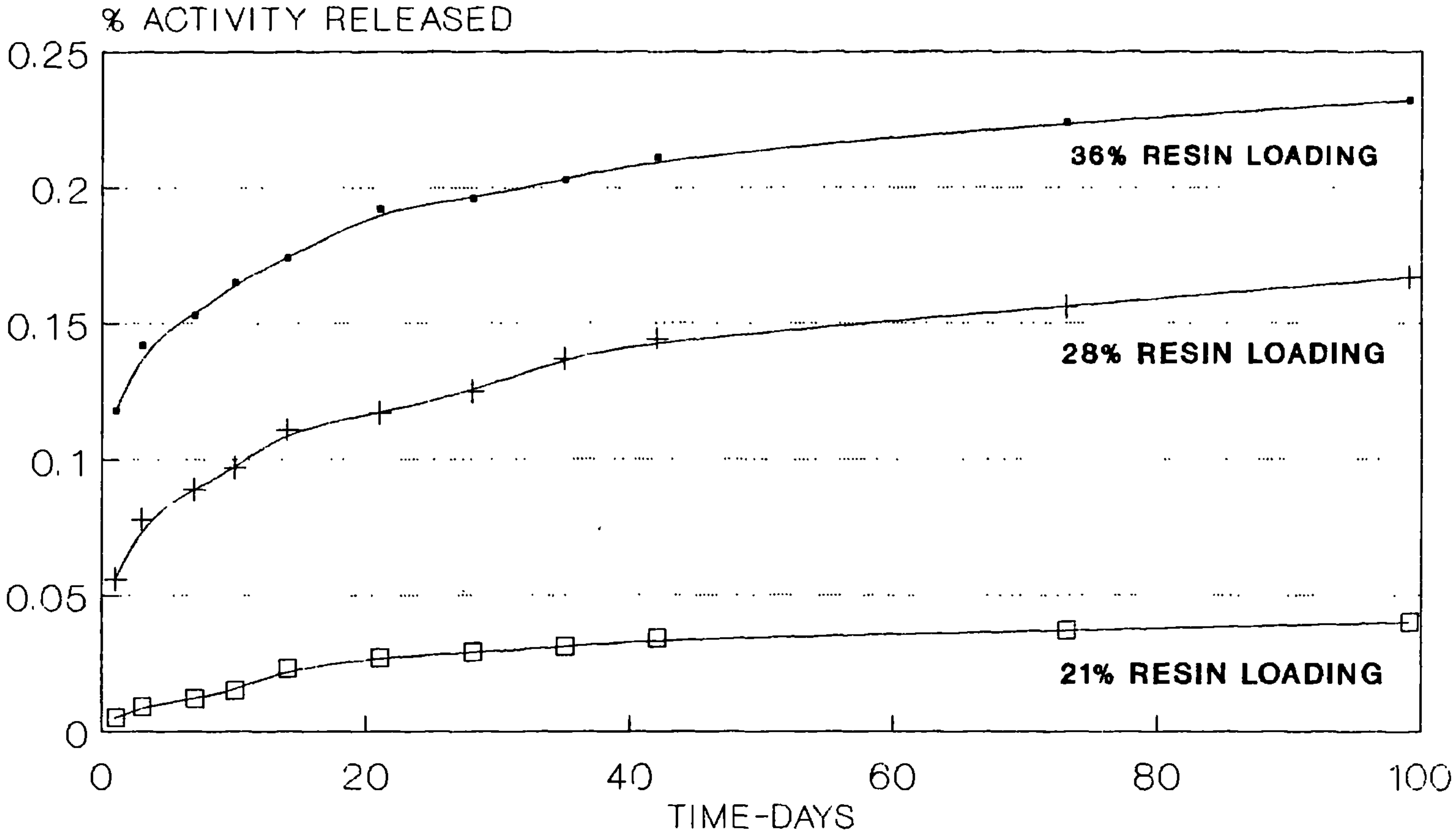


FIG. 1 CUMULATIVE Co-60 ACTIVITY LEACHED FROM CEMENTED RESIN

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
Third annual report (1988)

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 Caracterisation 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 1988 the influence of detergents, commonly used in Tihange 1, on the flocculation process has been examined.
The flocculation of different types of effluents has also been studied and in particular:
- regenerant solutions of ion exchangers with a low contamination
- effluents of decontamination with high activity.

The centrifuge pilot plant has been installed in Tihange 2 and some different types of sludges have been treated.
- supernatant of a flocculation
- effluent without flocculation
- sludge resulting from 4 successive flocculations
- sludge from a treatment of decontamination effluents.

Progress and results

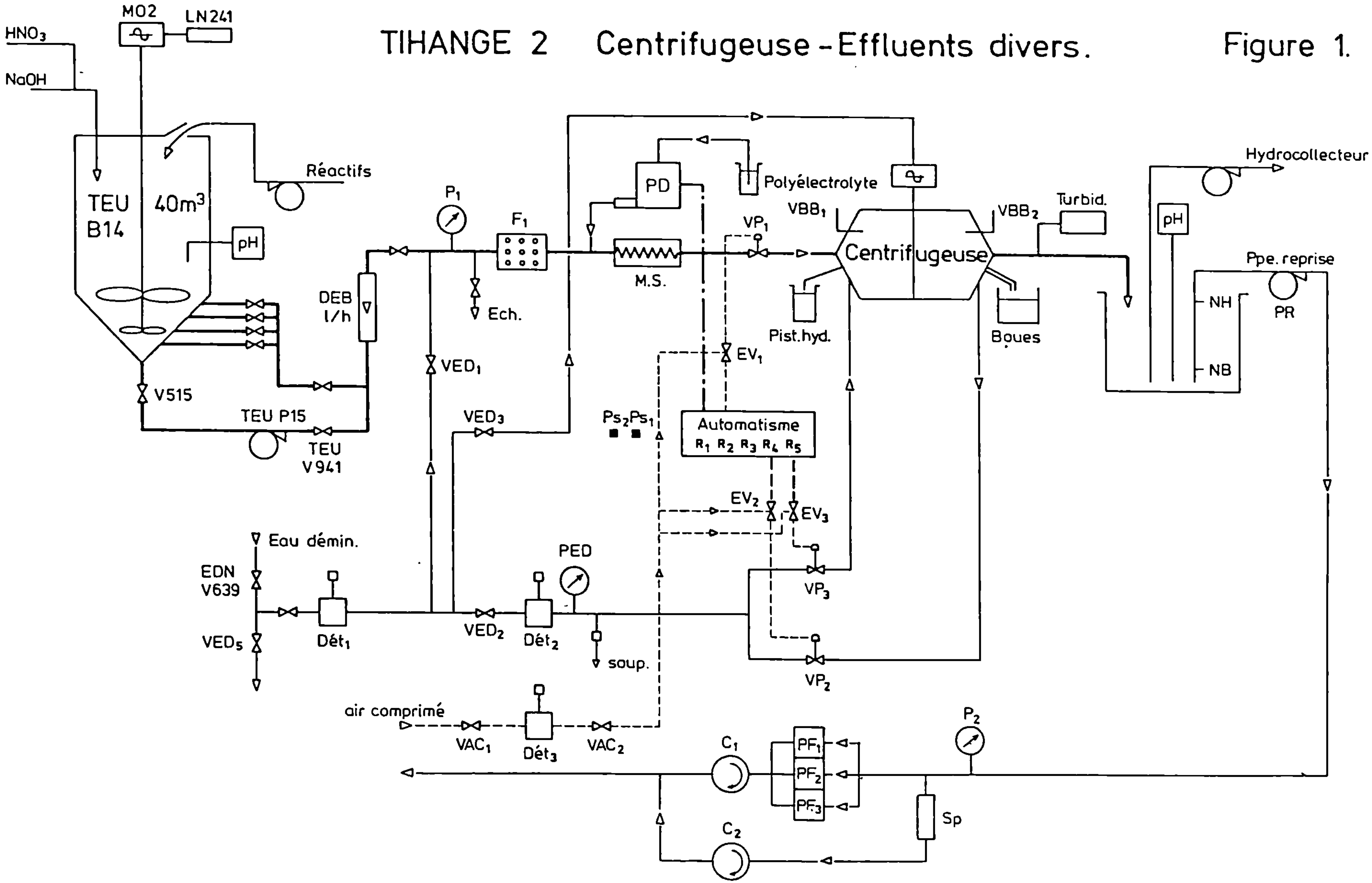
Detergents : the products normally used at Tihange 1 have no influence on the flocculation even at high concentrations. This means that a flocculation could be used on evaporator bottoms in order to further reduce the volume to be solidified.

Ion exchangers regenerants : the regenerants of a condensate polishing with low radioactive contamination can be treated by flocculation with $FeCl_3$. The activity of the supernatant was below 1 MBq/m^3.

Decontamination solutions : it has been possible to reduce the activity to values below 5 MBq/m^3. The volume of sludge (without centrifuging) ranges from 10 to 15 % of the initial volume of effluent.

Centrifuging : the flow sheet of the pilot plant that has been built in Tihange 2 is shown in figure 1.
The main results of the tests are :
- the amount of suspended solids in the incoming solution is low the efficiency can vary in large proportions (50-95 %)
- the amount of suspended solids in the treated water does not vary much with the flow rate if the amount is low at the inlet
- with high concentrations of suspended solids the efficiency of the centrifuge is always higher than 90 % and does not vary much with the flow rate (between 200 and 400 l/h)
- the activity at the outlet is always lower than 5 MBq/m^3 (inlet up to 700 MBq/m^3)
- the presence of polyelectrolyte is absolutely necessary but 1,5 to 2 ppm seems to be sufficient
- a safety filter (25 μ) improves the decontamination
- a delay coil between the injection of polyelectrolyte and the inlet of the centrifuge is useful.

TIHANGE 2 Centrifugeuse - Effluents divers. Figure 1.



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

Contractor:	ECN, Petten, The Netherlands
Contract No.:	FI1W/0008
Duration of contract:	June 1986-July 1988
Period covered:	January 1988 - September 1988
Project Leader:	A. van Dalen

A. Objectives and Scope

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

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

B. WORK PROGRAMME

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

B.1. Radiation resistance

B.2. Maximum loading capacity of modified sulfur cement with ashes, sludges, spent ion-exchangers regarding strength and leachability

B.3. Porosity regarding tritiated water.

B.4. Reactions with metal components of discarded equipment to be encapsulated.

C. Progress of work and obtained results

State of advancement

During the last period of the two years research contract sufficient data became abailable for reviewing the possibilities of modified sulfur cement MSC as a waste matrix material. A two year period proved to be a minimum for a correct judgement of the properties of MSC regarding waste encapsulation at laboratory scale. Due to the low permeability of the MSC formulations with aggregates or wastes the determination of realistic values for porosity and leachability cannot be accomplished within the time periods advised in standardized tests. (100 days to half a year). Practical results obtained from the variety of conditions can be used to indicate optimization of waste processing with MSC. In general the wastes produced by incineration and precipitation are preferred as a result of the findings that the compressive strength after water absorption remains high enough, and that the leachability is directly related to the solubility of the waste component in water. The MSC matrix proved to be inert. The prediction of actual wastes behaviour in MSC matrix based on the results with simulated wastes used in this laboratory study is possible regarding radiation resistance, leachability, porosity (permeability) and compressive strength.

The upscaling from laboratory tests to real size and introduction of MSC as a serious candidate material for waste encapsulation is hampered by the fact of inflammability of sulfur. However, due to the presence of an aggregate or waste material, the large volume of a waste form, the low heat conductivity, and the low heat of combustion the effect of a fire should be small. According to literature data on a MSC waste container only minor surface roughing was observed by a fire of 16 minutes /1/.

Progress and results

Most of the experiments carried out in this period were conclusive for the results obtained during the whole period of the contract. The following description of the items covers the progress and results of the last period and the interpretation including the results of the previous periods.

B.1. Radiation resistance

The gamma irradiation dose up to 20 MGy resulted in an increase of the compressive strength. No gaseous radiolysis products from samples containing PbJ_2, KEMA incinerator ash, and borate wastes could be detected. The total gamma dose is equivalent to the total dose to be received by the bituminized COGEMA reprocessing waste (1 kCi Ci α activity per m^3). The radiation effect of alpha emitters was simulated by the $^{10}B(n,\alpha)^7Li$ reaction. The six months simulation of 0.5 Ci/m^3 α activity did not show any radiolytic gas production.

The radiation experiments were carried out with dry samples, saturated with water the radiolytic gases H_2 and O_2 can be expected. The saturation time due to the low permeability is too long, small specimen need already a few years.

B.2. Maximum loading capaicity of MSC with ashes, sludges, spent ion-exchangers regarding strength and leachability.

Careful grading of the aggregates results in a loading of 75-80%; in fact the waste materials cannot be particle size graded and consist mainly of only fine particles. The maximum loading capacity regarding the workability of the paste at about 130°C is 60% of PbJ_2, 25% of the KEMA incinerator ash, 30% of waterpond sludges, 20% of borate waste, and 50% of Al_2O_3. Ion-exchangers destroy the waste form quickly by swelling due to water absorption (a few hours in water, a few days in humid air). Higher loadings with borate waste are possible but the compressive strength becomes too low and immersion in water results in cracks of the solidified material. Maximum loading is preferred to have minimum shrinkage at solidification of the paste at 120°C.

The leachability has been determined in analogy to the ANS leach test /2/. The time of leach testing had to be extended byond 300 days before reliable results could be obtained due to the low permeability of the MSC matrix. Typical results are summarized in the following table I.

Due to the inertness of the MSC matrix the diffusivities of the waste components are proportional to the squares of the solubilities of the components in water. The band width in figure 1 originates from differences in porosities.

B.3. Porosity regarding triated water.

Porosities of MSC preparations have been calculated from measured effective diffusion coefficients of HTO. The results are in accordance with H_2O absorption measurements. the effective diffusion coefficients fit also in the plot of figure 1. The porosity is present in the MSC fraction as dispersed air, maximal with asbestos or diatomite, and minimal with Al_2O_3 as aggregate in the matrix. the pore diameters are small, about 0,1 µm according to electron microscope images. Another form of porosity was also vissible: microcracks of about 1 µm diameter due to shrinkage as solidification. The effect of the two types of porosities is remarked in the effective diffusion and leaching results. The total porosities range from 0.5 for asbestos to 0.001 for Al_2O_3 as aggregate. Due to the small pore diameters the permeability is very low. The stresses induced in the material at solidification are released slowly in the solid state as was remarked by increase of compressive strength ater 2 years. Gamma irradiation shows a similar effect. Saturation of the pores with water results in a decrease of compressive strength from about 80 MPa to 20 MPa. Drying restores the compressive strength.

B.4. Reactions with metal components of discarded equipment to be encapsulated

Metal components can be covered with a layer of MSC-aggregate preparations by dipping in the melt. Experiments with metal strips showed that sulfide forming metals as Cu and Pb form a thin layer of CuS and PbS during the contact time with the melt. No reaction occurs with the other metals or alloys or after solidification. Storage in the chemical laboratory atmosphere resulted in tarnishing or corrosion of the uncovered metal parts. After removal by melting of the MSC coating clean metal surfaces became visible. The coating of metal components with MSC may be useful for temporary storage for radioactivity decay, or the long term storage in concretes to prevent corrosion and hydrogen development.

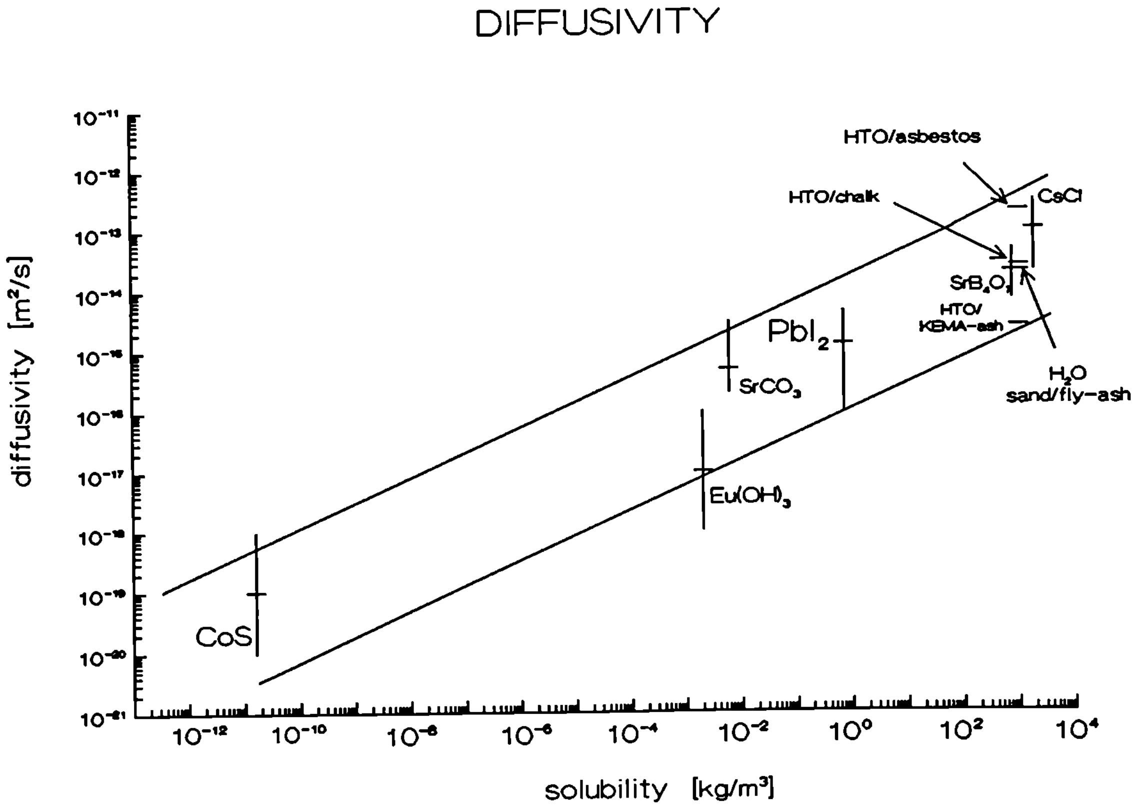
/1/ VROOM, A., Sulphur Research and Development 2, 15-18(1979).
/2/ Measurement of the leachability of solidified low-level radioactive wastes by a short-term test procedure. American National Standard ANSI:/ANS-16.1-1986.

Table I. Typical leach and diffusion results of MSC formulations with simulated wastes and aggregates.

	Cs	Sr	Co	Eu	HTO (H_2O)
borate waste	5E−14 8E−4	3E−14 4E−4	9E−19 2E−6		
KEMA ash	7E−14 1E−3	3E−15 9E−5	8E−20 6E−7	1E−17 1E−5	3E−15
asbestos					3E−13
$CaCO_3$					3E−14
ECN sludge	total β	1E−15 5E−5			
PbI_2	I	1E−15 7E−5			

D (=) $m^2.s^{-1}$
R_L (=) $g.cm^2.d^{-1}$

Figure 1. Relation between solubility and diffusivity and effective diffusion of waste components in MSC.



STUDY OF THE INDUSTRIAL OPERATION OF PLANTS FOR THE SOLIDIFICATION OF RADIOACTIVE WASTE WITH REGARD TO QUALITY ASSURANCE

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

Contract-No : FI-1-W-0009

Working Period: 01.01. - 31.12.88

Project leader: B. Ganser / R. Lang

A. OBJECTIVES AND SCOPE

Purpose of the R+D-programme is the investigation of the industrial operation of four different waste treatment plants with regard to quality control: compactor, evaporator/dryer, mobile cementation unit (MOWA) and stationary cementation system (continuous process). Within the programme the application of proposed controls at start up and active operation shall be systematically investigated, including comparisons of product qualities from industrial operation and lab-scale or inactive simulated full scale tests in available pilot plants and determination of acceptable bandwidths or product qualities. Expected results are the realisation of the proposed quality control procedures, which cover the commonly used waste treatment systems, and technical improvements of process control.

B. WORK PROGRAMME

1. Qualification of process and product control

2. Treatment of radioactive wastes
2.1 High force compactor (start up operation)
2.2 ROBE Biblis (active operation)
2.3 ROBE Gundremmingen (start up operation)
2.4 MOWA (active operation)
2.5 Continuous mixer (inactive test operation)

3. Additional investigations

4. Comparison of data and establishment

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

During the last year we terminated the experimental program by a technical demonstration of the continuous mixer system. We concluded the program by assembling the literature data and all experimental results to drafts of handbooks for the qualification of our waste conditioning plants.

Progress and results

- Qualification and product control (B.1)

  For the plants in industrial operation are the following ones meanswhile involved in qualification procedures /1/:

  - High force compactor of Arge TN/KAH in KfK-HDB
  - MOWA from Transnuklear (MOWA was overtaken by GNS in January '89)
  - Continuous mixing system by Siemens BW Hanau (ALKEM)

  The detailed description is given in our final report.

- Treatment of radioactive wastes (B.2, B.3)

  For all plants (B2.1 - B2.4) the experimental data and literature values were collected to define the experimental base for the qualification procedure. The corresponding experiments were perfromed; the results are described in detail in our final report.

- Comparison of data and establishment (B.4)

  The results of the experiments and of the practical experience were assembled to drafts of handbooks for the qualification of the plants (B.2.1, B.2.2, B.2.4).

For the ROBE a handbook could not be written because of the not completed list of requirements for the corresponding waste product group /2/. Details of the handbooks are attached to our final report.

References

/1/ J. Wolf KFA-ICT/PKS-IB-511/87

/2/ D. Gründler et al. GRS-A-1313

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. - 31.12.88

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 tests

5. Documentation

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

During the last year we installed and tested two different melting furnaces. Full scale tests were performed with all relevant ash simulates. The products were characterized concerning meltability, homogeneity, corrosion behaviour in deionized water and mechanical strength. Because of some constructive defects of the second furnace the second run of pilot melting experiments could not be completed within the time schedule. The delay can be estimated to about 3 months.

Progress and results

(B.2) Construction of a pilot plant

At the beginning of 1988, the special offer of LINN-Company, which was selected for the construction of a melting furnace, gave us the information of a longer delivering time. To save time, we decided to perform additionally pilot experiments in another pilot plant, which could be delivered within a short period (Naber-furnace), but which is nevertheless not according to our requirements for in-can-melting operation (special crucibles, fig. 2).

The Naber-furnace (fig. 1) is rectangular with a special fixation for the crucibles. The heated inner volume can be closed by a swing cover. In the cover we attached two openings for exhaust air (Ø 40 mm, center) and for the material feed (Ø 72 mm, half radius). The furnace has a programmable control. For the off gas cleaning we constructed a special filter device (particle deep bed filter).

The LINN-furnace was delivered at October 1988. Constructive defects concerning the bottom (light material, not suitable for weights of >100 kg), the heating space (no inner protection) and the electrical equipment (Ampère-meter, fuses) we had to shift the function tests to 1989.

The function tests of the Naber-furnace gave following results

- Heating time with filled crucible: 3 h/1050 °C, 5 h/1300 °C
- Cooling time with filled crucible: 1050 °C to 750 °C within 12 h
- Accuracy of temperature control: ± 50 °C
- Temperature gradient above crucible height: ≤ 50 °C
- Temperature at off-gas opening: 550 °C
- pH-value of condensed off-gas humidity: 2.5 (due to SO_2)
- Off-gas flowrate: 5.3 m^3/h
- Loss of pressure by off-gas filter: < 10 mbar

(B.4) Performance of fullscale tests

The ash simulates (AS) used for the fullscale tests were the same like used for the laboratory experiments (see annual report 1987). As melting temperature for the can-melting process we selected 1050 °C, which is the maximum temperature for stainless steel containers. One experiment (AS 8) was performed also at 1300 °C for comparison. The procedure was a batch process, i.e. the ash simulate was after homogenizing filled into the crucible and then heated to the final temperature. Because of the higher bulk volume of the ash simulate powder than of the crucible (50 l vs. 30 l), the residual amount was added to the melt within the first 2 hours of the melt experiment. Each product was kept at the maximum temperature for 10 h.

The melted products showed depending on the composition of the simulates different homogeneity. The products with rather low melting points were optical homogenious, the other products partially rough and unhomogenious surfaces. In the most products the upper part had a significant optical detectable porosity, as could be seen after core drilling. The product melted at 1,300 °C was mostly vitrified. The average densities were slightly below the densities of the labsamples and were between 1.9 - 2.7 g/cm³. The corrosion tests, performed according to ISO 6961, showed B and Al Diffusion coefficients, which were comparable to the lab samples (1.0 E-12 up to 8.3 E-18 m²/s after 28 days).

The mechanical strengths were clearly correlated to the structure. Porous samples had compressive strengths between 12 -34 N/mm², vitrified samples from 68 - 160 N/mm².

The results concerning volume reduction, corrosion and compressive strengths are summarized in tab. 1-3.

Ash Simulate No	Content of Na-Tetraborate concerning ash weight (%)	Weight (kg)	Temperature (°C)	Density (g/cm³)		Volume reduction factor
				Full scale tests	Lab tests	
AS1	50	63	1050	1.88	2.11	2.0
AS2	50	75.6	1050	2.31	2.52	2.5
AS3	50	58.5	1050	2.03	1.95	2.0
AS4	50	58.0	1050	1.81	1.92	1.9
AS6	50	60.0	1050	1.84	2.40	1.9
AS7	50	72.3	1050	2.20	2.41	2.4
AS8	50	74.7	1050	2.43	2.49	2.7
AS8	50	74.7	1050	2.41	2.49	2.7
AS8	30	74.7	1300	2.30	2.60	3.0
AS9	50	78.0	1050	2.44	2.60	2.7

Tab. 1 Results of volume reduction and density of the melted products

		Diffusioncoeffizient (m^2/s) after 28 d			
Ash simulate	Temp.	Full scale tests		Sample-position	Lab tests
	(° C)	Al	B		B
AS1	1050	4.7 E-16	2.2 E-13	above	2.1 E-16
		1.9 E-16	2.4 E-15	below	
AS2	1050	4.0 E-18	5.3 E-15	above	5.0 E-15
		4.3 E-18	2.1 E-14	below	
AS3	1050	5.7 E-17	7.0 E-16	above	1.2 E-15
		2.9 E-17	2.6 E-16	below	
AS4	1050	1.4 E-14	8.3 E-13	above	4.4 E-13
		1.6 E-14	1.0 E-12	below	
AS6	1050	4.5 E-16	2.0 E-14	above	
		3.0 E-17	2.6 E-16	below	
AS7	1050	3.2 E-17	1.9 E-15	above	7.2 E-17
		1.2 E-19	1.2 E-15	below	
AS8	1050	1.4 E-17	4.8 E-17	above	7.0 E-17
		1.4 E-17	5.9 E-17	below	
AS8*	1050	7.2 E-18	3.5 E-17	above	
		1.7 E-17	2.8 E-16	below	
AS8	1300	3.2 E-18	7.6 E-17	above	
		3.1 E-18	7.4 E-17	below	
AS9	1050	1.4 E-17	3.9 E-17	above	5.8 E-17
		8.8 E-18	8.3 E-18	below	

* Ash simulate was filled continuously within 10 h

Tab. 2 Results of the corrosion tests of the melted products
Comparison of lab and fullscale samples

Ash Simulate No	Contents of Na-Tetraborate concerning ash weight (%)	Temperature (°C)	Full scale tests bending and compressive strength (N/mm²) (Naber-furnace)		Remarks
AS1	50	1050	3.5	9.0	porous
AS2	50	1050	9.6	110	vitrified
			2.9	12.0	porous
AS3	50	1050	12.2	31.0	porous
AS4	50	1050	5.8	12.4	porous
AS6	50	1050	6.7	14.3	porous
AS7	50	1050	5.0	18.4	porous
AS8	50	1050	10.0	68.1	vitrified, sample broken
			7.5	121	vitrified
AS8*	50	1050	5.1	17.4	porous
AS8	30	1300	33.6	>140	vitrified
AS9	50	1050	46.4	>160	vitrified
			7.5	33.5	porous

* Ash simulate was filled continuously within 10 h

Tab. 3 Results of mechanical tests of the melted products

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 to December 89.

Period covered: January 88-December 88

Project leader: S.J. Ortiz

A. OBJECTIVES 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 objectives 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 resin-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.1. Bibliografic review.Origen and characteristics of the resins actual methods for their treatment and conditioning, and cements used for their inmobilization are studied in this review.

C.3. Dewatering experiments.

The image Analyzer (OPTAMAX V) technique has been used to measure the size grain of resins. Some of the initial problems have been solved.

Diference of size between dry and hydrated resins can be measured. However these diferences are not seen for resins satured with different cations not even no satured resins.

The change of size from dry to hydrated conditions is very fast. The hydration of the resin is realized with the atmospheric humidity in few minutes.

C.4. Properties of various resins cement mixtured. Mechanical properties on mixtures obtained with four selected cements and three ion exchange resins have been studied. The resins have been used like commercial form (H^+ and OH^-) and saturated with several ions (Ca^{2+}, Li^+, Cl^- and BO_3^{3-}).

Water cement ratio (W/C) 0.3, 0.4, 0.5 and 0.6 and resin/cement ratio (R/C) 0.16 for bead resins and 0.08 for powder resins have been studied.

C.4.1. Compressive and flexion strength. These test have been realized with two kind of samples: after a curing time of 28 days and similar specimens after and additional perios of 28 days under water.

C.4.2. Extended and shrinkage concrete have been detected only with some test sample.

C.4.3. Setting time. The begining and final of setting have been measured.

C.4.4. Volume increassing. This test relates initial volume of hydrated resin and final volume of cement-resin-water mixture.

C.4.5. Water porosity. The porosity is determined by weight difference between a dry and saturated sample. Very few samples can resist test conditions (dried during 48 h. at 105º C and inmersion in water during 7 days).

C.4.6. Fluidizes adition. The use of Plastiment BV-40 gives samples with good mechanical propoerties and till 15% dry resin content.

C.4.7. Water inmersion. Some samples have been inmersed 28 days in water after 28 days of curing time. The effect of this test on growing and mechanical resistance has been studied.

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

From tests carried out up to now, two cements (Blast Furnace and P-350 Y) have been selected for more specific studies with bed resins (DUOLITE ARC 9351 and AMBERLITE (RN-150).

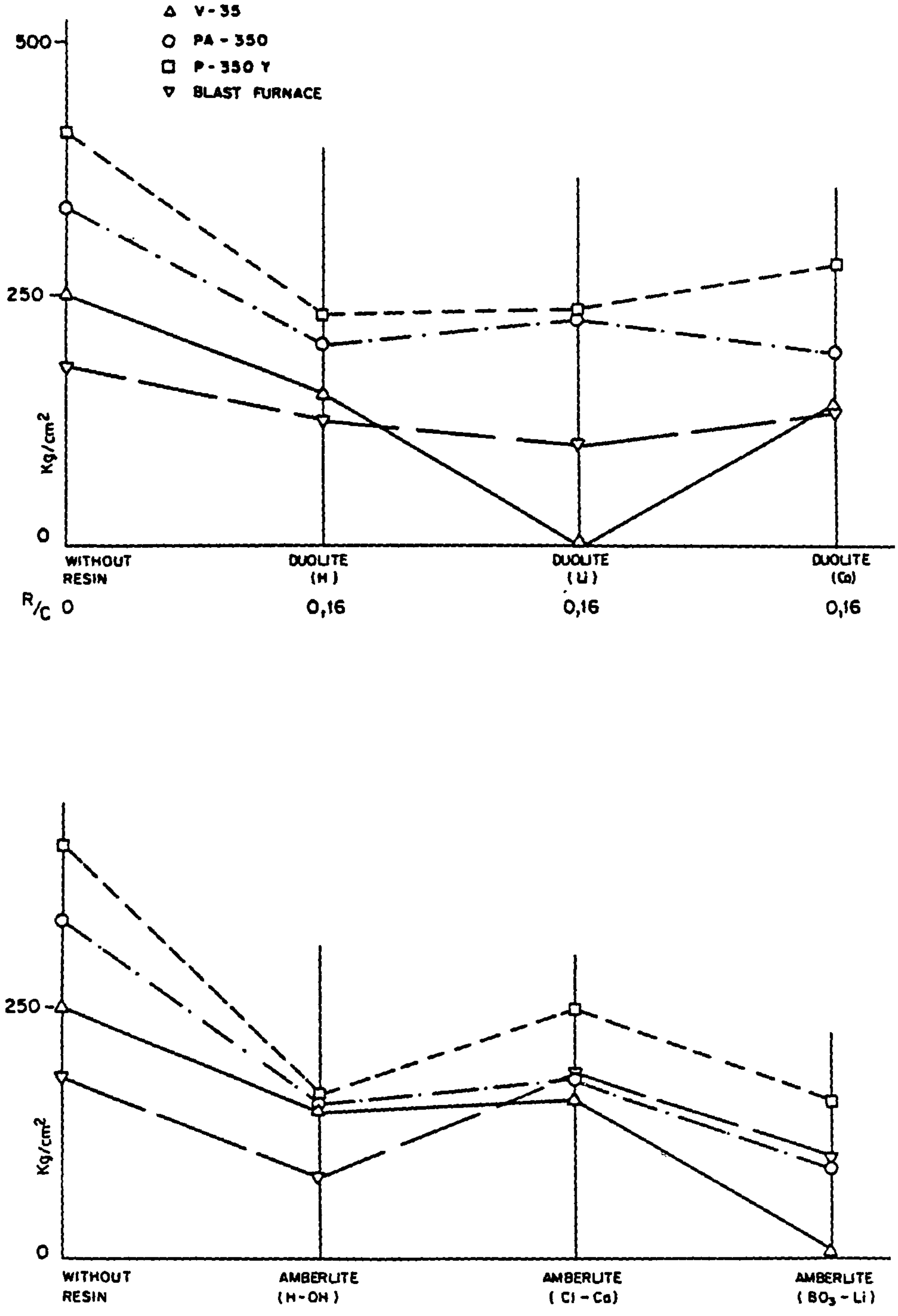


FIG. 1.- COMPRESSIVE STREGTH ($^{W}/_{C}$ =0,5)

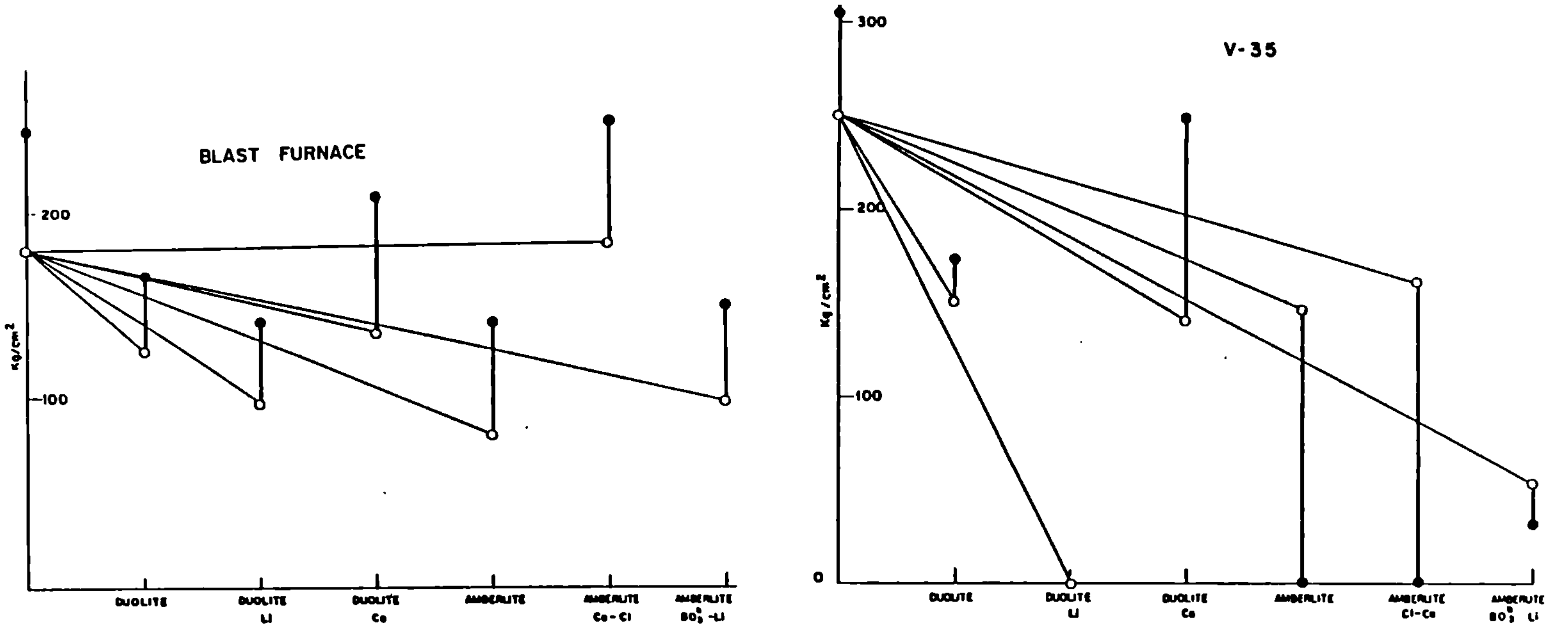


FIG. 2.- COMPRESSIVE STRENGTH

○ AFTER 28 DAYS CURING TIME
● AFTER 28 DAYS CURING TIME
AND 28 DAYS UNDER WATER

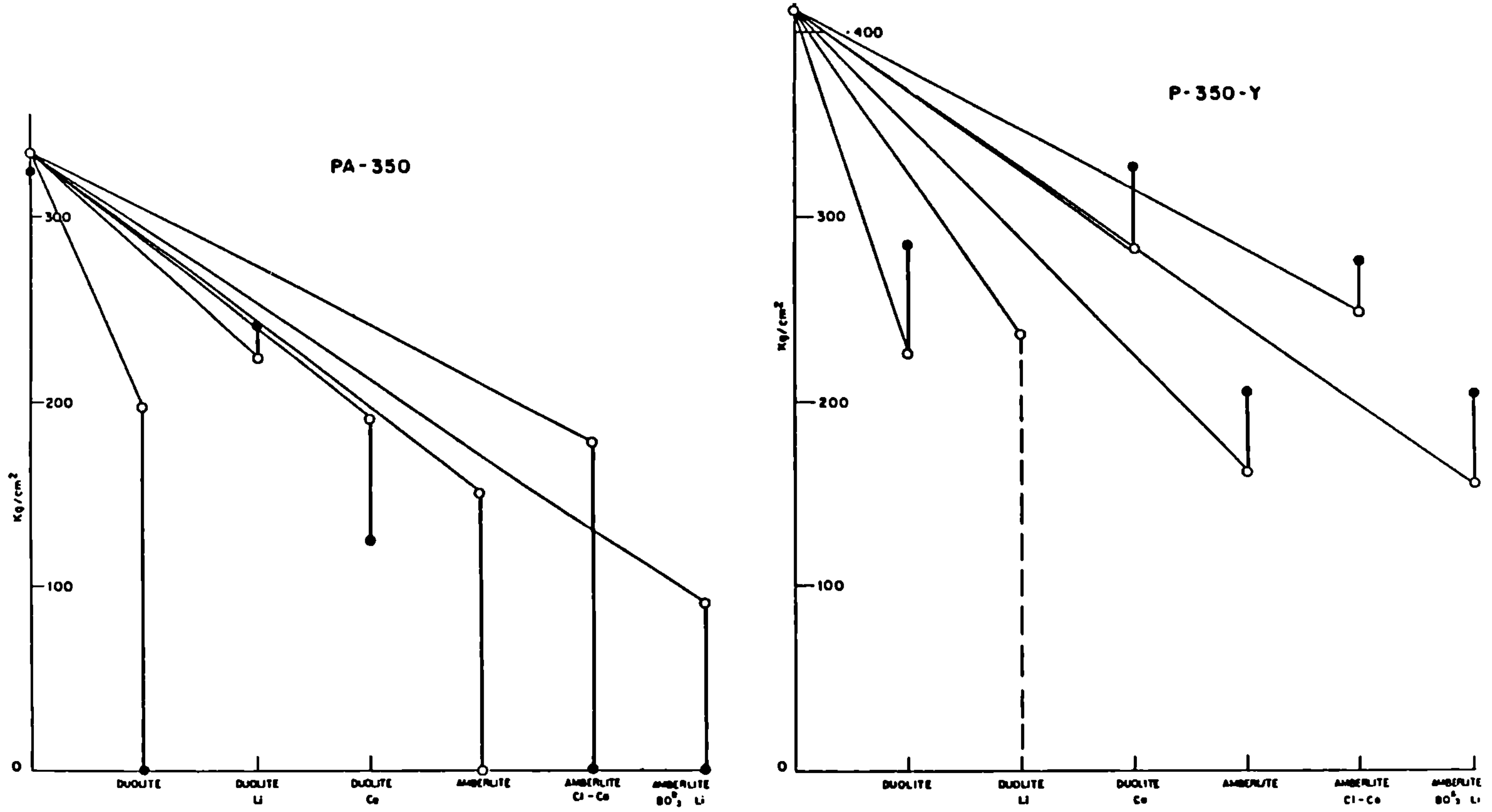


FIG.3 :- COMPRESSIVE STRENGTH

○ AFTER 28 DAYS CURING TIME

● AFTER 28 DAYS CURING TIME
AND 28 DAYS UNDER WATER

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° FI 1W/0005
Duration of contract : from 01.06.89 to 31.12.89
Period covered : July 87 to July 88
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 :

During the spent year -from July 87 to June 88- the following results have been obtained :

- On a 1 year leaching test, obtention of the data about leaching rate and total release of α emitters. The samples were 100 ml of volume : 3 of each were made in the 3 considered matrix, i.e. cement, epoxide resin and polymer cement compound. The α activity of the ashes was 50 Ci.t^{-1}, in agreement with the value calculated in the industrial project.

- We have also fabricated special samples containing, a high activity of ^{238}Pu, and started 2 kinds of tests :

  1) A direct leaching test, in order to appreciate the effect of α radiolysis and of water immersion.

  2) A radiolysis study, giving data on gas, generated by radiolysis and values of the $G(H_2)$ in the 3 solid ash forms.

- During the same time, a pilot plant has been received and started. This facility, able to produce solidificated waste form at the 200 l drum scale, can work with the 3 matrices : cement, epoxide or polymer cement.

PROGRESS AND RESULTS :

1) Feasibility of incinerator ash embedding

The formulation work is summarized in the following table :

EMBEDDING MATRIX	ASH CONTENT %	SOLIDIFICATION AGENT %
1) EPOXIDE CIBA (E : XF431 - H : XF348)	40	60
2) CLC CEMENT (OPC40 - BFS30 Flying ashes 30) Water/cement = 0,65	19	81
3) EPOXIDE-CEMENT COMPOUND - Epoxide CDF : E : MN201 H : D2000 - Cement CLC + water (W/c = 0,35)	40	60

2) Leaching test - conditions :

- α activity of the ashes 50 $Ci.t^{-1}$
- sample volume : 100 ml
- α activity of the samples :
  - . epoxide : 1.10^8 Bq (2,7 mCi)
  - . cement : 6.10^7 Bq (1,6 mCi)
  - . epoxide-cement compound : $1,3.10^8$ Bq (3.5 mCi).

The results are presented after 270 days :

Results	Epoxide	Cement	Polymer cement
α emitters total release	$1,2.10^{-5}$	$5,0.10^{-5}$	$6,6.10^{-6}$
Equivalent mass release in $g.cm^{-2}.d^{-1}$ (leaching rate)	$5,2.10^{-8}$	$2,7.10^{-7}$	$3,5.10^{-8}$

<u>NB</u> :

For this α leaching test, a new procedure has been set up : in the expressions of release and of leaching rate, the α activity A_i is a material balance :

$A_i = A_S + A_{IS}$

A_S = soluble α activity, in the leachant

A_{IS} = insoluble α activity, deposited on a strippable coating, covering the walls of the leaching tank

3) Embedded α ash forms, doped with ^{238}Pu. α internal irradiation behaviour study.

This accelerated test allows the delivery in 1 year, of the α dose integrated in 10^4 years, on samples at the nominal activity.

Three samples (100 ml volume) were fabricated in the 3 considered matrices : in each sample, incinerator α ashes mixed with the calculated amount of 238 plutonium dioxide, were encapsulated.

For each group of 3 samples, the distribution is the following :

- 1 sample, for a leaching test,
- 2 samples, for a radiolysis study.

3.1) Leaching behaviour :

This test gives data on the double effect of α radiolysis and water leaching [1]. The results are presented after 56 days.

Results	Epoxide	Cement	Polymer cement
Sample initial activity Ao	3 Ci	1.7 Ci	3.3 Ci
Total release at 56 days	$1,3.10^{-4}$	$1,5.10^{-5}$	$1,5.10^{-5}$
Leaching rate expressed in $g.cm^{-2}.d^{-1}$	$2,5.10^{-6}$	8.10^{-8}	5.10^{-7}

Conclusion :

In this leaching test, with this high ^{238}Pu content, the results after 56 days show a tendancy : cement and polymer cement seem better than pure epoxide.

3.2) Radiolysis test :

2 samples of each embedded form were put in a proof container under argon atmosphere. Samples of this argon were analysed once a month : the main component was found to be hydrogen, with traces of nitrogen, oxygen and carbon dioxide.

The results are presented after 6 months, in the following table :

Type of the sample	Specific activity	Absorbed dose	Hydrogen in ml	$G(H_2)$
Epoxyde form	$2.1.10^4$ Ci t^{-1}	$1.07.10^7$ Gy	160 ml	0,05
Polymer cement form	$2,0.10^4$ Ci t^{-1}	$0,9.10^7$ Gy	360 ml	0,10
Cement form	$1,0.10^4$ CI t^{-1}	$0,4.10^7$ Gy	320 ml	0,20

Nota :

The activity of the cement form is only the half of that of the two others, due to the poorer embedding capacity of the cement matrix.

4) Starting up of the pilot plant for incinerator ash embedding (PICC).

A pilot plant has been started in April 1988. The facility is designed to work with the process defined at the laboratory scale, using cement, or epoxide or polymer cement as bonding agent : this process has been described in a paper presented at the international meeting of Stockholm in May 88 [2].

The receiving tests of the pilot plant have run from March to July 1988 : they are composed with 2 steps :

1) Checking of the apparatus performances :

- calibration of the volume of the tanks of the flow meters, of pressure meters, of vacuum,

- hold up determination in the different parts of the process :

  . powder circuit (ash and cement),
  . liquid circuit (epoxide, water),

- checking of the electronic weighing system indeed, the fiability of this device is being important, since the quality of the final product depends on its massic composition.

2) Demonstration step, using each of the 3 matrices: cement, epoxide, polymer-cement. Several full scale drums of each embedded waste form were made. It can be noted that all the products, fabricated under vacuum as described [3], show better hardness and compacity.

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

Contractor:	ENEA-CRE CASACCIA, Rome, Italy
Contract n°:	FI1W-0011
Duration of contract:	July 1986-March 1989
Period covered:	January - December 1988
Project leader:	Loris Pietrelli

A. OBJECTIVES AND SCOPE

The purpose of this research project is to simplify the pre-disposal management of the stored liquid HLW at the EUREX pilot plant. This waste consists of the aqueous raffinate of the first extraction cycle (1AW) from the reprocessing of MTR-type fuel. The 1AW-MTR liquid waste consists of 85 m^3 (stored in two stainles steel tanks) of 1.1 M HNO_3 solution with 27 g/l of Al and other minor constituens, including fission products and reprocessing chemicals. Table I gives the chemical and radiochemical composition of the 1AW-MTR waste.

The direct vitrification of this waste would require a complex vitrification plant and result in a large amount of vitrified waste. Therefore the objective is to separate this liquid waste into two parts: 1) a small-volume, highly radioactive fraction, including the Cs, Sr and Actinides; 2) a larger-volume, low level waste fraction containing the majority of the inactive salts present in the waste.

In Figure 1 is shown a conceptual flowsheet for the management of 1AW-MTR waste.

The high-level fraction must be suitable for vitrification, with the objective of immobilizing the waste in the smallest possible volume of glass. From preliminary studies on glass composition /1/ the aluminum and sulphate in the high level fraction should be minimized (Al < 13% w/w as Al_2O_3).

The low-level waste fraction must be suitable for cementation, and it should be reduced to the smallest practical volume. Scope of research work under this CEC contract is to study and compare the proposed chemical processes by technical and economical criteria.

B. WORK PROGRAMME

B.1 Development of chemical flowsheets, by using simulated waste solutions, for the quantitative separation of Cs, Sr and Actinides from the 1AW-MTR solution.

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

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

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

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

B.6 General considerations and Final Report.

C. PROGRESS OF WORK AND OBTAINED RESULTS

B.1 Development of chemical flowsheets.

Taking into account the chemical and radiochemical composition of the MTR waste solution some chemical processes (based on the ion exchange and precipitation both in acidic and alkaline medium) were previously investigated in laboratory scale with simulated solution /2,3/. The ranking criteria (Decontamination Factors, volume reduction,safety problems, etc.) showed that the acidic processes did not meet the adequate performances, while the alkaline processes were adequate and essentially equivalent.

B.2÷B.3 Sampling equipment to analyse the MTR waste and realization of a hot minipilot plant.

In order to make the sampling, the analyses and than the "hot tests", ENEA has designed and realized a sampling equipment consisting essentially of a vacuum system to provide the transfer of the solution into a special sample container 8 litre capacity and 15 cm Pb shielding (Cendrillon).

At the same time in order to allow the realization of tests on real samples a hot cell has been equipped with a glass reactor (with stirrer, pH and Temperature control), peristaltic pumps, centrifuge and usual laboratory equipment. The mini pilot plant has been operated by remote controls and telemanipolators /4/.

B.4 Chemical and radiochemical analysis.

Table I gives the estimated (by ORIGEN code and/or process analytical data) chemical composition of the total waste, and the real composition of the solution stored in the first tank (F-710/D).

The significant differences between estimated and found chemical composition may be explained considering that:

- the estimated composition refers to the average composition of all MTR liquid wastes (tanks F-710/D and F-710/C);
- the found composition refers to liquid waste contained in the tank F-710/D, where the liquid effluents coming from the first "cold" runs with inactive fuels (carried out at EUREX plant before the hot startup) were collected.

As a consequence, a significant increase of aluminium concentration and a dilution of radioactive components, with respect to the average estimated composition, is to be expected. As soon as possible, the liquid waste of the second tank (F-710/C) will be sampled and analysed. In this case, it has to be expected to find higher values for radioactive components and lower values for aluminium.

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

Experimental procedure

The chemical treatment processes were performed by using 300 ml of real MTR waste solution each time.In order to semplify the Sr determinations on the supernatant after the chemical process, the real waste has been traced with Sr-85 (gamma emitter).

The solid separation was carried out by centrifugation at about 3000 rpm for 5-10 minutes.

The ion adsorption process was performed by using glass column, filled with IE-96 (Union Carbide) zeolite, at 25-27 °C. A 2.5 ml/h flow-rate was fixed by using a peristaltic pump with changeable head to allow every liquid tansfer from and to cell equipment.

Results and discussion

Both alkaline declassification processes (AZE=Alkaline and ZEolite, ATE=Alkaline and TEtraphenylborate) are based on alkalinization with NaOH of the MTR solution to pH>13 in order to transform the aluminum nitrate into soluble sodium aluminate.

Special attention must be devoted to minimize the volume of precipitate, and to obtain it in a suitable physical form for an easier solid-liquid separation. The best results have been verified by adding the acidic MTR solution to the NaOH concentrated solution (10 M) and not *viceversa*: in fact the mean value of 7.3 g of dry sludge per litre of MTR solution was obtained during the hot tests.

In the alkaline medium, the iron present in the waste solution precipitates as ferric hydroxide, and the strontium and the actinides are separated by coprecipitation-coagulation with it. Decontamination Factors (FD) > 170 and 44000 respectively for strontium and plutonium were performed. A volume ratio V_{MTR}/V_{NaOH} of 1.30 and an alkalinity excess of ≈0.9 M was used during the hot tests (see Table II).

The glass column was filled with 4.00 g of IE-96 (25-50 mesh) zeolite (from Union Carbide).

Material balance considerations, show that the area between the break through curve and the horizontal line at $Cs/Cs_{in} = 1$ is proportional to the total solute which is adsorbed when the outlet flow has reached a concentration equal to the inlet flow: the zeolites are therefore completely exhausted. This area is obtained by numerical or graphical integration.

In Table III the main results for the hot tests, the laboratory columns and for the SERSE pilot plant columns are reported: the capacity of the zeolites is calculated at 50% of the break through curve.

In figure 2 the break through curves for cesium from Hot test, SERSE pilot plant and laboratory tests are reported.

The significant difference of Cs capacity between the real MTR solution and other solutions is due to the higher Na content (Na=4.5 instead 3.5 M) and to the lower Cs equilibrium concentration in the supernatant (see table III). In fact the presence of Na competing ion has a dramatic effect in reducing cesium adsorption and this behaviour is particularly negative at low Cs concentration /5/. In order to solubilize the aluminum (37 g/l, more than the aspected value) a significant amount of NaOH was added (Na/Cs = 10^{-5} vs 3.9×10^{-4} estimated).

Cs separation by Sodium Tethraphenylborate (NaTPB)

The attractive features of the Cesium recovery by NaTPB is its ability to provide a high Cs DF from alkaline supernatant in a single batch precipitation. In fact an advantage of this process is that alkalinizaztion and Cesium precipitation could be carried out in the same reactor tank.

Cesium recovery using NaTPB as reagent is dramatically improved when the mole ratio Na-TPB/(Cs+Rb+K) is greater than 1. This indicates that there is a strong competition between the cations in the precipitation reaction. Once the cation concentration is equivalent to the NaTPB concentration, the recovery of Cs is very efficient. Some problems during the precipitation, due to high Potassium concentration, coming mainly as an impurity of NaOH, could occour during the alkalinization: therefore it is very important to add a NaOH with low Potassium content in order to avoid problems with Cs competition for NaTPB.

The precipitation and the process parameters were previously described on the other Progress reports /6,7/.

Cesium DF>1000 was carried out during the "hot tests" and the decontamination of other radionuclides were essentially the same of other precipitation tests. In Table II the main results of tests are reported.

Conclusions

The experimental work carried out with reasl waste has shown thet it is possible to perform a selective separation of radionuclides from liquid MTR waste solution obtaining high decontaminatio factors.

The high radioactive fraction is reduced to a smaller volume and the final glass volume is estimated to be only 1/10th of the volume which would be necessary without the selective separation.

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Table I:Estimated and real composition of MTR HLLW.

Elem.	**Estim. conc.**		**F-710/D conc.(*)**	
Al	27.01	g/l	34.42	g/l
Hg	1.34	g/l	0.79	g/l
Fe	0.56	g/l	0.43	g/l
Si	0.14	g/l	-	
Cs	17	mg/l	11.6	mg/l
U	6.5	mg/l	4.8	mg/l
Sr	7.8	mg/l	5.8	mg/l
Pu	2.5	mg/l	0.27	mg/l
Am	4E-3	mg/l	n.d.	
H+	1.1	M	0.92	M
SO4=	6E-3	M	1.7E-2	M
NO3-	4.1	M	4.65	M
d(25°C)	1.2	g/ml	1.236	g/ml
Residual	(dried to 120°C)		149.1	g/l

Radiochemical composition of sampled waste:

Cs-137	10.7	GBq/l	Co-60	1.8	MBq/l
Sr-90	9.3	GBq/l	Np-237	n.d.	
Eu-154	19.2	MBq/l	Am-241	n.d	
Pu8.0	MBq/l	(wt39%=90.45)	gross ß	39.2	GBq
Cs-134	3.0	MBq/l	gross α	13.8	GBq

(n.d.) = out of detectability; (-) = not analyzed

Table II: Main results of tests performed with real MTR HLLW.

	AZE	**ATE**
Vol. (ml)	500	500
OH- (M)	0.90	0.97
Na (M)	4.33	4.33
Al (g/l)	18.82	18.90
Fe (g/l)	1.5 E-6	1.5 E-6
Hg (g/l)	0.4	0.4
Pu tot	0.3 kBq/l	0.3 kBq/l
Eu-154	n.d	n.d
Cs-137	(*)	0.6MBq/l
Cs-134	n.d.	n.d.
Co-60	0.22 kBq/l	0.22 kBq/l
Sr-90	<25 MBq/l	<50 MBq/l
gross beta (§)	3.10 MBq/l	84 MBq/l
gross gamma (#)	2.10 MBq/l(**)	2.6 MBq/l

(*) see break-through curve
(**) after about 100 ml eluted
(§) referred to Sr/Y std.
(#) refered to Cs-137 std.

Table III: Continuous tests in columns with different alkaline supernatants /5/.

Column type	Sol. type	Temp. (°C)	Cs_{in} (mg/l)	50%b.t. (mgCs/g)	BCT(*) (hour)
Laboratory	CsCl	21	5110	220.8	1
Laboratory	MCE alk	21	13.5	1.01	1
Pilot Plant	MCE alk	25	13.5	0.93	1
Hot test	MTR	25	5.7	0.43	2-3

(*) Bed Contact Time

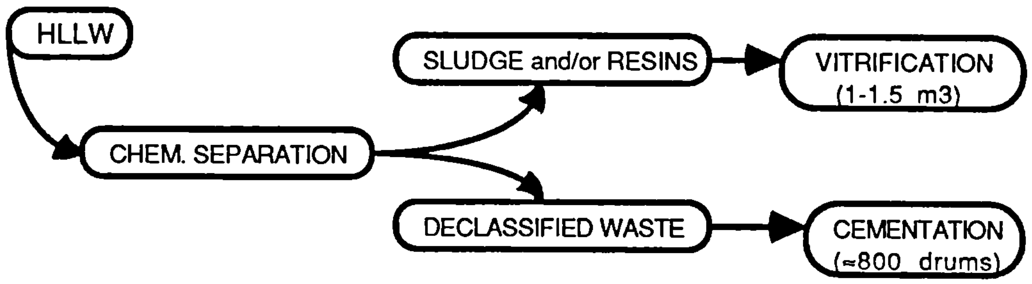


Figure 1: General scheme of the waste treatment.

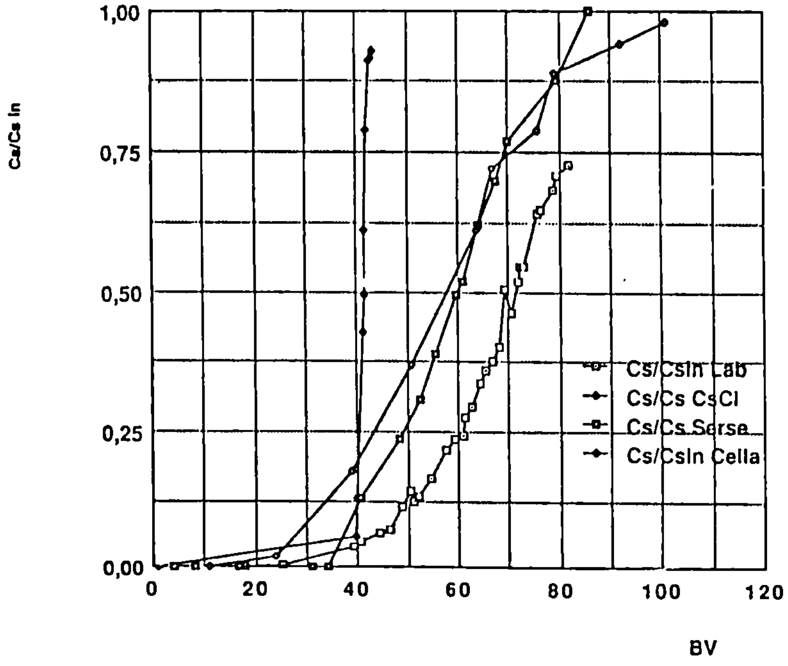


Fig. 2 : Break through curves for Cs adsorption tests

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

Contractor : CEA, CEN-FAR FRANCE
Contract No : FIW/0013
Duration of contract : October 1986 - December 1989
Period covered : January 1988 - December 1988
Project leader : G. KOEHLY

A. OBJECTIVES AND SCOPE

Nuclear activities in the Radiochemistry building of Fontenay-Aux-Roses nuclear research center concern principally the study of fuel reprocessing and the production of transuranium isotopes. During these activities solid wastes are produced that are contaminated with α β γ emitters for hot-cells studies and with α emitters only for glove-boxe experiments.

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

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

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

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

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

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

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

B. WORK PROGRAMME

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

2.1. 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 optimisation 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. RECOVERY 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 1988, about 1 tonne (= 6 to 7 m^3) of active solid wastes have been treated in ELISE : these wastes were subjected to the sorting and crushing operations. In PROLIXE 555 kg of α β γ solid wastes have been sorted and about 470 kg crushed.

Lixiviations campaigns were performed = 3 in ELISE involving = 30 kg of PCW and 6 in PROLIXE related to α β γ contaminated solid wastes (high ^{241}Am and ^{244}Cm contents), and about 1 m^3 of leachates have been concentrated using the cyclone concentrators.

Concerning the laboratory studies the state of advancement is the following :

1/ AgII OXIDIZING DISSOLUTION : a new utilization of that technique has been considered : the decontamination of MOx pins for the MELOX facility,

2/ REDUCING DISSOLUTION : the application of the concept using U^{3+}, U^{4+}, V^{2+} and Cr^{2+} reducing agents for the treatment of PCW is possible.

Progress and results

1. Wastes crushing (B.2)

Hot experiments done either in ELISE or in PROLIXE (note that these two facilities are equipped with the same crusher) have been realized without any difficulties : 1 tonne (ELISE) and about 470 kg (PROLIXE) were treated in 1988.

For the wastes treated in PROLIXE an apparent volume reduction factor of = 2.6 was obtained after the crushing step.

2. Leaching tests (B.4)

2.1. Laboratory studies

A new application of the AgII dissolution method was considered during that period. It consists in the decontamination of the zircaloy clad of the pins loaded in $(U,Pu)O_2$ for MOx fuel preparation. This technique is devellopped in collaboration with Cadarache.

The development of the reducing dissolution technique for PCW treatment was performed and definite proofs of the validity of the concept were obtained. The efficiency of the decontamination in plutonium of solid wastes during the electrogeneration of reducing agent has been determined with U, V and Cr solutions.

2.2. ELISE experiments

Three campaigns, involving each about 10 kg of PCW have been done. Successive HNO_3 lixiviations were realized and it was demonstrated that in this case the "extraction-like behavior" of the Pu during the lixiviations. This phenomenon is certainly connected with the presence of liquid TBP in the treated wastes. It must be noted that the objective of the exhaustive decontamination of the wastes was not obtained during these HNO_3 leaching tests.

2.3. PROLIXE experiments

About 104 kg of solid wastes (63 kg crushed and 41 kg non crushed metallic wastes) initially highly contaminated with ^{241}Am and ^{244}Cm have been washed : 6 campaigns were done. These wastes were produced in a hot-cell where (α,n) neutrons sources involving $^{241}AmO_2$ and $^{244}CmO_2$ are prepared.

A total of 30.52 g of ^{241}Am and 4.1 g of ^{244}Cm was dissolved in the leachates, thus the mean initial level of α contamination of these wastes was > 4200 $Ci.t^{-1}$. The determination of the decontamination factors corresponding to these tests is underway.

3. Equipment design (B5)

An AgII large electrolyzer was conceived and realized. AgII generation cold tests were done and the composition of the gas generated in the cathodic compartment was determined : the presence of H_2 is at the limit of detection ; the electrolysis mainly generate NOx.

This type of AgII electrolyzer will be used in ELISE and PROLIXE facilities and also in the new apparatus to be built for MOx pins decontamination.

4. Secondary wastes (B6)

The management of the leachates is working well in ELISE. Using the new cyclone evaporators about 1 m^3 of active leachates were concentrated during 1988 with good epuration factor. The distillates produced were reused for new lixiviations.

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 - March 1989
Period Covered: January 1988 - December 1988
Project Leader: N. 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

Four stainless steel ingots with an average unit weight of 3.6 kg were produced from actual *Phénix* reactor clads. For a more precise volatility balance the crucible head was disassembled and rinsed after the 4th ingot. Cesium was the only element volatilized in appreciable quantities. The ingot α decontamination factor has not been accurately determined. The general work progress status is as follows:

- B.1: Completed.
- B.2: Nearing completion. Some characterization results have not yet been obtained (oxygen, nitrogen and fluorine content of the ingots).
- B.3: The 4 contractual melting operations have been completed. The ingots must still be characterized, and the flux incorporated in glass in the *Vulcain* cell.
- B.4: Melting of the zirconium ingots has not begun. The work can only be approved after the results of an ongoing safety investigation are available: a significant delay is likely.

Progress and Results

1. Inactive Reference Tests (B.2)

The ingot characterization work is nearly finished. One of the pair of ingots produced by melting each material (stainless steel, zircaloy 4, and a zircaloy-steel-inconel mixture) was cut up for examination. Initial optical microscope observations (× 5, × 25 and × 175) after metallographic etching were followed by scanning electron microscope examination using an X-ray analyzer. The results clearly revealed the existence of a solidification front, and a change in grain size related to the cooling rate. No porosity was observed in general (a shrink cavity was found at the top of all but one ingot) and the specimens were generally uniform at macroscopic scale. In the zircaloy-steel-inconel ingot, however, a few hulls or inconel scraps could be distinguished that were not fully digested because of the fast drawing rate.

The apparent densities calculated throughout the ingot corresponded to the actual densities of the materials used, indicating a very good volume reduction factor (7 to 9).

Aqueous corrosion resistance at 100°C was measured using a glass Kumagava device: the mass loss and solution ion analysis results did not indicate significant corrosion of the elements from the metal matrix (the leach rates were below 10^{-9} $g \cdot cm^{-2} d^{-1}$).

The 3 types of flux recovered during the inactive ingot reference process tests were incorporated into R7T7 (SON 68 18 17 L1C2A2Z1) glass in amounts ranging from 2 to 4 wt%, corresponding to the extreme values liable to be obtained per ton of reprocessed LWR fuel. Glass specimens melted by Joule effect at 1200°C in a platinum crucible were homogeneous, with slightly higher density and lower viscosity than the basic glass without flux additives. Devitrification as estimated by differential thermal analysis did not appear to increase; only the glass transformation temperature dropped by a few degrees as the flux content increased. Chemical analysis of the glass showed that only fluorine was subject to volatilization (50% with the test procedure). Glass specimens containing $CaO\text{-}CaF_2$ and $CaF_2\text{-}BaF_2$ flux showed slightly increased alterability under Soxhlet conditions at 100°C.

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

The four planned active ingots have been produced from 3 kg of *Phenix* FBR fuel clads with a mean burnup of 32 000 MWd·t^{-1} reprocessed in 1980. Based on the results of analyses performed at the Marcoule pilot facility before this contract began, the specific activity is about 4.5 mCi (β) and 22 μCi (α) per gram of clads.

2.1 Ingot Fabrication and Appearance

Process conditions were generally similar to those under which the steel reference ingots were produced, except that the melting time was significantly extended to 80-120 minutes instead of 45 min. During melting, after half of the ingot was drawn, a cooler dark zone formed around the periphery of the molten bath and the upper portion of the ingot was capped with a metal crown that sometimes contained 1 or 2 incompletely melted hulls (Figure 1). Increasing the flux quantity during tests CI 05 and CI 06 did not eliminate this phenomenon. Two attempts (CI 03 and CI 04) did not result in the production of an ingot, as the available power was not sufficient to induce melting. An open shrink cavity was generally found at the top of the ingot.

2.2 Material Mass Balance

The results did not differ substantially from those obtained during the inactive reference test (Table I). The slag mass again increased (+14.7% for the active tests compared with +13.0% for the inactive ingots) probably from dissolution of oxides or elements adhering to the hulls.

2.3 Volatilization

As clearly indicated in Table II, the total volatilization (excluding tritium) was around 3.9% of the initial β activity and 1.0% 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. No tritium balance was determined for these clads.

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 values obtained for the first ingot (CI 01) based on the theoretical hull activity level indicate a decontamination efficiency of 85% α and 5.4% β (65% for Sr and 32% for ^{137}Cs).

2.5 Ingot Characterization

The first ingot (CI 01) has been cut up for characterization.

		Mass balance (g)			
	Materials	CI 01	CI 02	CI 05	CI 06
Before melting	Phenix hulls	3030*	3020*	3023,8	2980*
	Start up metallic load	634,6	633,8	636,7	634,6
	Slag CaF2 : 75 % MgF2 : 25 %	113,1**	120,1**	162,8**	161,7**
After	Non used hulls	-	-	7,1	-
	Non used slag	5,1	-	-	19,8
	Slag recovered on ingot :				
	by spontaneous removing	96,2	98,5	170,1	155,6
Melting	by slight hammering	22,5	31,0	20,8	13,4
	Slag recovered :				
	in dust separator	1,5Δ	0,5	0,8	0,3
	Total	120,2	130,0	191,7	169,3
	Final ingot	3574,9	3627,5	3614,2	3558,0
	Slag recovered on :				
	head cold crucible		0,6		
	top cold crucible		1,6		
	total		2,2		

* weighted mass to within 100 g

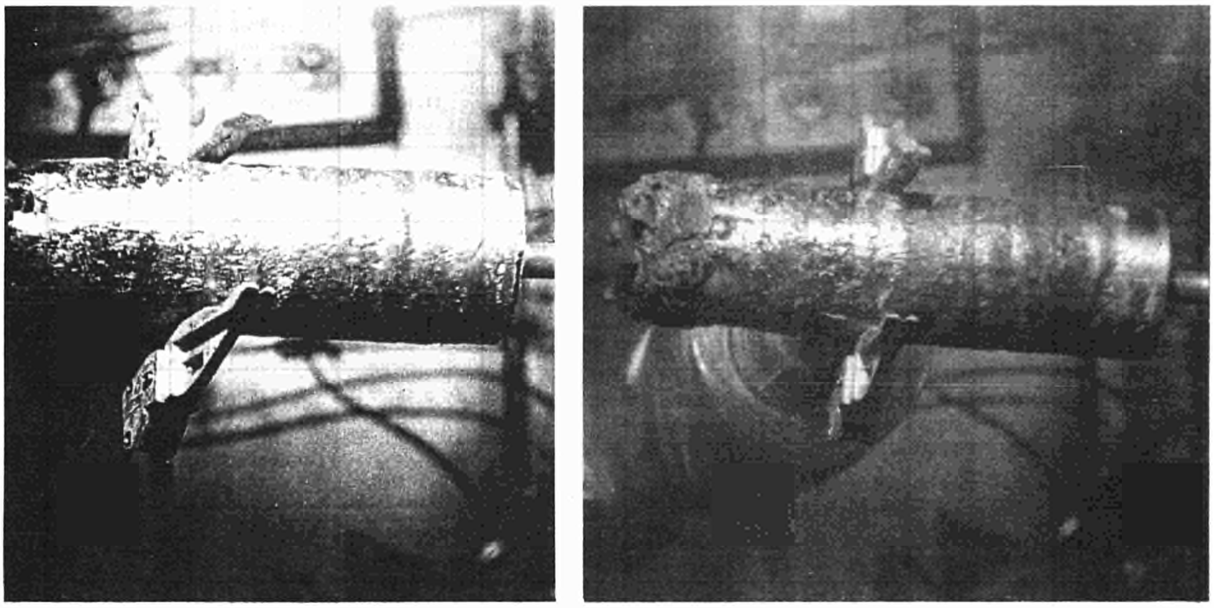
** included 1,7 g of Keplane for isolation of Startup metallic load

Δ two successive washing

Table 1 - Mass balance for melting of 4 Stainless Steel Ingots CI 01, CI 02, CI 05, CI 06

	A	B	C	D	E=A+B+C+D	F	$\frac{E}{F}$ X 100
	Head Crucible	Dust Separator	Washing column	Millipore filter	Gross activiy	Activity of the melted hulls	Volatility %
$^{90}Sr + ^{90}Y$	3,37	7,81	$\leqslant 0,3\ 10^{-3}$	$\leqslant 10^{-5}$	11,18	598,5	1,9
^{137}Cs	135,4	257,5	$1,6\ 10^{-3}$	$\leqslant 8\ 10^{-4}$	392,9	631	62,2
^{134}Cs	0,86	2,00	$\leqslant 1\ 10^{-4}$	$\leqslant 5\ 10^{-5}$	2,86	14,4	19,9
$^{106}Ru + ^{106}Rh$	$\leqslant 0,95$	$\leqslant 1,54$	$\leqslant 3\ 10^{-4}$	$\leqslant 6\ 10^{-4}$	$\leqslant 2,49$	1120	$\leqslant 0,2$
$^{144}Ce + ^{144}Pr$	$\leqslant 1,29$	$\leqslant 1,69$	$\leqslant 3\ 10^{-4}$	$\leqslant 4\ 10^{-4}$	$\leqslant 2,98$	0,45	(< 662)
^{125}Sb	2,58	$\leqslant 0,9$	$\leqslant 1,1\ 10^{-3}$	$\leqslant 2\ 10^{-6}$	$\leqslant 3,48$	730,5	$\leqslant 0,5$
^{60}Co	0,07	$\leqslant 0,2$	$\leqslant 8\ 10^{-4}$	$\leqslant 1\ 10^{-6}$	$\leqslant 0,27$	8013	$\leqslant 3\ 10^{-3}$
^{54}Mn	$\leqslant 0,17$	$\leqslant 0,3$	$\leqslant 5\ 10^{-5}$	$\leqslant 2\ 10^{-4}$	$\leqslant 0,47$	44,3	$\leqslant 1,1$
TOTAL BETA	144,7	271,9	$\leqslant 4,5\ 10^{-3}$	$\leqslant 2\ 10^{-3}$	416,6	11.152	3,7
$^{239-242}Pu$	0,20	0,07	$0,6\ 10^{-2}$	Nd	0,28	42,4	0,7
$^{238}Pu + ^{241}Am$	0,17	0,26	$1\ 10^{-2}$	Nd	0,44	25,9	1,7
^{244}Cm	$0,4\ 10^{-3}$	$0,3\ 10^{-3}$	Nd	Nd	$0,7\ 10^{-3}$	0,2	0,3
TOTAL ALPHA	0,37	0,33	$1,6\ 10^{-2}$	Nd	0,72	68,5	1,0

Table 2 - Volatility (activity in mCi)



[redacted] [redacted] [redacted] [redacted]

Ingot CIO1 Ingot CIO2

[redacted] [redacted] [redacted] [redacted] [redacted]

Ingot CIO5 Ingot CIO6

Fig 1 : FBR PHENIX HULLS MELTED IN "CELL 73"
(FAUR INGOTS)

HOT ISOSTATIC PRESSING OR MELTING OF Pu-CONTAINING ASHES

Contractor:	CEA, CEN-Valrhô, SDHA (France)
Contract No:	FI1W-0015 F CD
Duration of Contract:	October 1986 - September 1989
Period Covered:	January 1988 - December 1988
Project Leader:	A. Jouan

A. OBJECTIVES AND SCOPE

The purpose of this study is 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 is being carried out jointly with industrial firms where isostatic presses are available. The final phase will compare the end products obtained by pressing with melted ash products.

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 facility.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Progress and Results

- 1987:

Several kilograms of ashes were produced and the steps comprising the isostatic pressing procedure were defined. Various isostatic pressing tests were carried out at laboratory scale to optimize the operating conditions and investigate the effects of fluxing additives.

- 1988:

B.2 Determination of Pressing Parameters at Laboratory Scale

The optimum conditions for obtaining satisfactory sintering and good container wall adhesion without significant container distortion were defined as 2 hours at 800°C under a pressure of 150 MPa.

The use of fluxing additives was definitively rejected because of container deformation, the necessary allowance for the ash composition, and the resulting technological complications.

B.3 Production of Intermediate Scale Blocks

Three containers 450 mm high and 150 mm in diameter were prepared from a mixture of α ashes, untreated and heat treated (resulting in a different carbon content) airborne domestic waste incineration ashes. The specific gravity of the final product was about 2.4. The three containers were cut up for determination of the physicochemical and mechanical properties (Photos 1 and 2).

Equipment suitable for filling a container 800 mm high and 300 mm in diameter has been built, and heat treated airborne ashes have been delivered. Pressing is scheduled for the beginning of January, 1989.

B.4 Fabrication of Melted Ashes

Raw airborne ashes from a domestic waste incineration facility were melted by direct induction heating in 350 mm and 550 mm diameter cold crucibles to obtain blocks weighing 60, 120 and 200 kg containing up to 66% ash material and a primary glass additive. The production rate was 20 $kg \cdot hr^{-1}$ with an induction current voltage of 10 kV at a frequency of 163 kHz.

B.5 Comparison of Principal Conditioning Processes

This investigation will compare cement grouting with the isostatic pressing or melting processes, and has been assigned to a specialized department of the CEA. Given the dimensions of the final waste packages compatible with storage requirements and ash production rates (less than 400 $g \cdot hr^{-1}$), all the processes require interim ash storage and are operational only a few days each year. The first results of this study will be presented at the Madrid meeting on April 20, 1989.

LIST OF PUBLICATIONS

The work conducted in 1988 was presented in Avignon on April 21, 1988 and at Sallugia on October 6, 1988.

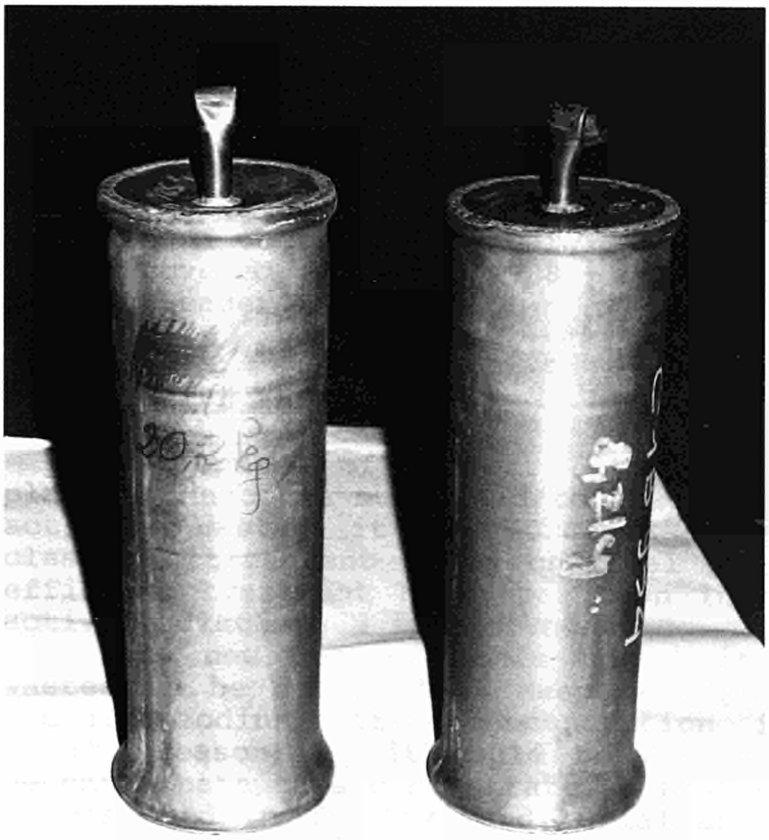


Photo 1

Two stainless steel containers 150 mm dia × 450 mm high after isostatic pressing for 2 hours at 800°C at 150 MPa

Photo 2

Cross section through a 150 mm dia container showing α ash content

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 1988 - December 1988
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 strontium 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 life-time of the S.L.M. and decrease the transfer of acidity through the S.L.M.

2.3. Extraction of cesium :

2.3.1. Synthesis of B21 C7 : for removal of cesium

2.3.2. Choice of the diluents able to dissolve substituted benzo crowns.

2.4. Laboratory scale experiments on hollow fibers modules.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Extraction of 98-99 % of actinides is obtained by using one S.L.M. constituted by the mixture CMPO (0.25 M) TBP (0.75 M) in decahydronaphtalene (Fig. 1)

Hexylbenzene is the most suitable diluent for S.L.M. impregnated with DC18 C6 because it is very sparingly soluble in water and transfers very low acidity (Fig.2).

The only crown ethers compound able to extract cesium from 4 M $NaNO_3$ solution are the benzo substituted crowns not available. B21 C7 was synthesized at the University of Strasbourg.

Tests were carried with plane membranes (Fig. 3) and hollow fibers modules (Fig. 4).

D. PROGRESS AND RESULTS

For some special fuels of graphite gas natural uranium reactor fuel, the clads must be chemically dissolved. The concentrate, according to the nature of the clads, results in three different compositions : MAR 400, MAR 400 (Al), MAR 400 (Mg).

Table I. Compositions of waste solutions.Molar concentrations

	MAR 400	MAR 400 Mg	MAR 400 Al
HNO_3	1 M	1 M	1 M
$NaNO_3$	3.8 M	3.4 M	3.5 M
$Mg(NO_3)_2$ 6 H_2O	0.078 M	0.62 M	
$Al(NO_3)_2$ 9 H_2O	-	-	0.41 M
$Ca(NO_3)_2$ 4 H_2O	0.03 M	0.015 M	0.015 M
$Fe(NO_3)_3$ 9 H_2O	0.015 M	0.0032 M	0.0032 M
NaCl	0.0032 M	0.012 M	0.012 M
NaF	0.076 M	0.017 M	0.017 M
Na_2O SiO_2 5 H_2O	0.023 M	0.001 M	0.001 M

Na_3PO_4	0.14 M	0.021 M	0.021 M
Na_2SO_4	0.165 M	0.021 M	0.021 M
NH_4NO_3	-	0.1 M	0.1 M
TBP	-	0.00056 M	0.00056 M

The présence of aluminium or magnesium does not modify the coefficients of distribution of uranium and plutonium but improves that of americium with CMPO and that of strontium with DC18 C6.

Table II. Distribution coefficients

	MAR 400	MAR 400 Al	MAR 400 Mg
$D_{UO}{}^{2+}$	400	500	550
$D_{Pu}{}^{4+}$	1000	1000	1000
$D_{Am}{}^{3+}$	14	35	55
$D_{Sr}{}^{2+}$	12	18	19

For the actinides extraction the compounds and the concentrations chosen by DANESI were used : mixture of CMPO (0.25 M) and TBP (0.75 M) diluted in decalin (decahydronaphtalene). With a stripping solution of sodium citrate 0.5 M actinides are transfered almost quantitatively (> 98 %).

A second membrane constituted by a long chain primary amine, transfers nitric acid but not the actinides from the first stripping solution to the second stripping solution (NaOH). The second membrane may enable less concentrated complexing to be used. But this double liquid membrane is difficult to utilize for the decontamination of concentrate : if the concentration of complexing agents is too low in the stripping solution a part of actinides extracted returns in the feed solution. If sodium citrate in the first stripping solution or soda concentration in the second stripping solution is to high, pH remains high in the first stripping solution , then precipitation occurs in some pores of the membrane leading to a decrease of transfer of ions through the membrane (Fig. 5).

Hexylbenzene is a good diluent for the dicyclohexano crown ether. Its very low solubility in water and its low volatility lead to an excellent stability of the membrane. Compared to the previously diluent used (decanol) hexylbenzene presents another advantage, it does not transfer acidity. To avoid formation of a third phase when hexylbenzene is in contact with the concentrate, an alcool or a phenol must be added. Nonylphenol is of interest in the obtention of a stable S.L.M. for several experiments carried out with a S.L.M. constituted of DC18 C6 diluted in the mixture hexylbenzene/nonylphenol the results are entirely satisfactory :

- high extraction of strontium (95 %);
- low transfer of acidity through the membrane;
- long life-time of the S.L.M.

B21 C7 only crown ether able to remove cesium from high sodium content concentrates, not commercialy available, was synthesized.

The synthesis, very tedious, is carried out in two steps, to obtain a satisfactory yield, the various reagents have to be previously purified.

First step : in pyridine medium, at ice bath temperature, tosylation of hexathyleneglycol :

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

The precipitate obtained is washed and deshydrated.

Second step : in aprotic solvent (acetonitrile), reaction of tosylation in presence of cesium (template effect):

$$TsO\ (CH_2OCH_2)_6\ Ts + OH - C_6H_4 - OH \qquad B21\ C7 + 2\ CsOTs$$

The final product is purified by chromatography over alumina.

The greatest part of the tests were carried out with polypropylene flat membranes from Celanese : CELGARD 2500. To obtain more important areas of membrane, hollow fibers modules have to be used.

Experiments carried out with different modules show that modules used for ultrafiltration are not suitable for S.L.M.:the glue used to tighten the UF modules are dissolved by the organic phase after some days of circulation of fluids.

<u>Publication</u> : JF. DOZOL - Use of liquid membranes for treatment of nuclear wastes. Symposium on Futural industrial prospects of membrane processes. Brussels, 6-7 décember 1988.

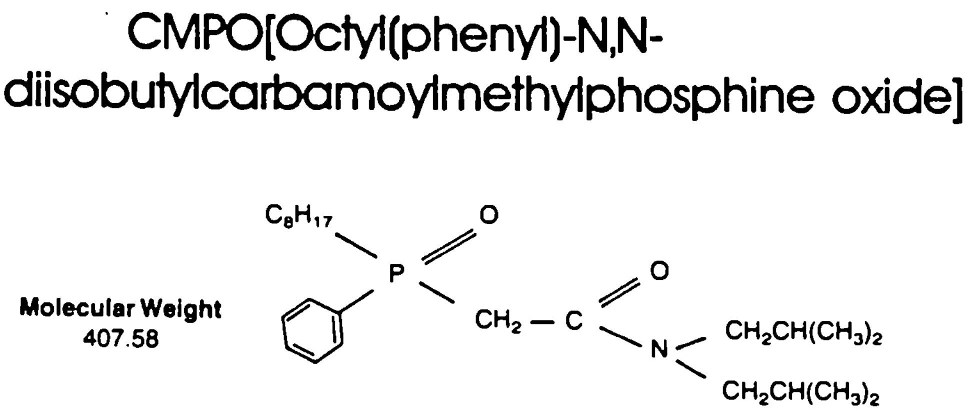


Figure 1 - CMPO

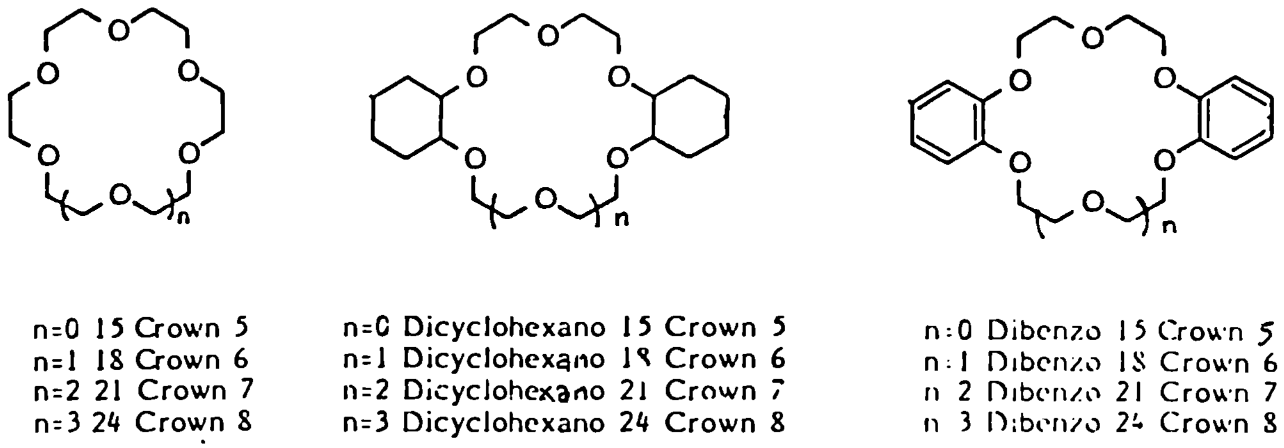


Figure 2 - Crown ethers

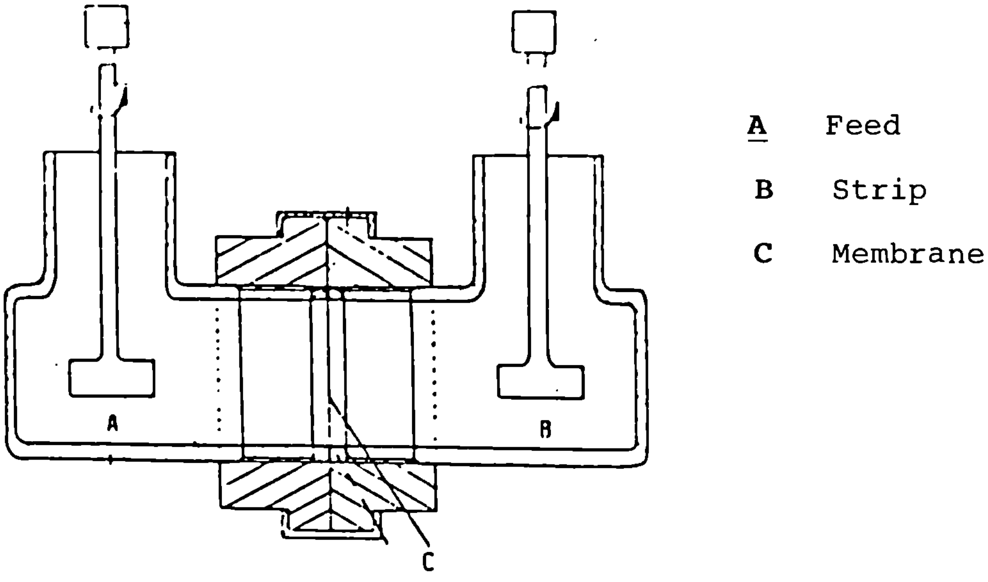


Figure 3 - Flat membrane modules

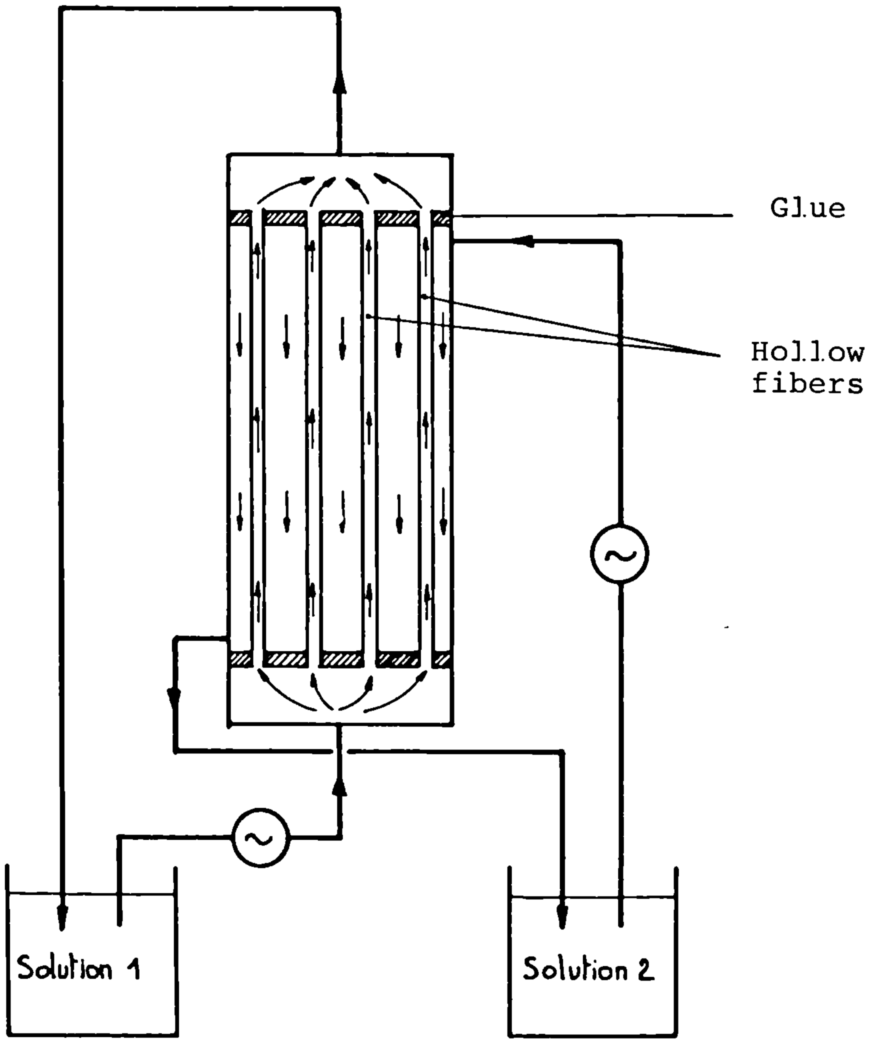


Figure 4 - Hollow fibers module

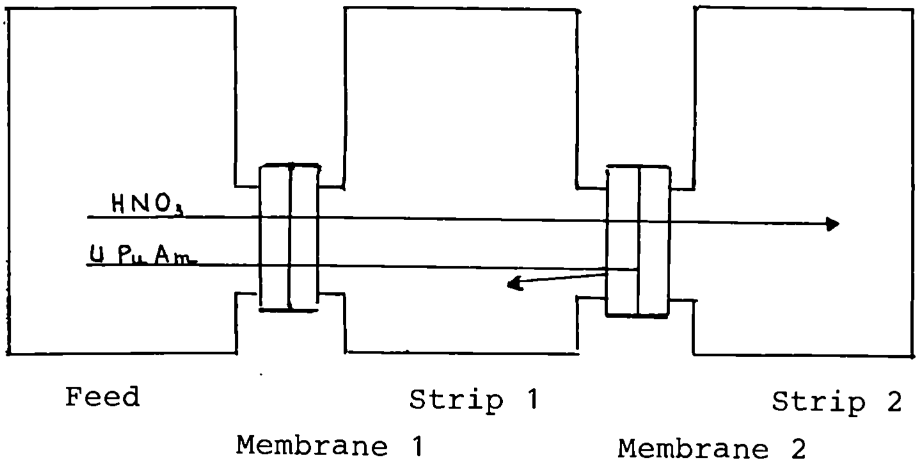


Figure 5 - Double membrane module

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

Contractor: UKAEA, HARWELL; U.K.
Contract No.:FI. 1W.0017 UK(H)
Duration of contract: July 1986-December 1989.
Project leaders: I W Cumming/A D Turner

A. OBJECTIVES AND SCOPE

The overall objective of this programme is to improve the design and operation of membrane plant for radioactive waste treatment by 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.

C. PROGRESS OF WORK AND OBTAINED RESULTS

STATE OF ADVANCEMENT

The most effective absorber for removal of βγ activity from Harwell low level waste (LLW) has been shown to be a combination of copper ferrocyanide and zirconium phosphate. Tests in pilot scale processing of Harwell LLW dosed with these two additives have given a consistently high Cs^{137} removal with, however, a variable Co^{60} removal. The pilot plant has now been modified to accept two direct membrane cleaned (DMC) modules one containing Tech Sep M4 membranes and the other a stainless steel fibre membrane. Inactive commissioning tests using the Tech Sep M4 membrane indicated that flux enhancement using DMC was similar to that achieved previously in small scale laboratory experiments.

Laboratory tests have been carried out treating two other wastes by crossflow filtration. One of the effluents was the Harwell medium level waste (MLW) and optimal α and βγ removal was achieved by dosing the waste with copper ferrocyanide and zirconium phosphate and then ultrafiltering at pH9. The other waste which arises at another UK nuclear site gave the highest removal by ultrafiltering at pH 9-10 after dosing with hydrous titania.

Accelerated life time tests on the effect of DMC on both Tech Sep M4 and stainless steel MAI membranes indicated that their performance was maintained for a period equivalent to more than five years operation. Studies have been carried out on the application of DMC to a number of different stainless steel membranes. These tests showed that fines rejection was maximised by operating the membrane with the wide pore side in contact with the waste stream. The operating conditions have been optimised to give maximum flux. The application of DMC has also been shown to be applicable to other mixtures of activity absorbers such as hydrous titania, zirconium phosphate, nickel ferocyanide and ferric hydroxide.

PROGRESS AND RESULTS

2.2 New precipitation Agents

Previously reported tests /1/ showed that βγ removal was maximised by dosing Harwell LLW with copper ferrocyanide and in-house prepared titanium phosphate (TiP) before ultrafiltering at pH4.5. Tests have now compared this form of TiP with a zirconium phosphate (ZrP) powder supplied by Magnesium Electron. This powder is free flowing with 95wt% of the material with 30-100 μm size range. Dosing the waste with ZrP at a concentration of 10g/m^3 gave a removal of 93% of Cs-137 and 81% Co^{60}. Combined dosing of ZrP and copper ferrocyanide at concentrations of 10 g/m^3 ZrP and 8 g/m^3 Fe(CN)$_6$ improved the removal to 99% Cs^{137} and 97% Co^{60}. These results indicated that the powdered form of ZrP was superior to the in-house TiP. Higher concentration of ZrP did not significantly improve the βγ removal.

Pilot plant tests have been carried out dosing Harwell LLW with copper ferrocyanide and ZrP. The plant was fitted with a 0.2μm alumina Membralox membrane operating at a crossflow velocity of 4.5m/s and a transmembrane pressure of 3 bar(g). Seven different batches of waste were processed at ~ pH5 whilst dosing with copper ferrocyanide and ZrP at concentrations of 20g/m^3 Fe(CN)$_6$ and 10g/m^3 ZrP. The results of these tests are given in Table I. The removal of Cs^{137} was consistently high whilst the Co^{60} removal was variable. This meant that averaging the results for six of the permeates gave a β content of ~ 50 mBq/mℓ. The seventh batch which had a high content of Co^{60} and also gave a poor Co^{60} removal brought this average value up to 115mBq/mℓ. Work is continuing to try and improve the Co^{60} removal.

Tests have been carried out on the treatment by ultrafiltration of Harwell medium level waste (MLW). The removal of α and βγ activity was found to be maximised by processing at ~ pH9. The use of copper ferrocyanide and ZrP has been compared with a conventional calcium phosphate /ferric hydroxide/ copper ferrocyanide floc treatment. A summary of the results of these tests are shown in Table II where the average results of tests on three different batches are presented. These results show that the α removal by U.F. is about ten times higher than floc treatment and the use of copper ferrocyanide or ZrP gives some improvement in βγ removal. The combined use of ZrP and copper ferrocyanide on one of the batches gave a small further improvement in βγ removal. To test the ultrafiltration process at more realistic conditions a minature active pilot plant has been consructed and commissioned. This unit can be used to concentrate MLW about 100 times.

A waste which arises at another UK nuclear site has been assessed for α removal by ultrafiltration. The best removal was achieved using hydrous titanium hydroxide at pH 9-10. The alpha removal being at least three times better than a calcium phosphate ferric floc treatment.

2.4 TESTS WITH ELECTRICALLY ASSISTED PROCESSES

Pilot scale modules

From laboratory scale tests on Harwell site LLW concentrated to 1% solids, the periodic electrolytic cleaning of Tech-Sep M4 membranes (ZrO_2 supported on carbon) maintained an enhanced permeability of 1 m/d/bar - even with the substantially reduced crossflow velocity of 1 m/s. This was achieved with cathodic pulses of 50 mA/cm^2 of only 1 s duration applied at 15 minute intervals. From analysis of the permeate, the α DF was unchanged from conventional crossflow filtration - with a residual level < 1.5 mBq/mℓ.

A pilot scale module based on this membrane has been fabricated and commissioned in the ultrafiltration pilot plant. It comprises three 1.2 m tubes of total area 680 cm^2 with axial platinized titanium wire anodes as shown in Figure 1. Due to a reduction in crossflow volumetric flow rate to 0.3 m^3/h, the recirculation pump also had to be changed to a Lowara type CK 70/5 centrifugal pump. The HP 6456B (100A/36V) power supply used to supply 11.3A/tube cleaning current at 20.5V is activated by the plant management computer. In order to maximize cleaning effectiveness, this is synchronized with the opening of the recirculation loop. The feed pump is inhibited 11 out of 12 pulses in order to permit concentration of the feed to 1-2% solids. The electrolytic gases produced during cleaning pass out in the dissolved state with the permeate. Subsequent degassing requires a 1ℓ/h air purge to dilute H_2 to below 2%. Inactive commissioning tests have demonstrated similar flux enhancements to those observed in the laboratory. Active trials, however, have been delayed due to a short circuit caused by an adventitous sliver of swarf remaining after manufacture.

While this unit is being repaired, a second module, based on a 3 µm sintered stainless steel fibre membrane (MAI) is being installed in the plant. This comprises three 60cm tubes of 18 mm diameter with a 10 mm central platinized titanium tube anode. Each membrane has a surface area of 340 cm^2 - giving a module area of 0.1 m^2. The power supply is able to deliver cleaning currents of up to 300 mA/cm^2 to each tube in turn. The electrical switchgear to accomplish this is currently being designed.

Membrane life under DMC

Accelerated tests have been carried out to assess the effeect of DMC on the life of both Tech Sep M4 and stainless steel MAI membranes in simulant feeds of 0.1M $NaNO_3$ at pH 10 and 10mM $NaNO_3$ at pH5. For the M4 ultrafilter, 50 mA/cm^2 was passed for 30 hours either continuously or as 1s pulses with 5s intervals. Weight loss, water permability and visual examinations were carried out. No significant changes attributable to the DMC could be detected - giving permeabilities in the range 0.05-0.08 m/h/bar and weight losses equivalent to 5 µg/cm^2/h current passed. These tests correspond to 5.6y of elapsed time, assuming four 1s cleaning pulses/hour for a 24 h/d, 200 day working year. As no signs of degradation could be detected, useful lives of beyond this may be possible, particularly as the reduction in crossflow velocity during filtration will minimise any erosive wear of the ZrO_2 filtration layer. The equivalent experiments with the 316L stainless steel MAI/SS membrane used a current density of 150 mA/cm^2 also for 30 hours - both continuously and as 5s pulses with 20s intervals. In the DMC tests, a 1.4% weight loss was detected, though on microscopic examination, little corrosion of the fine fibres was apparent. With the pulsed current, two tests were carried out - one where the membrane was allowed to float on open circuit after the DMC pulse, and a second where the membrane was electrically repassivated. The corresponding weight losses were 3.6% and 0.9%. The 30h passage of current corresponds to 1.1 year of elapsed time for four 5s pulses/hour. On the basis of the repassivated system results and SEM examination of the membrane, lifetimes in excess of 10 years are anticipated.

New membrane examination

A series of sintered stainless steel fibre membranes have been examined for their filtration and DMC characteristics. These included MAI, MAI/S, MAI/SS (3 µm absolute) and FM5, FM5/S (2 µm absolute). These have an asymmetric structure produced by fine fibre in-filling on one side. The membranes with an 'S' postscript have a coarse mesh embedded in the surface.

After SEM examination, filtration trials were carried out using a 100 ppm $Fe(OH)_3$ dispersion in 0.05M $NaNO_3$ at pH 10. The main conclusion of these tests is that in order to maximise fines rejection, the wide pore side of the membrane should be in contact with the waste stream. The effectiveness of DMC was optimized under conditions were the electrolytic bubbles were able to grow under the fouling layer thus removing it from the surface. To prevent bubbles escaping into the permeate, the transmembrane pressure should be reduced essentially to zero during DMC pulse application. Higher current densities leading to more rapid bubble growth were also more effective. These factors are of particular relevance at high solids contents in the feed (~ 5%).

A series of optimization tests demonstrated that 5s was the maximum pulse duration required for cleaning, and that depending on the nature of the fouling solid, current densities in the range 100-300 mA/cm^2 were satisfactory.

Seeded microfiltration

Mixtures of hydrous titania, zirconium phosphate, nickel ferrocyanide and $Fe(OH)_3$ have been filtered at a 3 µm membrane. At 200 ppm total solids, permeabilities of > 0.5 m/h/bar were determined, giving a permeate turbidity of only 0.11 NTU. DMC was able to maintain filtration performance up to 5.5% solids, although due to the increasing solids content the permeability had fallen to 0.08 m/hbar by this stage. The flux was approximately half that measured for $Fe(OH)_3$ alone at an equivalent solids content due to the incorporation of the finer nickel ferrocyanide precipitate.

References

1. Cumming I W, Turner A D, Holdroyd S D, Junkison A R, Davison C G and Kavanagh P. 'Treatment of radioactive wastes by a combination of precipitation and crossflow membrane filtration - Annual report for 1987'. AERE-G4576.
2. Turner A D, Junkison A R and Bridger N J. 'Electrical processes for liquid waste treatment IAEA-SM-303/20'. Symposium on Management of Low and Intermediate Level Radioactive Wastes (Stockholm, 16-20 May 1985).
3. Cumming I W and Turner A D. 'Recent developments in testing new membrane systems at AERE Harwell for nuclear applications'. Symposium on Future Industrial Prospects of Membrane Processes (Brussels, 6-7 December 1988).
4. Cumming I W and Turner A D. 'Optimization of an UF pilot plant for the treatment of radioactive waste'. Symposium on Future Industrial Prospects of Membrane Processes (Brussels, 6-7 December 1988).

TABLE I: PILOT PLANT TRIALS OF
$\beta\gamma$ REMOVAL FROM HARWELL LLW

Batch No.	Copper Ferrocyanide g/m^3 $Fe(CN)_6$	ZrP g/m^3	Present Removal		
			β	Cs^{137}	Co^{60}
1	-	10	83	95	65
1	20	-	83	99	76
2	20	10	65	99	80
3	20	10	70	97	49
4	20	10	49	> 96	67
5	20	10	68	99	32
6	20	10	76	99	60
8	20	10	20	> 88	25

Processing at ~ pH 5

TABLE II : LABORATORY TESTS TREATING
HARWELL MLW

pH	Treatment	Permeate activity Bq/mℓ	
		α	β
9	U.F.	0.3	39
9	U.F. - dosing with copper ferrocyanide at $10g/m^3$ $Fe(CN)_6$	0.23	8.4
9	U.F. - dosing with $10g/m^3$ ZrP	0.48	10.4
9.5	Calcium phosphate/ferric hydroxide/copper ferrocyanide floc	4.7	11.1

Average data from three different waste batches.

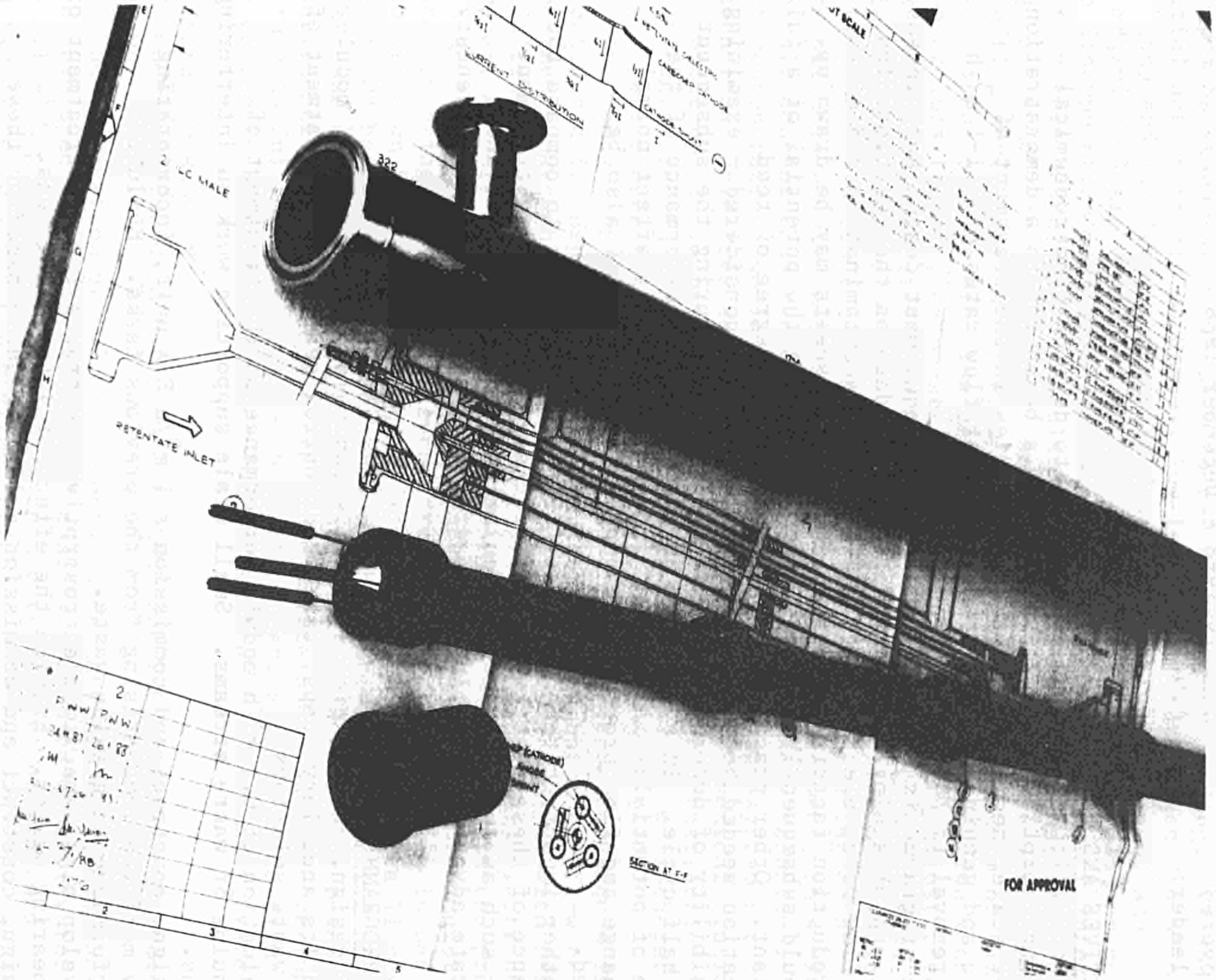


Figure 1 Tech Sep M4 membrane with direct membrane cleaning system fitted.

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 1988 - December 1988
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 $\beta\gamma$ 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 $\beta\gamma$ waste solutions.

2.3 Evaluation of 0.1 m^3/h module performance on the treatment of genuine $\beta\gamma$ 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 /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 wastes. Evaluate performance on genuine waste.

C. PROGRESS OF WORK AND OBTAINED RESULTS

SUMMARY

After successful manufacture, full scale 0.2 m^2 zirconium phosphate (ZrP) EIX electrodes have been incorporated into the 0.1 m^3/h pilot plant situated in the Harwell effluent treatment centre. During a detailed inactive commissioning programme, Cs DFs of > 5000 were obtained from a 100 ppm Na stream at > 5.5 BV/h to beyond 8% cation loading. Although initial active trials on Harwell low level waste have given DFs of only 1.7 (Co) and 1.3 (Cs), the residual activity of 22 mBq/mℓ (Co) and 11 mBq/mℓ (Cs) are considerably less than with the normal floc process. The disappointing performance is attributed to the presence of interfering ions in this batch - in particular an unusually high concentration of Na_2SO_4 - which led to a significant fall in pH and a consequent decline in efficiency. Small scale work has confirmed that this form of EIX is best suited to feeds with low cation content (< 10 mM) and with weak acid counter ions (borate, carbonate). This has been recently illustrated with PWR waste simulants giving Co DFs ≥ 300 in a 1-5 ℓ/h bench top flow cell. This will be compared with active tests on genuine wastes at Tihange, Belgium early in 1989. A modified form of EIX incorporating anion absorption is able to maintain the feed pH during treatment, thus extending the salt content that can be effectively treated by this technique. High salt concentrations would require a hybrid ion-exchange system for conventional selective absorption, followed by electrochemical elution.

Scale-up of EIX has continued with the design and construction of a fully engineered multi-modular cell. This 5 module unit will therefore give a performance representative of a much larger plant.

The removal of α activity by three electrosorptive techniques is being investigated in comparative glove box tests. Both batch and flow cell experiments have shown removal of Pu and Am to below 1 Bq/mℓ with DFs of 23-75 from dilute acid streams at a zirconium phosphate EIX electrode. However, as this technique has been shown to be unsuitable in the presence of high salt contents, the hybrid IX absorption/electrochemical elution system is being evaluated for such streams. The third system is based on adsorption on HTiO grown as a thin film on a high surface area Ti mesh. Kds of 10^4 have been determined from batch experiments - similar to the bulk phase obtained from Ti(IV) salt hydrolysis. On polarity reversal, quantititative recovery is achieved into dilute HNO_3, thus recovering the Pu in a useful form. Several methods of preparing thick oxide film layers are currently being investigated for evaluation in a flow cell system.

PROGRESS AND RESULTS

2.2 COMMISSIONING OF A 0.1 m^3/h EIX PLANT FOR THE TREATMENT OF βγ WASTE STREAMS

The fabrication of 0.2 m^2 zirconium phosphate EIX electrodes has been developed to a high standard of quality and reproducibility for use in the 0.1 m^3/h pilot plant. This has been extensively commissioned inactively to define the preferred variables of flow rate, current density and electrochemical mode of operation prior to fully active trials. Inactive demonstration of every aspect of operation and potential malfunction was also required under new safety regulations before the plant could be operated actively. Several modifications were found necessary to minimize any airborne contamination and also in the handling of the more active concentrate eluant. Work on the selective performance of ZrP EIX at both pilot and bench-top scales has demonstrated that with higher cation content feeds (> 4 mM), the polarity switching selectivity enhancement technique is not able to offer the performance required in an economically sized plant. However, exceptional Cs decontamination results have been obtained in the desalting mode from a 100 ppm Na stream - with DFs > 5000 at flow rates > 5.5 BV/h to beyond 8% cation loadings (Figure 1). Elution on polarity reversal has been demonstrated to give VRFs $\gg 100$.

2.3 TREATMENT OF GENUINE WASTES IN THE 0.1 m^3/h EIX PLANT

The first genuine active waste runs have now been conducted in the pilot plant using Harwell site low level liquid waste. In this particular batch, Co (37 mBq/mℓ) and Cs (14 mBq/mℓ) were the principle radionuclides - somewhat lower than the average levels of 94 mBq/mℓ Cs and 125 mBq/mℓ Co. Even so, initial results of performance were somewhat disappointing - with DFs of 1.7 (Co) and 1.3 (Cs) - although discharge levels were considerably less than the normal floc process. This is thought to be due not only to the low initial activity of the feed but also to the unusually high inactive salt content of this particular batch of feed (> 12 mM Na_2SO_4). Not only is the absorption of more ionic material required to give a high DF, but the corresponding fall in pH also reduces process efficiency.

Small scale supporting work on the effect of interfering ions has shown that Ca (60 ppm) and Mg (4 ppm) present in local hard water can be absorbed satisfactorily to $> 90\%$ in addition to Na and Cs. However, while the elements with soluble hydroxides can be successfully eluted at pH > 7 (Na,Cs,Ca), Mg required an eluant of pH 2-3 for successful desorption. Transition metal elements (Co,Fe,Ni) have shown similar trends of behaviour. The effect of the nature of anions present has also been investigated. Weak acid anions are able to buffer the feed pH during treatment, thus preventing a large fall in pH and hence a significant drop in process efficiency, which also influences the effectiveness of the overall process. Strong acid anions (eg sulphate, nitrate) at large concentrations, on the other hand, can lead to a degradation in effectiveness. This explains the poor active feed results. While normal waste compositions with a low Na_2SO_4 concentration should be treated more successfully, the existing system could be modified by the inclusion of an anion absorption EIX electrode to maintain the feed pH during treatment - thus enabling these exceptional wastes to be treated as well.

PWR low level waste simulants (1000 ppm B, 1 ppm Li) have been successfully treated in a bench-top flow cell (1-5 ℓ/h) - demonstrating Co DFs $\geqslant 300$. This is in preparation for active tests to be carried out on the LLW stream from the Tihange PWR in Belgium during March 1989.

2.4 SCALE-UP OF $\beta\gamma$ EIX PILOT PLANT TO 1m^3/h

A novel multi-modular EIX flow cell has been designed and constructed after evaluation of the concept at a laboratory scale (480 cm^2 electrode area/module). The large plant is based on the parallel use of 0.4 m^2 modules, similar to those used in the 0.1 m^3/h plant (Figure 2). A 5 module system will therefore represent the performance expected of a moderate sized plant. The ancillary plant equipment has been procured and assembly is currently in progress.

2.5, 2.6 ELECTROSORPTIVE TREATMENT OF α WASTES

Three approaches for the electrically enhanced treatment of α containing waste streams have been investigated. Conventional EIX based on ZrP has been successfully demonstrated on the removal of Pu from low salt streams. Batch experiments at pH 3.7 gave a DF of 8.5 after 4 hours treatment, leaving only 0.6 Bq/mℓ. Subsequent flow cell experiments at 1 BV/h (0.2 ℓ/h) gave a mean α DF of 23 from a pH 3.4 feed (116 Bq/mℓ), with an Am DF of 74. A pH 4.5 feed (9 Bq/mℓ) was reduced to 1 Bq/mℓ at 1 BV/h. These experiments are continuing over a range of pHs, flow rate and current densities in a flow cell identical to the one used for small scale βγ trials in order to simplify an intercomparison of results. However, the effectiveness of the system was greatly reduced in 0.1M NH_4NO_3 due to the 10^6 molar excess of NH_4^+ swamping any selectivity effects. A hybrid system relying on selective absorption by conventional ion-exchange and electrochemical elution is being investigated to circumvent this problem. Preliminary experiments have confirmed that zirconium phosphate, known to be controllable by EIX, has a Kd for Pu and Am of $\sim 10^4$ - in line with literature values.

The third system being investigated uses absorption on high surface area oxide films grown on an extended surface area titanium electrode. Batch experiments confirmed this material to have a Kd of $\sim 10^4$ - similar to that reported for HTiO, with rapid absorption kinetics (first order in Pu concentration). On polarity reversal, quantitiative Pu recovery into 1M HNO_3 was observed. While simple anodization at 17V gave only a thin oxide film, three methods have been investigated for thicker film growth - including potential cycling between 0-20V in 0.1M HNO_3, anodizing in Ti(III) solution and thermal oxidation at 750°C. These are currently being assessed under batch conditions prior to evaluation in a flow cell identical to that used for ZrP.

List of Publications

/1/ TURNER, A.D., BRIDGER, N.J. and JUNKISON, A.R., Electrochemical ion-exchange for medium active liquid waste treatment - Annual Progress Report 1987, AERE-G4533.

/2/ TURNER, A.D., JUNKISON, A.R. and BRIDGER, N.J., Electrical processes for liquid waste treatment - IAEA-SM-303/20. International Symposium on Management of Low and Intermediate Level Radioactive Wastes (Stockholm, 16-20 May 1988).

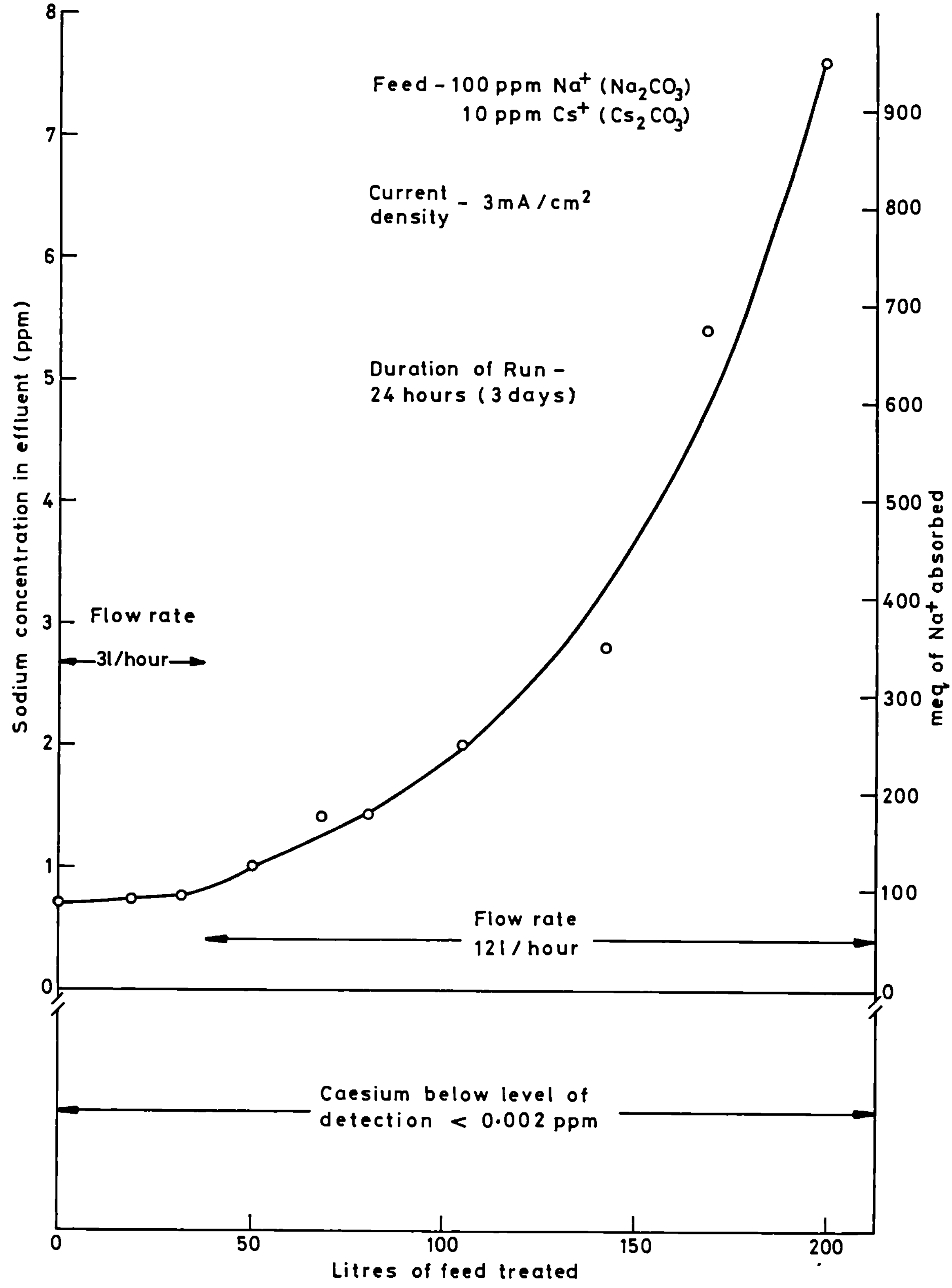


Figure 1 Cs decontamination during a desalting run on a Na containing simulant feed in the FC/6/Sim flow cell.

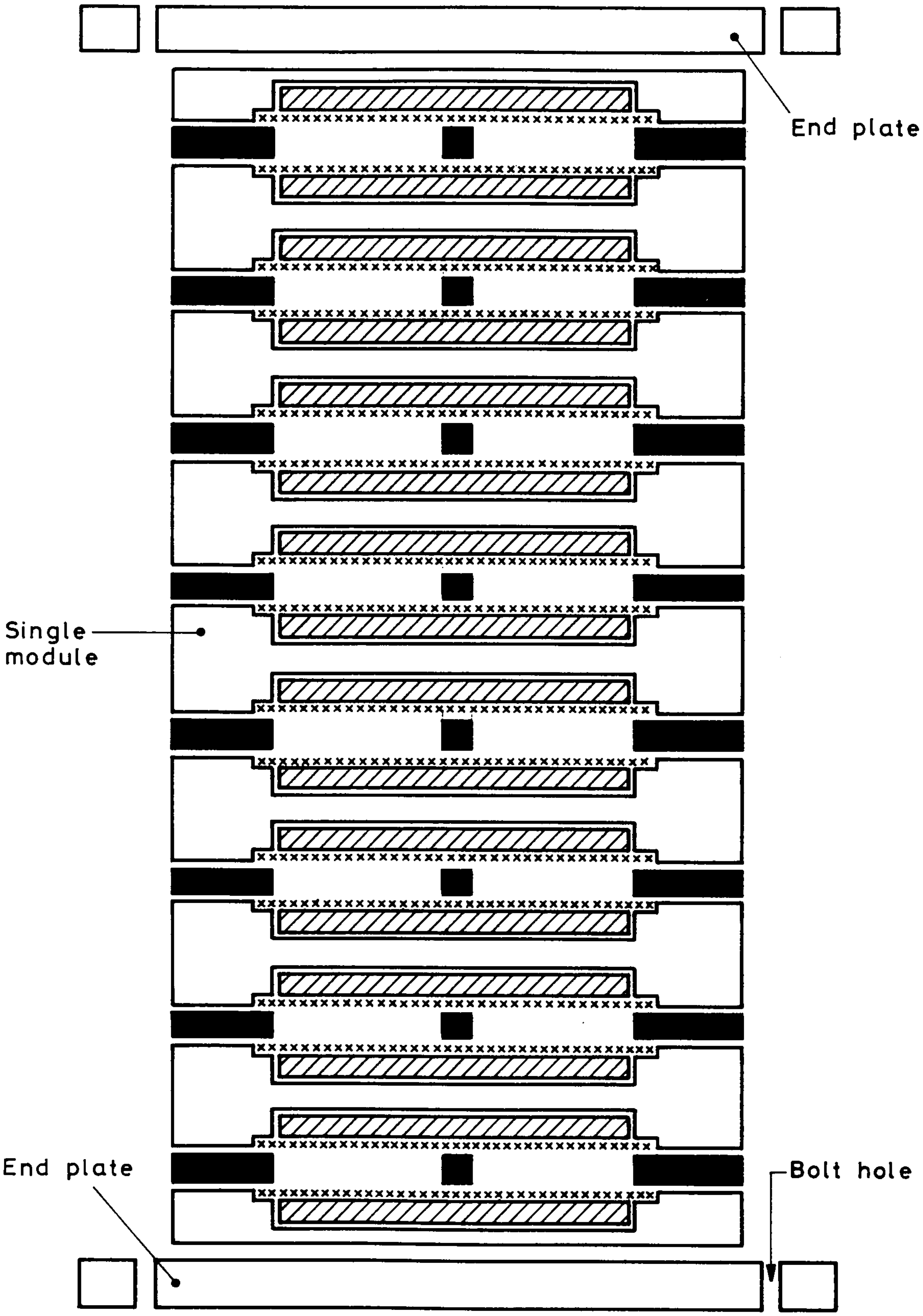


Figure 2 Multi-module EIX flow cell for a scaled-up plant.

IMMOBILISATION OF CLADDING WASTE BY PRESS COMPACTION AND CONDITIONING FOR FINAL DISPOSAL BY ENCAPSULATION IN A LEAD CONTAINMENT

Contractor : S.C.K./C.E.N., Mol, Belgium
Contract No. : FI1W-0019-B
Duration of contract : May 1986 - December 1989
Period covered : January 1988 - December 1988
Project Leader : L. Geens

A. OBJECTIVES AND SCOPE

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

The main aims of the actual project are :

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

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

B. WORK PROGRAMME

2.1. Further development of press compaction technology under inactive conditions.
2.2. Equipment of a hot cell facility for press compaction and conditioning of radioactive cladding hulls.
2.3. Transport of representative cladding waste and compaction products.
2.4. Press compaction of radioactive hulls.
2.5. Conditioning of compacted radioactive hulls in a corrosion resistant containment.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The equipment of the hot cell facility for the active demonstration of the compaction-encapsulation technology has been continued. The construction of the cell has been finished. The alpha-box was installed and all the concrete shielding has been mounted. The box was connected to the different passages for peripheral equipment and to the control room. All the in-cell equipment has been installed, the major parts being the positioning frame of the gamma scanner, the compaction press, the welding apparatus and the jib-arm. The cell has been closed and connected to the ventilation system.

A lot of attention has been paid to the development of and cold tests with the in-cell equipment. The gamma scanning apparatus has been tested under simulated conditions, which resulted in the definition of a reference radioisotopes solution for calibration and absorption measurements. Procedures have been drawn up for the in-cell press compaction and for the welding of the containers. The jib arm is controlled manually, via a personal computer. The necessary soft ware for in-cell control has been developed. Cold tests in the cell have been performed, which revealed the necessity of development of new tools for remote operation.

The radioactive hulls for the active demonstration will be obtained from the WAK. A rather complex transportation scheme has been drafted. The hulls will be transported from WAK to KfK, where they will get a double packaging for transport to S.C.K./C.E.N. At S.C.K./C.E.N. the hulls will be received in the water pool of the BR2 reactor. Via the BR2 hot cell the hulls can then be transferred to the hulls processing cell.

Progress and results

1. Equipment of a hot cell facility for press compaction and conditioning of radioactive cladding hulls (2.2.)

For the active demonstration of the hulls conditioning technology, a hot cell facility has been equipped. The stainless steel alpha-tight box was installed and the 1 m thick concrete shielding was mounted. All connections with windows, doors, passages and other peripheral equipment have been made. The necessary ventilation equipment has been constructed and installed. Two transfer systems for active materials have been provided. The in-cell equipment has also been installed : the feeding tray for portioning of the hulls, the positioning device of the gamma scanner, the compaction press, the welding apparatus, the vacuum container for the He leak test and the jib-arm, as lifting device. The cell has been closed and connected to the ventilation system. The ventilation system itself is being tested now.

The further development of the cell equipment has been continued inside and outside the cell. The gamma scanning apparatus has been tested in a mock-up under simulated cell conditions. These measurements resulted in the definition of a reference solution of various radioisotopes, which is necessary for the calibration of this apparatus and particularly for absorption measurements.

The jib arm is controlled manually, via a personal computer. A programme has been developed, which translates the operator's commands to the power control unit of the electrical motors for the mechanical movements. Additionally, the PC checks if there are no incompatibilities between the operator's command and the spatial restrictions in the cell. The hook coordinates are displayed and the position of the arm is graphically visualized on the PC screen.

A new semi-automatic TIG welding apparatus has been purchased. Tests showed that modifications were necessary for remote operation and maintenance in the cell. An experimental programme was carried out to determine the optimal welding parameters : torch diameter, torch distance, rotation speed, torch oscillation frequency and amplitude. These parameters are different for the three types of containers to be welded.

After installation of the equipment in the cell, a series of cold tests with the different units has been performed. As a result, certain operation parameters had to be modified. Furthermore, new procedures for in-cell operation have been drafted. These cold experiments also revealed the necessity of development of new tools for remote operation and maintenance of the units.

2. Transport of representative cladding waste and compaction product (2.3.)

The radioactive cladding waste for the active demonstration will be obtained from the WAK in Karlsruhe. The incompatibility between the shipping and handling facilities in Karlsruhe and the reception and handling systems in Mol have necessitated the drafting of a complex transportation scheme. The following steps are foreseen :

- loading of the hulls in 5 dm^3 primary containers and stacking of 6 primary containers in a 125 dm^3 drum at WAK;
- packaging of 125 dm^3 drum and transport to KfK;
- reception of 125 dm^3 drum at KfK/HDB and packaging of 3 primary containers in a DD-container;
- packaging of 6 DD-containers in a transport container and transport to S.C.K./C.E.N.;
- under water reception of the transport container at the BR2 reactor;
- transfer of the DD-containers to the BR2 hot cell and emptying of the DD-containers;
- packaging of the primary boxes and transport to the hulls processing cell;
- reception of the primary containers in the hulls processing cell.

LIST OF PUBLICATIONS

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- Semestrial Report July-December 1988.

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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 1988 - December 1988
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 reprocessing plant (WAK) is analogous to the WAK process with the difference that the wastes are embedded into concrete in 330 l insert drums and packaged into 400 l barrels.

A drawback of this method is that a relatively 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

2.3.6 Conceptual design of a press facility for active H+S waste compacting

From a number of realistic press concepts three favourable concepts were selected. Basis of these concepts was a design study awarded to NUKEM /1/. The criteria of selection were the minimization of the dimensions, weight, loadings of individual components, and contaminated press surfaces. Another decisive criterion was the lowest possible expenditure in terms of remote handling in maintenance work.

Figure 1 and 2 show favourable concepts for situations in which a ready-planned or already existing hot cell is to be retrofitted with a hull press. The particular advantage of the horizontal variant is the free access from top during all remote maintenance procedures. Moreover, the design principle of the dual cylinder press implies lower weights of the individual parts as compared to the single cylinder presses.

For cases where hot cell planning can still be influenced, Fig. 3 shows the more favourable concept compared to that in Fig. 1. The press cylinder is installed outside the hot cell and the piston sealing is provided by bellows. Consequently, the contaminable surface is smaller. The staff has direct access to carry out maintenance work on the piston cylinder unit.

The calculation of dimensions of these designated presses is based upon an axial compaction pressure of 200 MPa. It is an optimal compaction pressure. Higher pressures cause expensive equipment which reduce the cost savings resulting from the smaller waste volume. Lower compaction pressures effect that the density distribution in the compact is not uniform enough.

LIST OF PUBLICATIONS

/1/ H. Frotscher, KfK:
Presentation at the progress meeting of working group No 2
on October 4-7, 1988 in Saluggia (I)

Fig. 1: UPRIGHT SINGLE-CYLINDER PRESS

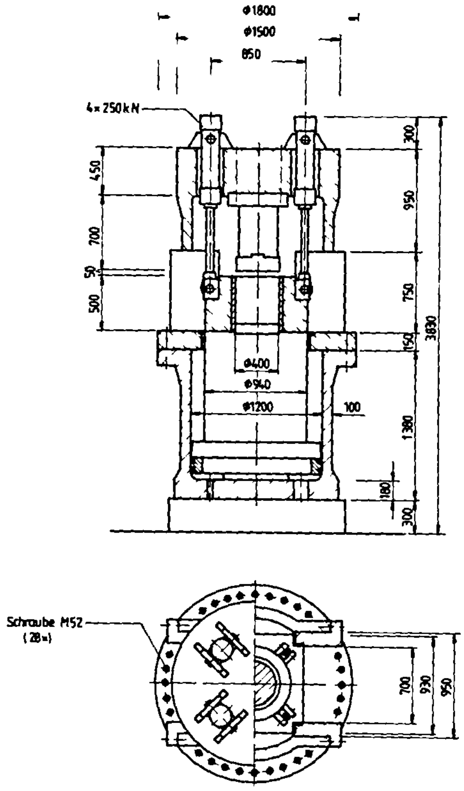


Fig. 2: HORIZONTAL DUAL-CYLINDER PRESS

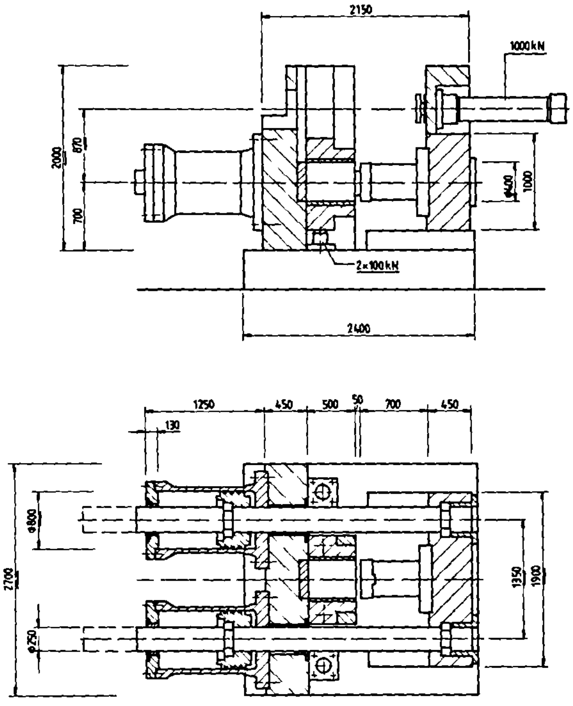
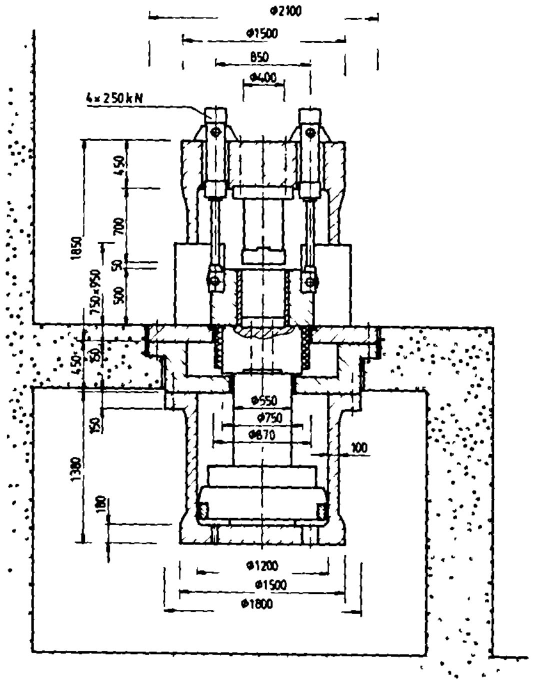


Fig. 3: UPRIGHT SINGLE-CYLINDER PRESS WITH BELLOWS



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 1988 - December 1988
Project Leader	: A. Loida

A. OBJECTIVES AND SCOPE

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

This way of TRU-waste immobilization has been demonstrated using all kinds of original TRU-waste known until now on lab-scale. The leach rate for actinides is less than 10^{-7}g/cm²d in water and salt brines at room temperature, the average open porosity < 5 vol%, the compressive strength > 50 N/mm².

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 items during the year 1988 were the preparation, respectively the characterization of very high TRU-waste loaded alumosilicate-based ceramics KAB 78 containing

- TRU ashes from the dry incineration of burnable waste,
- TRU slurries, precipitated from original solutions of the acid digestion process,
- TRU-slurries from simulated filtrate solutions, generated in the frame of the fuel elements fabrication.

X-ray powder diffractometry, optical light microscopy and scanning electron microscopy were the mostly applied investigation methods.

Progress and results

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

The product characterization of the ceramic specimen series loaded with TRU-ashes (20-60 wt%) have been completed by microstructure investigations, as well als leaching tests.
By means of image analysis the size, distribution and shape of the closed porosity have been determined to be more or less independent from the waste loading degree.
The sample characterizations, performed by scanning electron microscopy yielded the distribution of the elements Al, Si, Ca, Na, Ti, Te, Pu which was found to be according with the phase composition, obtained by X-ray-diffractometry. Additionally the formation of a plutonium zirkonolite ($CaPuTi_2O_7$) has been detected.
Leaching tests according to the ISO-draft using Q-brine as leachant yielded plutonium leachrates around 5 E - 7 g/cm²d after 74 days of total leaching time with a tendency to lower values.

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

Ceramization experiments using slurries, precipitated from waste solutions from the acid digestion process have been successful. A specimen series of ceramics KAB 78 loaded with 20-50 wt% of waste could be produced by mixing the washed and dried precipitates in the required ratio with the ceramic raw material KAB 78, formed by cold pressing and sintering at T_{max} 1350°C with 30 minutes holding time.
The average density of these pellets is about 2.85 g/cm³, their compressive strength varies from 263-123 N/mm² and the open porosity has been determined in the range from 1.1-11.8 Vol%. Leaching tests and ceramographic investigations are under preparation.
The ceramographic investigations of the KAB 78 ceramic products loaded with 20, 30, 40 and 50 wt% of TRU-slurries, precipitated from original solutions of the acid digestion process, have been performed by using X-ray diffractometry, optical light- and scanning electron microscopy and half automatically working image analysis. Due to the chemical composition of these specimen, the phase composition of these series were determined by means of X-ray diffraction to be corundum (Al_2O_3), spinel ($Zn(Fe^{3+},Al)_2O_4$) and a possible glass phase. By means of image analysis

it was found that the amount, the size and the shape of the closed porosity could be almost independent from the waste loading degree.
The microstructure of these ceramics consists of a very fine grained matrix (< 1 µm), where mainly the elements Al, Si and much less iron, zinc and calcium are present and inclusions (Ø up to 250 µm), where iron and zinc are the elements with the highest degree of enrichment and the aluminium-silicon-concentrations were significantly decreased. These results agreed with those of the X-ray diffraction investigations.

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

Preliminary experiments concerning the ceramization of TRU-slurries precipitated from filtrate solutions originated during the fabrication of MOX-fuel elements have been performed using a 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 3.11(5) to 3.80(5) g/cm^3,
- open porosities increase from 3.8(1) to about 10.0(2) Vol%,
- compressive strenght decrease from 533(20) to 138(19) N/mm^2.

The preparations of ceramization experiments using active simulated solutions from the MOX-fuel element fabrication have been completed.

TREATMENT OF REPROCESSING CONCENTRATE BY EXTRACTION CHROMATOGRAPHY AND INORGANIC ION EXCHANGE

Contractor: Kernforschungszentrum Karlsruhe, 7500 Karlsruhe, F.R.G.
Contract No.: F1IW-0022 D
Duration of Contract: July 1986 - June 1989
Period covered: January 1988 - December 1988
Project leader: W. Faubel

A. OBJECTIVES AND SCOPE

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

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

Therefore the main objective of this contract is to assess the performances of these alternative treatment processes for decontamination of reprocessing concentrate. 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 Inactive 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)
2.8 Joint intercomparison exercises
2.8.1 Marcoule reprocessing concentrate and simulants treatment
2.8.2 Liquid alpha waste treatment from ENEA-Casaccia

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 not possible for Sb and Ru due to chemical reasons. Therefore larger experiments in a 20 l scale with genuine ILWC were required to do.

In this year scaling up experiments have been performed in 20 and 100 l scales with simulated MAW in a pilot plant.

Furthermore, active experiments in a 20 l scale were done in a hot cell for the filtration step on glasswool, the absorption of organics on the Bio Beads SM 7 and the removal of cesium using ammonium molybdato phosphate.

The general work programme status is as follows:

2.2, 2.3, 2.4	are completed.
2.5	is in progress and will be completed in February 1989.
2.6, 2.7, 2.8	are processing normally.

Progress and results

Experiments in 20 - 100 l scale (2.2, 2.3, 2.4, 2.5)

First of all the hydraulic behaviours of the columns were tested by increasing the volumes pumped through the columns, constructed for the 1 l scale, up to 100 l 1 M HNO_3.

The best results for the suspended bed column has been reached for a ratio of the length / diameter of 7.5 / 1 and a throughput of 10 column volumes. Also the filters (solid/organics), the CMPO and the DMG columns could be handled in the same manner as earlier described for the 1 l scale, only by enlarging the volumes pumped through.

The metal oxide columns (Sb_2/MnO_2) need higher hydraulic pressures (up to 3 bar) and, as mentioned earlier, that is not a disadvantage because of the slow kinetics of exchanger materials (throughput: 0.6 l/h).

As next 20 - 100 l experiments with simulated ILW solutions have been performed. Up to 97 l of a representative simulated MAW solution, traced with Ce-141, Co-58, Cs-134, Eu-152 and Sb-125, were treated in three steps:

1. The solids/organics have been removed on glasswool/SM 7, whereas the cesium has been separated with AMP-1 employing the "suspended bed" column.
2. Molybdenum and antimony have been retained on metal oxides.

3. Actinides/lanthanides with the valence state 3+ and cobalt have been separated by using columns filled with CMPO and DMG, respectively.

Furthermore, experiments with genuine concentrated MAWC have been started in a 20 l scale. The concentrate was produced by reprocessing of a spent fuel element of the Light Water Reactor power plant Neckarwestheim (GKN) by the German reprocessing plant WAK in Karlsruhe. The burn up was 32,700 MWd/t and the cooling time 3 year.

A total amount of 20 l MAWC has been passed through glasswool/SM 7 and the "suspended bed" columns with the result that the waste was cleaned up from solids/organics and that 99.97 % of the cesium have been removed (table I).

Table I: γ-Activities of ILWC before and after treatment

Nuclide	Half life	γ-activities of ILWC Bq/l		
		genuine	after treatment with	
			SM 7	AMP-1
Am-241	432.6 a	7.8×10^{7}	7.0×10^{7}	5.8×10^{7}
Ce-144	284.8 d	2.3×10^{8}	1.4×10^{8}	1.0×10^{8}
Co-60	5.3 a	5.3×10^{6}	2.6×10^{6}	2.6×10^{6}
Cs-134	2.1 a	8.6×10^{8}	8.6×10^{6}	1.3×10^{5}
Cs-137	30.7 a	3.4×10^{9}	3.4×10^{9}	9.2×10^{5}
Eu-154	8.8 a	1.9×10^{7}	1.8×10^{7}	1.1×10^{7}
Eu-155	5.0 a	2.0×10^{7}	1.9×10^{7}	6.8×10^{6}
Ru-106	368.0 d	3.9×10^{9}	2.7×10^{9}	1.8×10^{9}
Sb-125	2.8 a	1.4×10^{9}	1.4×10^{9}	1.2×10^{9}

List of publications

/1/ W. Faubel, P.-M. Menzler, Sameh A. Ali, Int. Symp. Manag. Low- and Intermediate Level Wastes, Stockholm, IAEA-SM-303/13 (1988).

/2/ W. Faubel, R.-M. Menzler, Sameh A. Ali, Report KfK-4476, p. 409 - 422 (1988).

/3/ W. Faubel, P.-M. Menzler, Sameh A. Ali, 2nd Int. Conf. Nucl. Radiochemistry, July 11 - 15 (1988), Brighton/UK.

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

Contractor: KFA, Jülich, Federal Republic of Germany
Contract No.: FI1W/0139
Duration of contract: September 1987 - December 1989
Period covered: January 1988 - December 1988
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 cementitious 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. Particulary the narute 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

2.3.2.1 The experiments concerning the performance and lifetime using an electrolyser operating with a Solid Polymer Electrolyte (SPE) were continued and finished.

2.3.2.2 Comparative studies were carried out with a TELEDYNE hydrogen generator model HG 501 operating with 35 % KOH as the electrolyte solution.

2.4.1 The experimental equipment of the tritium laboratory for handling up to 185 TBq (5000 Ci) of tritium has been completed.

2.4.2 First experiments on the bonding of protium to small zirconium sponge samples were undertaken in the experimental facility in order to fix protium/tritium to zirconium sponge.

C. PROGESS OF WORK AND OBTAINED RESULTS

Progress and results

2.3.2.1 CONTAMINATIONS IN THE GENERATED HYDROGEN AND OXYGEN BY ELECTROLYSIS

In the previous experiments it has been established that in the pretreatment of slightly contaminated, tritiated excess water from a reprocessing plant 1 % of the radionuclides I-129 and Cs-137 are transferred to the distillate.

The major fraction is fixed at the SPE (NAFION foil) during electrolysis by ion exchange and adsorption. Analysis by gamma spectrometry determined that up to 80 % of the Cs-137 and to most of the I-129 is fixed at the foil.

For the experimental implementation with I-131, 2.5 litres of the solution to be electrolyzed contained 7.4×10^{7} Bq Na-131-I with 2.8×10^{-9} g Na ions and 1.6×10^{-8} g I ions. The ion concentration was therefore a little below that of the distilled reference solution. The experimental results are compiled in "Table I". The experiments show that only an extremely low iodine contamination is present in the hydrogen flow generated by electrolysis. The alkali ion concentration was than increased to approx. 8.5×10^{-9} g/l in one case by adding CsI in order to study the possible influence of residual alkali and iodine ion concentration on the hydrogen contamination. In a further experiment, the iodine ion concentration was increased to approx. 3.15×10^{-7} g/l by adding HI. The experimental results are compiled in "Table II". The results show that there is no significant influence from various alkali and iodine ion concentrations on the iodine contamination in the hydrogen flow of the electrolyzed water. For the experimental implementation with Cs-137, two litres were electrolysed with 7×10^{5} Bq/l corresponding to 2.1×10^{-7} g/l Cs-137. In the course of several experiments it was not possible to establish any contamination of the hydrogen obtained by electrolysis.

In order to determine any possible contamination of the oxygen flow with I-129, two litres were prepared with 1.85×10^{7} Bq/l corresponding to 4.03×10^{-9} g/l I-131 of which 64 ml was electrolysed. The oxygen flow was fed into a washing receiver filled with 1n NaOH where I-131 was detected by gamma spectrometry. This experiment shows that in the case of an electrolysis of the excess water from a reprocessing plant with an SPE, about 30 % of the I-129 still present as contamination is released together with the oxygen generated.

2.3.2.2 ELECTROLYSIS EXPERIMENTS WITH A TELEDYNE HG-501

Comparative studies were carried out with a TELEDYNE hydrogen generator HG-501. In contrast to the electrolyser with solid polymer electrolyte, this device requires 35 % KOH as the electrolyte solution and operates with bipolar electrodes. According to the manufacturer's data, the solution to be electrolysed must display a conductivity of < 1 µS. Since the device was to be used with radioactive solutions, modifications had to be made to the hydrogen generator. After the starting-up phase of the TELEDYNE generator, 3.7×10^{7} Bq of I-121 was added to the distillate of the crude waste solution in order to study its behaviour in the generator. The volume in the reservoir amounted to 200 ml of 35 % KOH + 1790 ml of distillate with 1 mCi I-131. After electrolysing 600 ml of the solution-corresponding to an operating period of 25 hours only 1 % of the initial activity was measured in the residual volume. No I-131 was detected in the hydrogen flow and in the oxygen flow. Although the electrolytic cell had not been in contact with the total volume of the solution spiked with I-131, nevertheless 99 % of the I-131 used was present in the electrolytic cell. In experiments with Cs-137 in the distillate of the crude waste solution no Cs-137 was detected in either the generated hydrogen or oxygen. 82 % of it was measured in the residual solution. The difference can be explained by adsorption effects at the container walls.

After that fast-motion log-term experiments began with simulate solutions based on the distillate of a crude waste solution with an increase in the concentration of the I^-- and Cs^+-ions even up to the point that 2.6 g I^- and 6.5×10^{-2} g Cs^+ had been passed through. The generator did not show any alteration in operation values. The solution drained off displayed a strong brown coloration. The investigation with respect to corrosion products revealed: 126.2 mg Cr/l and 421.6 mg Fe/1. In relation to the quantity of solution passed through, the following quantities of corrosion products resulted during this experiment: 94.6 mg Cr and 316.3 mg Fe. In experiments with the crude waste solution without previous purification by means of distillation the TELEDYNE hydrogen generator operates without difficulty even with 200 times the concentration of the solution. If one then includes the concentration of the corrosion products, relative to the ion concentration, in the operating life then a verified lifetime of the electrolytic cell of approx. 5 years is obtained.

2.4.1 TRITIUM LABORATORY

The installations in the tritium laboratory has been completed concerning the tritium measuring and adsorption devices.

2.4.2 EXPERIMENTS ON ZIRCONIUM HYDRIDE FORMATION

First preparatory experiments were carried out with hydrogen in order to fix tritium/protium to zirconium sponge. These experiments served the purpose of determining suitable parameters for a trouble-free loading of zirconium sponge with tritium. The aim was to realize the concept of a tritium fixation plant "TRIFIX" proposed by N. Ebeling /1/. This concept envisages the bonding of hydrogen enriched with tritium to zirconium sponge in batches of 4500 g of zriconium in stainless steel cylinders serving both as the reaction vessel for hydrogenation as well as final storage casks. Hydrogenation is to be carried out at a constant H_2-pressure of max. 100 hPa starting the reaction at room temperature. The reaction heat to be expected from the exothermic reaction of zirconium hydride formation, is to be removed by water cooling. The most optimum results in our experiments for the hydrogenation of zirconium sponge to $ZrH_{1.8}$ were always achieved whenever 10 % the total required quantity of H_2 was supplied to the speciem; in the case of 1 - 2 g speciems approx. 500 hPa in the apparatus used. In the vast majority of experiments a spontaneous exothermic reaction starting from room temperature took place heating the material to 850 - 1000 °C. The reaction led to the desired stoichiometric hydride formation and at the end a good vacuum was present in the loading apparatus. The experiments show that a hydrogenation of zirconium sponge in quantitites of 4500 g does not seem possible without difficulty at a continuous hydrogen pressure of 100 hPa and a starting temperature of 25 °C.

The Ebeling design for the TRIFIX facility assumes that the exothermic reaction of Zr hydride formation at an H_2 pressure of 100 hPa starting from room temperature immediately reaches a temperature of 544 °C and after 60 s 792 °C /1, p. 152, 57 and 64/. Our experimental results obtained with 50 g of Zr sponge specimen under these conditions do not confirm this assumption. The initial H_2 uptake leading to a temperaure increase of approx. 250 °C either comes to a standstill after 20 minutes with cooling of the material or in the case of a further reaction only understoichiometric quantities of hydrogen are taken up.

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Fusion Technology, Vol.14, Sept. 1988, p.1000-1004

TABLE I: ^{131}I CONTAMINATION IN ELECTROLYTIC HYDROGEN

electrolyzed ^{131}I spiked H_2O quantity (ml)	^{131}I in the receiver (Bq)	^{131}I in the NaOH washing bottle (Bq)	^{131}I in H_2 gas (%)
250	1.65×10^6	4.2×10^2	0.025
250	1.54×10^6	3.35×10^3	0.22
180	1.25×10^6	1.86×10^3	0.15
180	8.95×10^5	3.25×10^2	0.038
250	4.2×10^5	6.5×10^1	0.015

TABLE II: INFLUENCE OF THE ION CONCENTRATION ON H_2 GAS KONTAMINATION

electrolyzed ^{131}I spiked H_2O quantity (ml)	^{131}I in the receiver (Bq)	^{131}I in the NaOH washing bottle (Bq)	^{131}I in H_2 gas (%)
500 Cs+ added	6.89×10^4	6.5×10^2	0.9
250 Cs+ added	3.66×10^4	1.03×10^2	0.28
250 I- added	3.36×10^5	1.0×10^2	0.03
250 I- added	2.44×10^5	6.7×10^2	0.027

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 1988 - December 1988
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. 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 values (up to 10 wt.-%) their disposal could become problematic in the light of disposal criteria set up by safety authorities. Likewise, it may be valuable to recover Pu from these ashes for recycling purposes in LWRs. Therefore, the development 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 developing a suitable process.
- Assessment of the perfomance of the new process.
- Preliminary cost evaluation for a plant prototype.

B. WORK PROGRAMME

2.3. Literature survey

2.4. Evaluation of the experiments performed in the ALONA plant.

2.5. Experiments

2.5.1. Characterization of the incinerator ashes from KfK and Marcoule.

2.5.2. Ashes pretreatment
- effect of particle size on leachability of ashes.

2.5.3. Pu recovery from ashes
- influence of leaching temperature, leaching reagent, leaching reagent/ash ratio and furnace temperature during incineration on the leachability of the ashes and the dissolution of PuO_2.

2.5.4. Pu purification
- development of a purification process for Pu from leaching solutions with a view to Pu recycling.

2.5.5. Secondary waste
- evaluation of the secondary waste produced during Pu dissolution/purification and proposal for a waste treatment process.

2.6. Drawing up flowsheets
- on the basis of the experimental results flowsheets have to be drawn up for the treatment of alpha-bearing ashes.

2.7. Cost evaluation
- based on a simplified flow diagram, a preliminary cost evluation will be performed for a prototype facility.

C. PROGRESS OF WORK AND OBTAINED RESULTS

The sulphuric 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 sulphuric acid used in PuO_2 digestion had to be completely replaced as early as after a throughput of about 0.6 kg ash per litre, 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 sulphuric acid. Nitric acid is examined as an eligible solvent because it is used anyway to oxidize the carbon left in ashes.

During the period of reporting an ash produced during incineration of a synthetic waste mixture (ash 71-88) was characterized and its solubility in nitric acid as a function of various parameters was studied. Besides, ashes were investigated which had been produced during inactive trial operation of the new incineration furnace for alpha-bearing wastes installed at the Karlsruhe Nuclear Research Centre (ashes 1-7-88 and 1-8-88).

2.3. LITERATURE SURVEY

Different possibilities of PuO_2 dissolution were discussed including the systems HNO_3, HNO_3/HF, $HNO_3/KF/Ce^{4+}$, HI and electrochemical methods (Ag^{2+}, Ce^{4+}). As a result, only few systems are available for dissolving PuO_2 from incineration ashes which would be compatible with the usual methods of purifcation of Pu, such as extraction with TBP, and which would be effective, without addition of foreign substances which are not tolerable in technical-scale operation.

2.4. EVALUATION OF THE EXPERIMENTAL TEST PERFORMED IN THE ALONA PLANT

In the ALONA facility at EUROCHEMIC about 10 kg of Pu-bearing incineration ashes from EUROCHEMIC were treated during a campaign in Semptember/October 1985. It was possible to convert into $Pu(SO_4)_2$ up to 99% of the insoluble PuO_2. The digestion acid (H_2SO_4) had been saturated with residue after a throughout of 0.6 kg of residue per litre of acid, and had to be exchanged completely. These drawbacks are offset by the advantage of this method and the method of Pu-purification, tested on a technical scale and insensitive to such disturbing elements as chlorine and carbon. The rate of Pu recovery is as high as it is with other methods. The application of this process could be further enhanced by extending the residence time of the digesting acid.

2.5.1. CHARACTERIZATION OF THE INCINERATOR ASHES FROM KfK AND MARCOULE

- Ash D EUR 1/1 from Marcoule:

The main inorganic component of the ash of about 165 mg/g is Si followed by Al and Ca of about 95 mg/g. It contains 244 mg/g carbon and nearly 50 mg/g chlorine. The radioactive compounds are Pu, Am and U. The concentration of Pu is about 90 mg/g, of Am and U about 2 mg/g (Table I).

- Ashes from KfK:

Up to now, no Pu bearing ashes from the new KfK incinerator have been characterized, because active operation has not yet started. Three inactive ashes have been investigated, one from incineration of a synthetic waste mixture (71-88) and two which had been produced during inactive trial operation of the new KfK-incinerator (1-7-88 and 1-8-88). As in the ash from Marcoule, the main inorganic component is Si followed by Al and Ca (Table I).

2.5.2., 2.5.3. ASHES PRETREATMENT AND INFLUENCE OF DIFFERENT PARAMETERS ON THE ASHES LEACHABILITY OF ASHES

In the experiments on the solubility of the ash 71-88 it was found that the solubility increased with increasing temperature. Parameters such as the HNO_3 concentration, the grain size, the time needed for dissolution and the ash/HNO_3 ratio did not exert a noticeable influence under the selected experimental conditions. The solubility of ashes produced during incineration at 950 °C was poorer by about 5-9% than that of ashes from incineration at 750 °C whose solubilities at the boiling temperature of nitric acid were always in the 36-46% range.

Dissolution experiments with water and nitric acid at different concentrations were performed with the ash 1-7-88. According to expectations, the solubility is lowest in water. Only Ca, Al, K and Na can be detected at concentrations between 0.02 and 0.1 g/l. If 2 M HNO_3 is used, the concentration of the dissolved oxides already increases considerably. The maximum concentration of more than 10 g/l is attained by calcium, followed by 4-5 and 1-1.4 g/l, respectively for aluminum and magnesium. Sodium, potassium, barium, iron and zinc occur at concentrations of about 0.1-0.4 g/l, whereas the strontium and cerium concentrations are less than 0.1 and 0.01 g/l, respectively. The solubility of the compound increases with rising HNO_3 concentration. It attains the maximum values at 10 M HNO_3 and slightly decreases again at 14.5 M HNO_3 (except for cerium). Figure 1 shows the percentage of dissolved elements during pre-treatment with water and nitric acid, respectively.

Table I: COMPOSITIONS OF THE INCINERATOR ASHES D EUR 1/1 (MARCOULE) AND 71-88, 1-7-88 AND 1-8-88 (KfK)

Element	D EUR 1/1 [mg/g]	71-88 [mg/g]	1-7-88 [mg/g]	1-8-88 [mg/g]
C	244	n.m.	2	1
Na	35	8	4	13
Mg	14	7	31	19
Al	97	158	128	133
Si	167	189	195	219
Cl	48	-	-	-
P	n.m.	12	<0,4	2
K	n.m.	22	9,0	11
Ca	95	64	113	77
Cr	3	3	<0,7	3
Mn	1	n.m.	n.m.	n.m.
Fe	59	20	19	25
Ni	6	n.m.	n.m.	n.m.
Cu	1	n.m.	n.m.	n.m.
Zn	30	37	7	3
Sr	n.m.	2	n.m.	n.m.
Ba	10	23	55	8
Pu	94			
Am	2.3	------inactive ashes------		
U	2,2			

n.m.: not measured

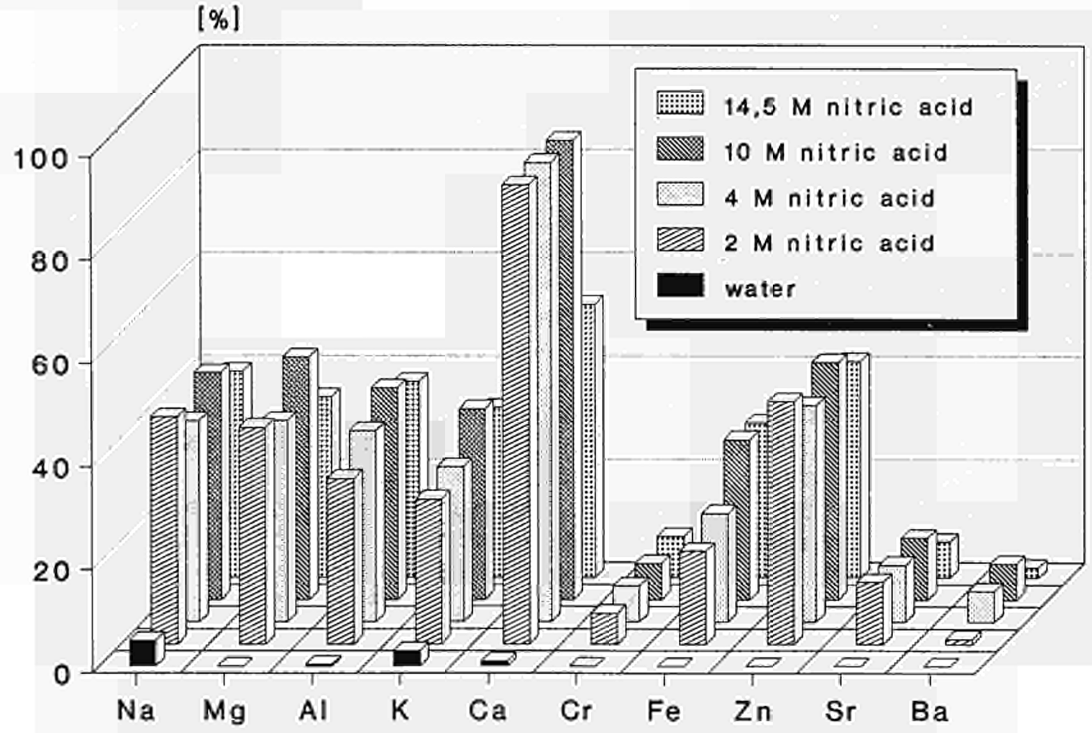


Figure 1: PERCENTAGE OF ELEMENTS DISSOLVED BY LEACHING OF THE INCINERATION ASH 1-7-88 WITH WATER AND NITRIC ACID

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 1988 - December 1988
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. The most important problem was to position the injection apparatus. We preferred to begin by experiments on a transparent scale-model to perfect the injection and to determine the fluidization conditions. The first results show that positionning the injection nozzle vertically, inside the fluidized-bed, would be the best solution.

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 concerns the position of the injection apparatus, which is described in figure 2. We have decided to carry out experiments on a transparent scale-model. In this way, it was easier for us to control the spraying on the bed and the quality of the fluidization after the injection. With the first results, we can conclude that positionning the nozzle vertically, inside the fluidized-bed, seems to be a satisfactory solution. Indeed, if it is above the bed, the nozzle gets quickly blocked after the beginning of the atomization.

Then, we can reach flows of liquid wastes between 0.5 and 2 l/h , as it was planned.

All these experiments have been carried out with inactive products (just sand and water) , in discontinuous working, with non (or lightly) heated particles.

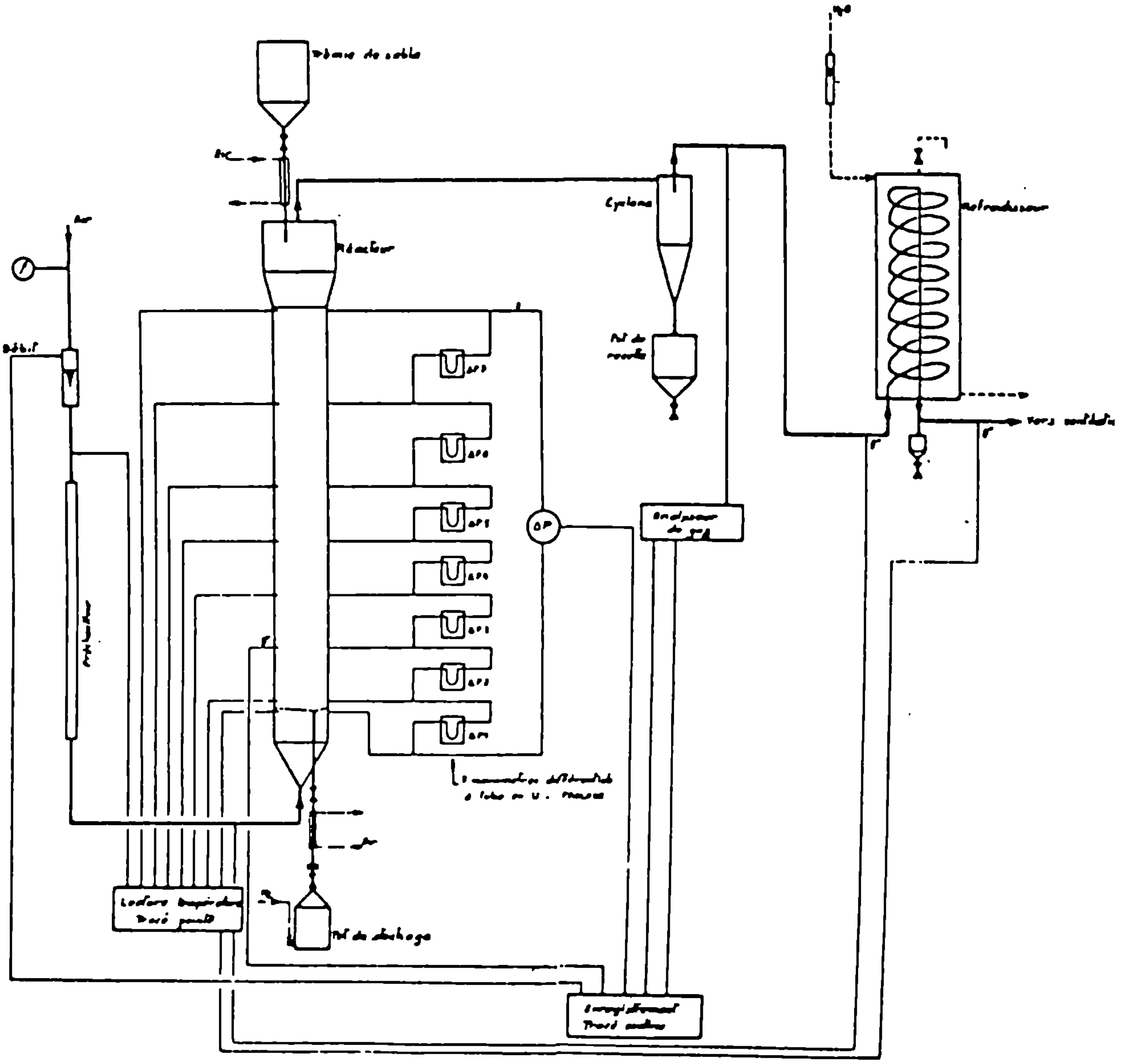
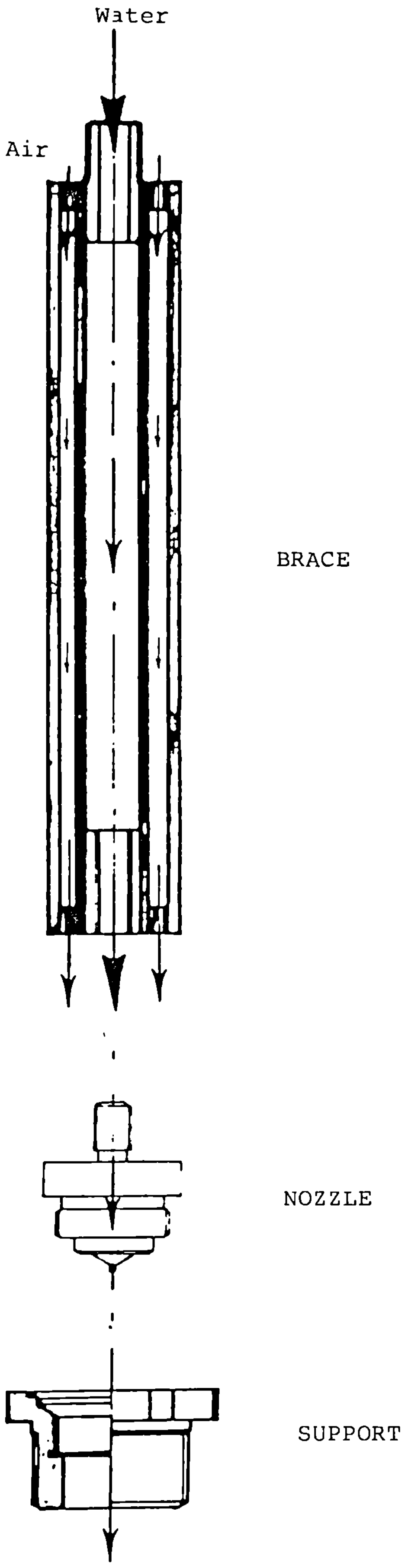
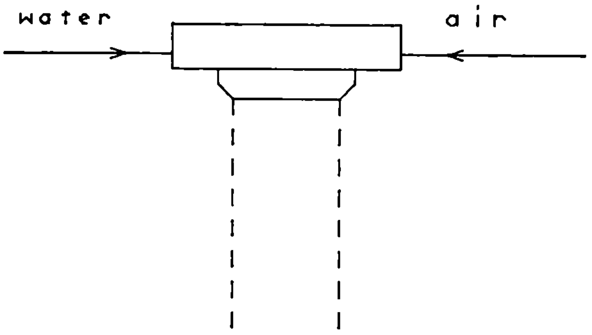


Figure 1 : Schema of a calcinator

Figure 2 : Schema of the injection apparatus



Top of the injection apparatus



TASK N. 2

2.C. OPTIMIZATION OF WASTE MANAGEMENT AT SOURCE

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

Contractor : BELGONUCLEAIRE N.V., Dessel, Belgium
Contract N° : FI1W/0024
Duration of contract : May 1986 - October 1988
Period covered : January 1988 - December 1988
Project leader : H. Pauwels

A. Objectives and Scope

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

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

B. Work Programme

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

B.2. Results from the application of techniques, concepts and systems for :

B.2.1. -the confinement of Pu bearing powders within tight equipment.

B.2.2. -the limitation of the contamination within the glove boxes.

B.2.3. -the transfer of Pu bearing materials in reusable containers.

B.2.4. -the transfer of Pu bearing materials using new purged posting systems.

B.2.5. -the reduction of waste with high Pu content by the gradual replacement of destructive testing by non-destructive testing.

B.3. Qualitative and quantitative characterization of the waste generated at a Pu fuel fabrication plant; identification of the waste producing fabrication steps; classification of the waste as a function of the conditioning and final disposal criteria.

C. Progress of work and obtained results

No report received.

TASK No 3

Evaluation of conditioned waste and qualification of engineered barriers

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

A. Objectives

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

Establishment of quality assurance in radioactive waste management.

Integration of European research effort in the above fields.

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

Characterization of medium-activity waste forms:

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

Characterization of solidified high-activity waste forms:

- Several reference materials (e.g. borosilicate and vitreous ceramic glasses) were defined and investigated in the framework of a coordinated Community action. The investigations concerned:

. the leaching of glasses,
. the effects of leachants,
. thermal stability,
. radiation damage,
. mechanical strength and fracture mechanics.

Work on engineered barriers:

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

- Selection and characterization of suitable buffer materials.

C. 1985-1989 programme

1) Research on medium-active waste form characterization

- Long-term leaching behaviour:

  . Modelling of nuclide release phenomena in various repository environments.

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

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

2) Research on high-active waste form characterization

- On the basis of the results of the preceding programme, characterization research on solidified high-level waste is being carried out on several reference borosilicate glasses.
- The data obtained from the above mentioned research will be validated and the relevant mechanisms will be modelled.

3) Other engineered barriers

- The following subjects are being investigated:

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

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

. Long-term effects of irradiation on barriers.

4) Development of standard test methods

The EC Repository Systems Simulation Test, in which 15 laboratories have participated, has been in operation over the past year. The prime objective of this test is to provide a test method which could be used by laboratories interested in evaluating waste performance in different host rock materials, i.e. granite, salt and clay. Progress and results will be treated in a separate report.

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

D. Programme implementation

The available information on 50 contracts is listed thereafter.

3.1. Medium-active Waste Form Characterisation

MEDIUM-ACTIVE WASTE FORM CHARACTERIZATION: 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 Mar. 1990
Project Leader: Professor F.P. Glasser

A. OBJECTIVES AND SCOPE

Cement is used as a matrix material for the immobilization of low and medium-active radioactive wastes and as a constructional material. Its properties are markedly affected by time and temperature, by reaction with added material, including both wastes and pozzolanic additives (slag, fly ash, etc.), by the cumulative impact of radiation, and by its interaction with the near-field environment. The present project has as its goal the quantification of relevant factors, with the aim of developing a predictive capability. The programme is cooperative, with the radiation studies being conducted at Harwell Laboratories.

B. WORK PROGRAMME

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

2.2 Modified Cement Systems. Determination and characterization 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 characterization 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. The reaction between cement and steel will be studied, mainly by critical analysis 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, E_h, sorptive capacity and phase stability.

2.4.2 Thermal Effects. The effect of moderately elevated temperatures on the hydrate phases up to 70°C, 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-Nearfield Interactions. The role of corrosive ground waters and of brines will be assessed.

C. PROGRESS OF THE WORK

State of Advancement

Encouraging progress has been made on the solubility modelling of cements. This has been accomplished by determining the solubility of calcium silicate hydrates and developing a rational and integrated framework for their interpretation. One aspect of the slow polymerization of amorphous calcium silicate hydrate, with concomitant reduction in solubility, has been pursued by nuclear magnetic resonance (NMR). Examination of laboratory-cured and historic cements shows little difference in polymerization state in excess of that which is induced by partial dessication.

The solubility studies have also been exended to embrace within the modelling exercise, calcium aluminate and alumino-sulphate hydrates.

The work on cement performance in the repository environment has been extended to include two quite different aspects: chemical attack, as may be caused by ground water dissolution, and radioactive stresses. The latter have been simulated by irradiation under controlled conditions. The fate of two specific radwaste constituents in cement has been determined: uranium and iodine. Sorption and lattice incorporation controls observed iodine uptakes while U^{6+} tends to react with cement components forming solubility-limiting phases.

Progress and Results

The overall progress of modelling of cement systems in the first three years of the contract has been described in progress reports and in critical, refereed publications. Since work is well advanced on calcium silicates, the focus of activity has shifted to hydrated aluminates and aluminosulphates. Single-phase preparations of $4CaO{\bullet}Al_2O_3{\bullet}13H_2O$ (C_4AH_{13}), $3CaO{\bullet}Al_2O_3{\bullet}6H_2O$ (C_3AH_6), $6CaO{\bullet}Al_2O_3{\bullet}SO_3{\bullet}32H_2O$ (AF_t), and $4CaO{\bullet}Al_2O_3{\bullet}SO_3{\bullet}12H_2O$ (AF_m) were made and their solubilities determined. Minor impurities, almost inevitably present in these preparations, can be removed by redispersion. Solubilities and activities are given for solutions saturated at 20°C. One of the principal findings concerns the formation and dissolution of AF_t: in contrast to previous studies, it is congruently soluble. Figure 1 shows the solubility curve,with representative analytical points and the calculated position of the congruence line.

The solubility modelling is important as solubilities of cements control repository pH. Current solubility models depend largely on control by crystalline $Ca(OH)_2$ and an amorphous gel, designated C-S-H although only the latter may be present in aged,, blended cement systems. However, polymerization and crystallization can lower the pH of C-S-H. The polymerization state of amorphous materials is difficult to characterize: NMR has been applied. Figure 2 shows spectra obtained after about 4 weeks (^{29}Si). The polymer resonance (chemical shift ~ -85ppm) is enhanced by partial drying, and this appears to be an important effect.

Iodine can occur in cment systems in three speciations: I, I^- and IO_3^-. In practice, only the latter two are significant. Both sorption and lattice incorporation are important in controlling the fate of iodine in cement. This may be seen in practical experiments: Table II shows K_d values for I^- in OPC and in an 85% blast furnace slag blend. Throughout the measurements, OPC is the more efficient scavenger. Laboratory investigations are required to explain these and other phenomena. They show that (i) iodine is probably reduced to I^- in slag-rich blends (ii) iodine is not appreciably sorbed by either hydrotalcite or $Ca(OH)_2$; sorption on C-S-H increases with increasing C/S ratio and at lower concentrations (iii) C-S-H has stronger affinity for IO_3^- than for I^-, but the uptake into AF_m phase is the single most significant factor in controlling the iodine uptake by OPC. Table II lists some results. This Table also records Cl^- contents, achieved by spiking;

the AF_m phase has a strong preference for I^- even in the presence of Cl^-.

Uranium, as U^{6+}, is relatively insoluble in cement. In the short term, it is strongly sorbed into C-S-H gel. Provided the U/calcium ratio of preparations are low (<0.3), solubilities are less than 10^{-6}mol dm^{-3}; Table III gives typical data. However, at longer ages solubility limiting solid phases may also form as a result of reaction, leading to crystallization. Two such phases which appear important in this context have been characterized; one is isostructural with uranophane; the other, which has no natural counterpart, is Ca_2UO_5 1.3-1.7H_2O (its exact water content is somewhat variable).

Concretes in the repository are exposed to many chemical agents in ground waters. A survey of these have been made and a risk assessment suggests that higher priority should be given to attack by aggressive CO_2. Therefore a thermodynamic study has been undertaken of the relevant system. Previous approaches are empirical or at best, only semi-systematic. A more systematic and detailed treatment is nearing completion and results are expected to be completed in the framework of the contract.

The impact of radiation on concretes has been assessed in an experimentally based programme. In the absence of nitrate ion, it has been concluded that the effect of γ irradiation is (i) hydrogen is evolved with $G(H_2)$ in the range 0.06-0.21 for both OPC and BFS/OPC grout of normal water:solid ratio (0.36) (ii) PFA grouts suppress H_2 evolution from OPC, (iii) all grouts absorb oxygen, although OPC grouts may evolve O_2 after a cumulative dose >20MGy and (iv) oxygen is aborbed in BFS/OPC grouts without the presence of irradiation but is enhanced by it. During the current contract, three mechanisms of O_2 absorption have been investigated. Peroxide has been found to occur at 0.5MGy.(0.2KGy hr^{-1} in the pore fluid but in the solid at much lower doses (≥0.50MGyy). High dose rates result in high temperatures in the samples. Since high temperatures (>70°C) may also be encountered in the repository it is important to assess thermal effects in their own right, as well as in conjunction with irradiation. Phase changes in PFA/OPC and BFS/OPC blends have been followed at 20°C and 72°C for up to 2 years. Following cure, a high pH is maintained - Table IV shows data - but supplementary chemical and mineralogical studies show conclusively that the high pH is maintained by soluble alkalis and by C-S-H; $Ca(OH)_2$ disappears by reaction with the blending agent. The rate of reaction between cement and blending agent increases markedly with rising temperature.

Publications and presentations

Presentations. Materials Research Society, 10-13 Oct 1988, Berlin. Symposium "Scientific Basis for Nuclear Waste Management"

Publications. *Note. The list includes those papers either published or accepted for publication in 1988.*

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/2/ Modelling Approach to the Prediction of Equilibrium Phase Distribution in Slag-Cement Blends and Their Solubility Properties. F.P. Glasser, D.E. Macphee and E.E. Lachowski. Mater. Res. Soc. Proceedings 112, 3-12 (1988).

/3/ Polymerization Effects in C-S-H: Implications for Portland Cement Hydration. D.E. Macphee, E.E. Lachowski and F.P. Glasser. Advances in Cement Res. 1[3], 127-133 (1988).

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TABLE I: IODINE K_d VALUES CALCULATED FROM EXPERIMENTAL DATA (mls/gm)

Iodine:	~10^{-7}M		$10^{-3.7}$M	10^{-2}M
	(30d)	(60d)		
OPC	21	54	4.8	4.8
85% BFS	1.5	1.7	0.9	0.7

TABLE II: SOLID AND AQUEOUS PHASE CHARACTERISATION OF AF_m AND AF_t PREPARATIONS AFTER EQUILIBRATION.

sample	solids	pH	SO_4^{2-}*	I^-*	Cl^-*
1. 'AF'	AF_m (AF_t)	12	<0.15	0.33	1.10
2. '$AF^m{}_m$·pH 13'	AF_m	13	0.47	0.68	1.15
3. 'AF'	AF_t (AF^m)	8	8.0	f.a.	0.96
4. '$AF^t{}_t$·	AF_t (AF_m)	13	>8.3	f.a.	1.01
5. 'AF'	AF_m (AF_t·C_3AH_6)	12	<0.15	0.19	0.96
6. '$AF^m{}_m$·	AF_m (AF_t)	13	0.50	0.47	0.99
7. 'AF'	AF_t (AF_m)	8	1.0	0.92	0.96
8. '$AF^t{}_t$·	$AF^t{}_t$ ($AF^m{}_m$)	13	1.0	0.92	f.a.

* Concentration units 10^{-3}M

Table III: Solubility Data for Products in the $CaO-UO_3-SiO_2-H_2O$ System

Sample Ref.		G	I	J	A	B	C	D	E	F
Target C/S		1.0	1.25	1.5	1.7	1.7	1.7	1.7	1.7	1.7
Target U/C		1.0	1.0	1.0	2.0	1.0	0.3	0.15	0.074	0.036
FIRST DISPERSION	Age (Days)	35	160	37	28	36	15	15	13	13
	pH	11.97	11.70	11.95	10.12	11.54	12.25	12.34	12.35	12.38
	Ca	0.205	0.774	0.649	0.798	0.140	11.70	14.10	18.11	22.06
	Si	0.997	0.427	0.392	0.049	0.570	0.100	0.030	0.021	0.020
	U	15.5	17.2	10.5	(1.7)	10.0	5.5	7.1	6.3	4.2
	Na	17.62	3.92	7.61	30.88	6.31	29.36	29.58	24.14	25.23
	NO_3^{2-}	2.02	0.69	0.16	143.5	6.13	55.8	54.5	41.1	32.7
SECOND DISPERSION	Age	95	220	97	88	96	75	75	73	73
	pH	11.67	11.41	11.60	10.72	11.69	11.58	11.77	11.65	11.61
	Ca	0.245	0.923	0.724	0.948	0.265	1.821	2.770	2.345	2.495
	Si	0.856	0.339	0.303	0.143	0.303	0.161	0.089	0.125	0.107
	U	4.2	(1.3)	(2.1)	96.6	5.0	10.5	(1.7)	(0.8)	(0.8)
	Na	6.09	1.22	3.05	1.87	6.09	0.37	0.40	0.19	0.25
	NO_3^{2-}	0.04	0	0	0	0.12	0.05	0.11	0.04	0.09
	Age	135	260	137	128	136	115	115	113	113
	U	4.2	(0.8)	(1.6)	1596	5.5	(0.4)	(0.4)	(0.4)	(0.4)

Uranium concentrations in 10^{-6} mol dm^{-3}, all others in 10^{-3} mol dm^{-3}.

Parentheses for uranium analyses indicate absorbance values less than twice those of the reagent blank.

TABLE IV: pH VALUES EXPRESSED PORE FLUIDS (OPC B)

Hydration Time	Sample	Temperature/°C			
		20	40	50	72
3 months	OPC	13.8	13.7	13.7	13.8
	3:1 BFS/OPC	13.5	13.4	13.4	13.8
	9:1 BFS/OPC	13.2	13.5	13.6	-
6 months	9:1 BFS/OPC	-	13.4	13.6	13.6
	3:1 PFA/OPC	13.6	13.5	13.4	13.3

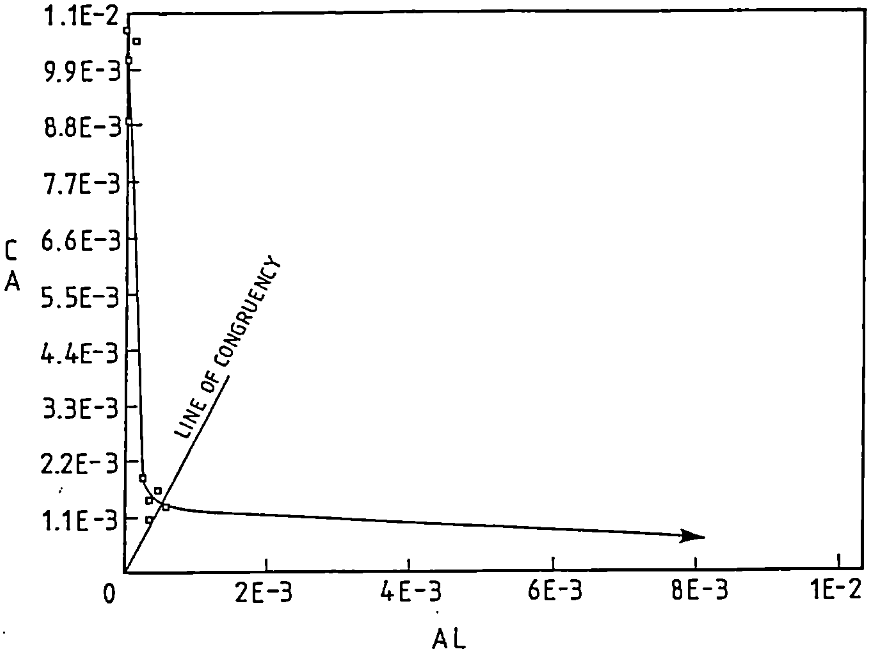

Figure 1. Calcium- aluminium plot for ettringite.

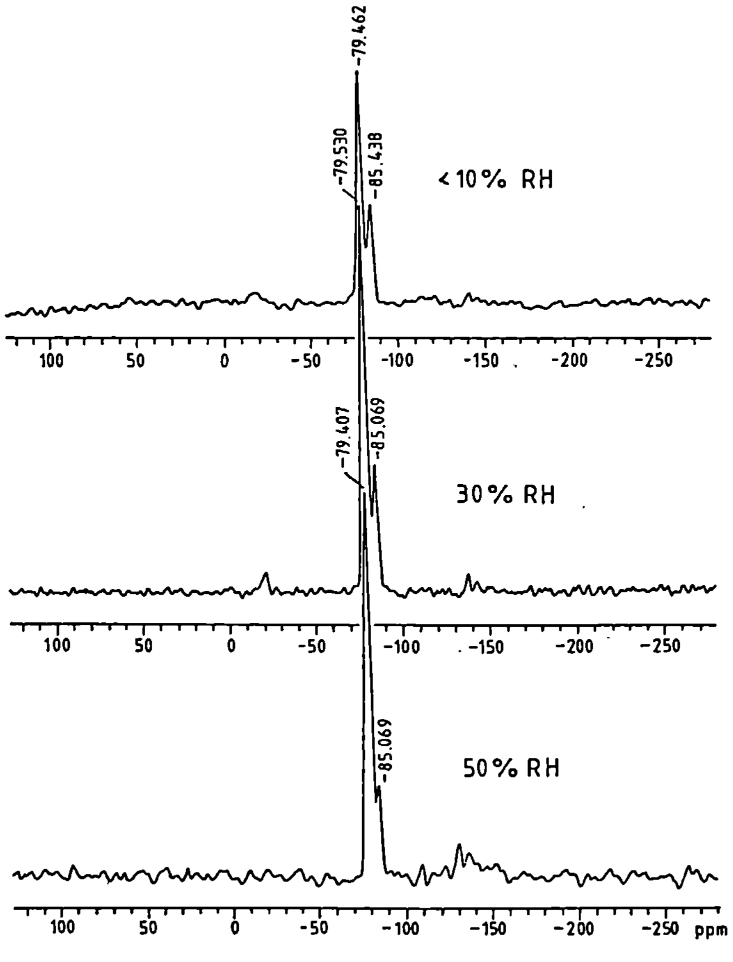

Figure 2. 29Si NMR spectra of C-S-H aged under various humidities for 4 weeks.

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
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 of inactive Cs or of Cs-137 from cement samples with distilled water at 30°C was continued. Further distribution profiles of Cs^+ along the axis of some of these samples have been obtained and compared with appropriate theoretical Fickian profiles. The study of the effect of temperature and of sample thickness on leaching kinetics of Cs has been nearly completed. An increase of the leaching temperature from 30° to 70°C resulted in a corresponding rise of the Fick diffusion coefficient by ca one order of magnitude. The Arrhenius activation energy (12-14 kCal/mol) calculated from these diffusion coefficient values, together with other evidence, shows that the leaching process of Cs^+ from the specimens under study is not a purely diffusion controlled phenomenon. Diminution of the sample thickness to ca 1/3 of the original value had no significant effect on leaching rate. The final portion of the elution curves (percentage of Cs eluted vs time) was found to fall below the Fick law prediction based on the initial portion of these curves (Figure 1). In order to examine the effect of atmospheric CO_2 on the elution of Sr^{++} in relation to the Sr content from cemented specimens, leaching tests were begun. Differential scanning calorimetry (DSC) measurements were also undertaken to obtain information about the state of water (freezable or non-freezable) within the cement samples. Our study of the elution kinetics of NaCl embedded in cellulose acetate was extended by examining the effect of different particle size. Leaching tests of $CsNO_3$ (which is substantially less soluble in water than NaCl) from cellulose acetate were performed using films of various salt contents.

Progress and Results

1. Studies with cemented specimens

B.1.1-B.1.4 Elution studies of Cs-kinetics

The cylindrical cement specimens (height (ℓ) = 4 cm, diameter = 4 cm) contained either ~3.4% by wt of 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) /1,2/. The thinner samples (diam.=4 cm, height=1.2 cm, series C) had the same composition as series A. All outer surfaces of each specimen, except one flat surface, were covered with epoxy glue. Leaching experiments were performed in stagnant distilled water at 30°C.

Typical examples of leaching results of series A, C and D are presented in Figure 1 where the fractional amounts eluted are plotted on a $\sqrt{t}$ basis. (For comparison, elution results at 70°C of specimens of the same composition and size as in series A are presented). In some samples of series A and D a distinct acceleration of the elution process is observed (in keeping with a detectable increase in porosity as leaching progresses). The experimental distibution profiles of non-eluted Cs at different stages of the elution process for series D (30°C) are presented in Figure 2 (where C=measured Cs concentration in a slice located at distance x from the exposed surface, and C_0=initial Cs concentration) and fitted by theoretical curves /2/. The resulting best-fitting values of diffusion coefficient (D) agree with those deduced from the corresponding elution curves. Both measured profiles are consistent with zero surface concentration ($C_1=0$), in contrast to what was observed in the case of series A, where $C_1/C_0 \simeq 0.2-0.3$.

B.1.5 Elution studies of Sr (atmospheric CO_2 effect)

The Sr-samples (diam.=4 cm, height=4 cm) contained 740 kBq of Sr-90 and 8% wt of $NaNO_3$ (Series E,F) or 740 kBq of Sr-90, 0.15% wt 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 with the other conditions being identical as in the case of Cs-samples.

The results of Sr-leaching tests are given in Figure 3. A strong depression of the leaching rate caused by exposure to the atmosphere is observed, thus confirming the behavior found previously in specimens of higher Sr-content ($SrSO_4$) /3a/. Incorporation of additional amounts of $Sr(NO_3)_2$ results in higher elution rates.

B.1.6 Characterization of the state of water in cement specimens by DSC

This technique yields information on the melting range of the (previously frozen) imbibed water and the heat absorbed by the melting process. Assuming the enthalpy of melting to be constant throughout the melting range, an estimate of the relative amounts of freezable and non-freezable water can be obtained. The former may be considered to be located within pores and is of primary importance for the elution process. The latter is made up of water molecules strongly interacting (physically or chemically) with the constituents of cement. Freezable water estimated in this way amounted to ca 25% of total (as estimated by drying at 106°C) imbibed water for a blank (no added salt) specimen (curve B of Figure 4) and ca 35% for a largely leached out specimen initially containing ~3.4% by wt of Cs_2SO_4 (curve C of Figure 4). Water in large pores is expected to behave like bulk water equilibrated with the powdered cement specimen (curve D of Figure 4). On this basis, it is concluded from curves A and B of Figure 4 that freezable water in an incompletely hydrated cement specimen is primarily located in small pores, but there is a considerable amount of water in large pores in a fully hydrated specimen.

2. Studies with polymer-salt systems

B.2.1 Cellulose acetate-salt system

Cellulose acetate films (thickness 300-380 µm, cast from a 20% by wt acetone solution) containing various amounts of powdered $CsNO_3$ (10%, 25% or 40% by volume) or NaCl (11.1% or 20% by wt) were prepared and subjected to leaching by agitating the sample (10 cm^2 area) in distilled water at 25°C /3b/. Elution results of $CsNO_3$ were interpreted according to the Higuchi equation and compared to analogous previous results with the much less soluble $CaSO_4$ and $SrSO_4$ /3b/. In the case of NaCl, the effect of using particles of different size (<25 µm or 53-80 µm) was also examined. Finely powdered NaCl was obtained by addition of acetone to stirred saturated aqueous solution of salt, followed by passing through a fine (25 µm) sieve. The majority of the particles was found by microscopical observation to be in the 3-10 µm range. The elution rate was much greater in the case of the larger particles (Figure 5).

B.2.4 Epoxy resin-salt system

Elution tests at 30°C by stagnant distilled water of epoxy resin samples (discs of thickness 0.7 cm and diameter 5 cm) loaded with NaCl or $SrSO_4$ (12%, 25% or 40% by vol.) were continued. Elution curves continue to be linear vs $\sqrt{t}$ in the case of $SrSO_4$ whereas those for NaCl show a distinct tendency to curve upwards.

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/1/ GLASSER, F.P. and McCULLOCH, C., Editors, Characterization of Radioactive waste forms, Progress Report 1986, EUR 11354 EN, Vol. 1, pp 32-41 (1988).

/2/ AMARANTOS, S.G., PAPADOKOSTAKI, K.G. and PETROPOULOS, J.H., Annual Report 1987, GREEK AEC-EEC Contract No. FI1W/0026/00 (February 1988).

/3/ POTTIER, P.E. and GLASSER, F.P., Editors, Final Report - 2nd CEC Program 1980-84: (a) p. 133-140, (b) p. 149-153 EUR 10579 EN (1986).

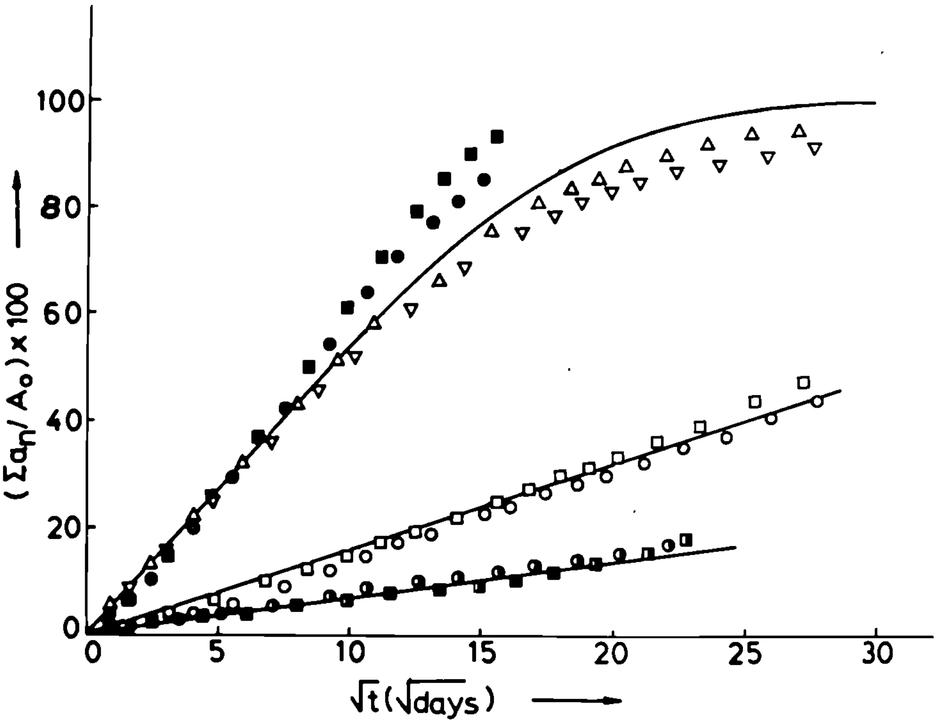


Figure 1. Elution curves of Cs from cemented specimens containing inactive Cs_2SO_4 (3.4% wt) at 70°C (●,■) or 30°C (Series A,C; o,□,∇,Δ) or Cs-137 (370 kBq/sample), $CsNO_3$ (0.017% wt) and $NaNO_3$ (8% wt) at 30°C (Series D; ◐,◨). Sample thicknesses: 1.2 cm (series C;∇ ,Δ) or 4.0 cm (o,□,●,■,◐,◨). The theoretical curve (full line, series C) was calculated by Fick's law with $D=3.7x10^{-8}$ cm^2s^{-1}.

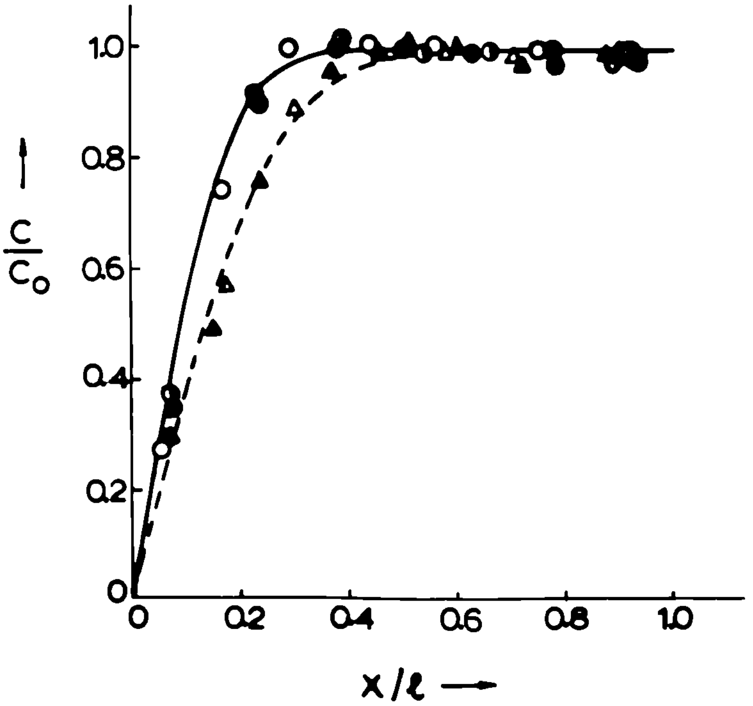


Figure 2. Distribution of Cs-137 in cement specimens (series D) after 203 (o, •, ⊙), or 377 (Δ,▲) days of elution at 30°C. Amounts eluted (%): 9.8 (o,⊙), 10.8 (•), 13.9 (Δ), 14.8 (▲). The theoretical curves correspond to D=0.8x10^{-8} cm^2s^{-1} (—) or 1.0x10^{-8} cm^2s^{-1} (---) and C_1/C_0=0.

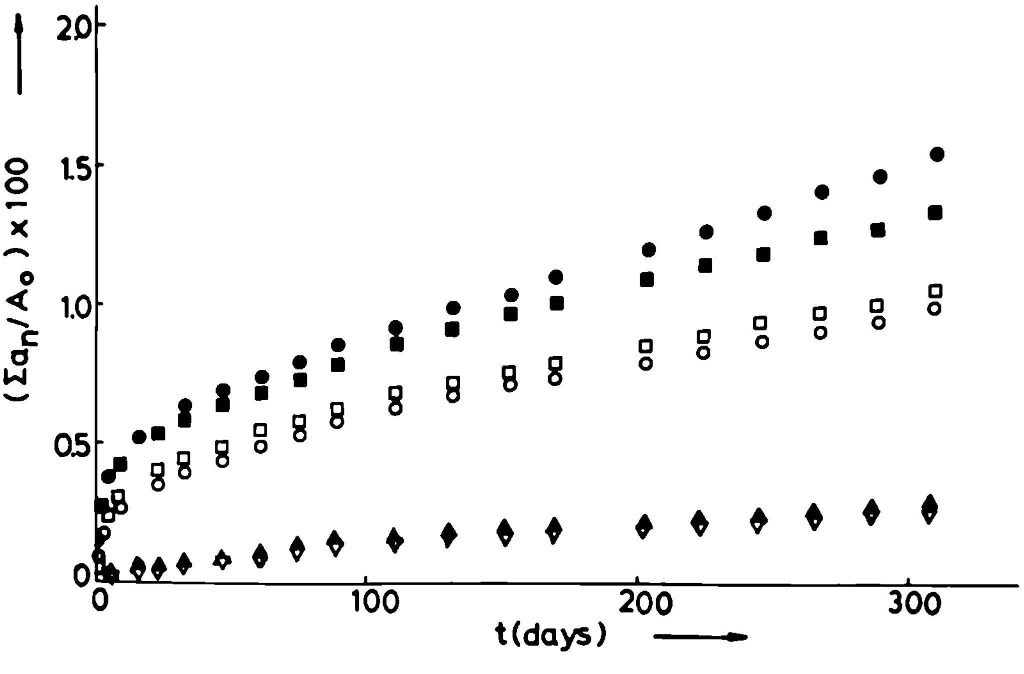


Figure 3. Elution curves of Sr-90 at 30°C from cemented specimens prepared and leached under full (∇ ,▲; series E,G) or minimum (o,□,•,■; Series F,H) exposure to atmospheric CO_2, containing Sr-90 (740 kBq/sample) and 8% by wt $NaNO_3$ (open points; series E,F) or Sr-90 (740 kBq/sample), 8% wt $NaNO_3$ and 0.15% wt $Sr(NO_3)_2$ (filled points; series G,H).

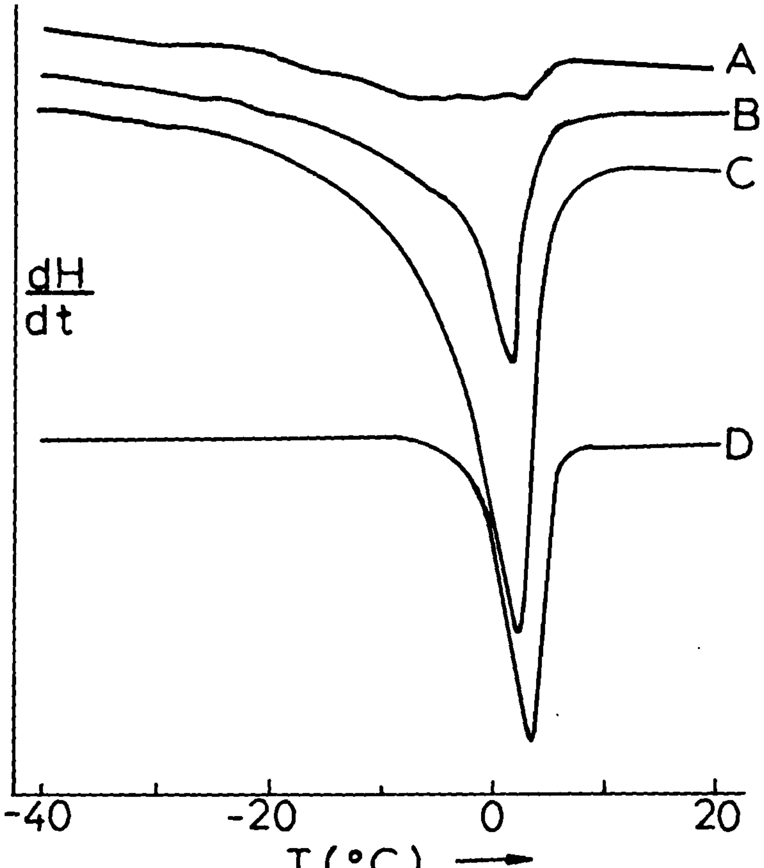


Figure 4. DSC melting thermograms of water imbibed in cement specimens exposed to 76% RH (curve A) or 100% RH (curves B,C); initial salt content: zero (curves A,B) or 3.4% by wt Cs_2SO_4 (~85% leached out, curve C). Curve D refers to bulk water equilibrated with the powdered blank specimen.

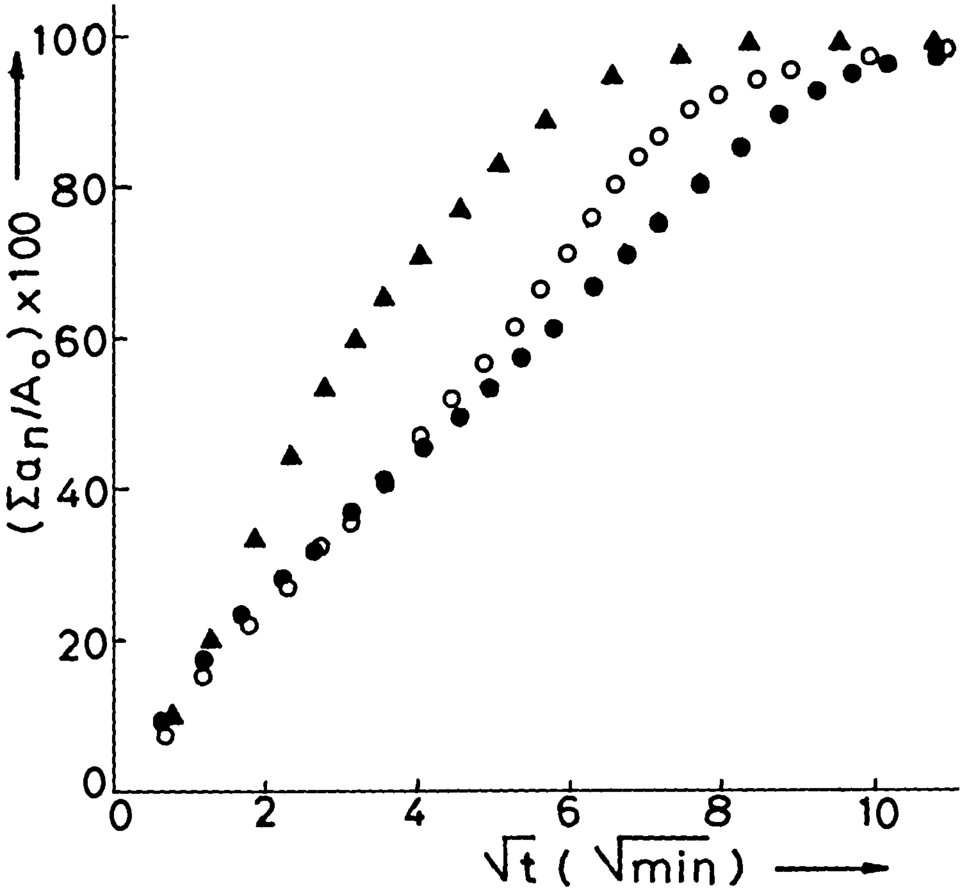


Figure 5. Elution curves of NaCl at 25°C from cellulose acetate films (~300 μm thick) containing 11.1% (o) or 20.5% (●,▲) by wt NaCl. Salt particle size: <25 μm (o,●) or 53-80 μm (▲).

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 - December 1988
Project leader : G. W. Marx
Group leader : Ch. Keiling

A. Objektives and scope

The influence of the organic complexing agents DBP, TBP, EDTA, citrate and oxalate on the solubility, sorption behaviour and migration of the elements iodine, cesium, uranium, neptunium, plutonium and americium has been investigated in order to obtain data relevant to safety aspects of ILW repositories. These synthetic organics are products resulting from fuel element fabrication, spent fuel processing and from chemical procedures performed in laboratories.

Leaching experiments on the real and simulated ILW forms have been performed for comparing them with those data, obtained from the compounds aforementioned. Within the frame of this project the matrices cement and bitumen used for vitrification have also been taken into consideration.

B. Work Programme

B.1 Source term solubility studies
B.1.1 Determination of equilibrium solubilities of silver iodide, silver iodate, cesium nitrate, sodium diuranate, neptunium(V), plutonium(IV) and americium(III) hydroxides in concentrated salt solutions 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 in cement and determination of their leachabilities
B.1.6 Solidification of complexed elements 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 the use of salt columns
B.2.3 Determination of the sorption behaviour of selected radionuclide systems upon salt by the use of batch-type experiments

C. Progress of work and obtained results

State of advancement

Up to the preseht state of this project the solubilities of silver iodide, silver iodate, cesium nitrate, sodium diuranate, neptunium(V)hydroxide, plutonium(IV)hydroxide and americium(III)hydroxide have been determined under the influence of the complexing organics mentioned above in saturated NaCl solution and Q-brine after contacting the matrices cement and bitumen.

Column experiments were performed with solutions, containing iodide or iodate, cesium, uranium, neptunium, plutonium or americium.

Analytical procedures were developed for investigating the leachates of real waste, which could cope with the problem of separation and measurement of the special radionuclides being present /1/.

The elements iodine, cesium, uranium, neptunium and americium were vitrified together with complexing organics, in order to investigate in detail the behaviour of cement samples leached by saturated NaCl solution and Q-brine.

Real waste forms solidified with cement and bitumen were leached by concentrated salt solutions, saturated with various complexing organics.

Progress and results during the time period January-December 1988

B.1 Solubility studies of the source term

The systems, used for the experiments, consisted either of saturated NaCl solutions or of Q-brine /2/. Both of the solutions were made by use of bidistilled water. Before adding the materials under investigation the solutions were equilibrated with ground Portland 35 F-cement matrix or crushed Shell Mexphalte R 80-100 bitumen. After filtrating suspended particles the solutions were saturated with the special complexing organics under investigation. Undissolved residues of the complexing agents were also removed by filtration.

The pH of the NaCl solutions containing cement was kept at 12 and that one of the Q-brine containing cement at pH 6 respectively. The pH of the solutions equilibrated with bitumen corresponded to these values being characteristic ones of these special systems.

The elements, the solubilities of which had to be determined, were added to the special solutions in form of the compounds AgI, $AgIO_3$, $CsNO_3$, $Na_2U_2O_7$, NpO_2OH, $Pu(OH)_4$ and $Am(OH)_3$. The systems were equilibrated by stirring at 298 K for several days. Saturation was verified by adding small amounts of the special compounds respectively.

In general suspended particles were removed by filtration with membranes, the poresizes of which were 450 nm.

B.1.1 Determination of solubilities at equilibrium

Solubilities of $AgIO_3$

The values obtained from the determination of the $AgIO_3$ solubilities in saturated salt solutions containing the various complexing agents aforementioned range from $1{,}6 \cdot 10^{-2}$ bis $4{,}4 \cdot 10^{-2}$ $mol \cdot dm^{-3}$.

Solubilities of neptunium

Investigations into the solubility of neptunium were performed with various saturated salt solutions which NpO_2OH was dissolved in (cf. table 1).

The results obtained show the strong influence of citrate on the solubility of neptunium. EDTA also increases the solubility of neptunium. Furthermore in NaCl solutions containing cement the solubility of NpO_2OH is significantly higher, when oxalate is present. This effect may be due to masking the Ca^{2+} ions leached from the cement matrix by CaC_2O_4 formation, increasing the CO_3^{2-}-concentration therefore, which enhance the complex formation of neptunium.

Solubilities of americium

Until now the solubilities of americium(III)hydroxide have been determined in NaCl/cement-solutions, the concentration found being near to $2 \cdot 10^{-9}$ $mol \cdot dm^{-3}$ when TBP is present and $2 \cdot 10^{-5}$ $mol \cdot dm^{-3}$ in case of EDTA. Furthermore the solubilities of americium in Q-brine were determined after contacting cement when DBP, TBP or citrate were present, the solubilities ranging from 10^{-6} to 10^{-5} $mol \cdot dm^{-3}$.

Americium was substituted by Eu^{3+} in those systems, which due to the pH a higher solubility was expected for, because sufficient amounts of americium were not available for saturation.

Solubilities of $Eu(OH)_3$ were determined in Q-brine after contacting bitumen in presence of DBP, citrate and oxalate, the data obtained ranging from $8 \cdot 10^{-5}$ $mol \cdot dm^{-3}$, when oxalate was present, to $5 \cdot 10^{-3}$ $mol \cdot dm^{-3}$ in case of citrate.

B.1.2 Ultrafiltration experiments

Ultrafiltration of solutions containing $AgIO_3$

When saturated salt solutions containing $AgIO_3$ were treated with filters, the poresizes of which were nominally 450 nm and 2 nm, an optimal decrease of the IO_3^- concentration to 7% was observed in the solution. This result showed that there was no significant filtration effect at all.

Ultrafiltration of solutions containing plutonium

For salt solutions containing plutonium filters were used with pore sizes ranging from 450 nm to 2 nm. In several cases the plutonium content of the solutions decreased. From reiterated filtrations sorption on filter materials could be observed to a certain amount. Further investigations are necessary to confirm this phenomenom.

B.1.3 Determination of leachabilities of radionuclides from conditioned ILW

Leaching experiments were performed on simulated waste containing plutonium, americium and fission products, added in form of inactive material /3/ with concentrated NaCl solution, which was previously saturated with DBP, TBP, EDTA, sodium citrate and oxalic acid. The americium- and plutonium-concentrations obtained from leaching experiments running for 21 days are listed in table 2.

The results obtained from the experiments on real waste forms can be seen on figures 1 - 3. Suspended particles were filtered with filters, their pore sizes being 450 nm.

Nearly constant concentrations of the various activities were already established after a relative short period of time.

B.2 Sorption and migration in the near-field

Column experiments on migration

The column experiments have been performed by use of the well known apparatus, consisting of a peristaltic pump, a chromatographic column and an automatic sampling device /3/.

Before adding the radioactive solutions the column packing consisting of NaCl GR is treated with the special saturated salt solution under investigation, equilibrated with bitumen or cement respectively.

The radioactive solution is added as a pulse, the volume of which is approximately 2 cm^3, followed by rinsing with equilibrated salt solution, the flow rate being 1,5 $cm^3 \cdot h^{-1}$.

B.2.1 Migration behaviour

Migration behaviour of $AgIO_3$

In the systems under investigation the recovery of iodate was in between 85 % and 100 % after passing the columns filled with NaCl.

Migration behaviour of neptunium

For the investigations of the neptunium compounds those solutions were added, which were prepared in order to determine the solubility of NpO_2OH.

The radioactivity passing through the column was measured either by taking an average sample or separately by use of an sampling device to register the break through curve.

In the NaCl/cement-system the recovery of neptunium was very small ($\leq$ 10 %), which might be due to the high alkalinity of the solutions.

In the NaCl/bitumen-system with its lower pH caused by containing DBP or citrate relative high recoveries were obtained ranging from 40 % to 70 %. The recovery was $\approx$ 26 % when oxalate was present. The other complexing agents influence the recoveries to become approximately $\leq$ 10 % in these systems.

In the system Q-brine/cement the recoveries obtained ranged from 2 % to 90 %.

In case of the investigated Q-brines equilibrated with bitumen the recoveries of neptunium were $\leq$ 20 % under the influence of DBP and TBP.

Migration behaviour of americium

After passing a column filled with NaCl GR the recovery of americium was up to 30 % in the NaCl/cement solutions on condition that oxalate was present. The lowest value obtained until now was nearly 4 % in these systems, in case of citrate being present. The recoveries were higher, on the other hand (> 80 %), for Q-brine equilibrated with cement and also when complexing organics were present.

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

Batch experiments

In order to investigate the sorption behaviour of various problem elements on sodium chloride, being the main component of a waste repository located in a salt dome, batch experiments were performed for which the ratio 'volume of the solution' - 'mass of solid NaCl' was fixed. The referring materials were shaken at 298 K by use of a coulter mixer located in an air thermostat. Before taking a sample suspended particles were removed from the solution by filtration with 450 nm membranes.

Sorption behaviour of $AgIO_3$

The distribution coefficients of iodate for systems consisting of salt solutions saturated with complexing organics and solid NaCl GR are very small (< 1 $cm^3 \cdot g^{-1}$).

Sorption behaviour of cesium

The solutions used for the batch experiments were made by dissolving solid $CsNO_3$ labelled with ^{137}Cs in the special saturated salt solutions.

The distribution coefficients obtained show that only a small quantity of cesium is adsorbed on the NaCl used for the batch experiments. The R_s-values for the adsorption of cesium on NaCl are smaller than 1 $cm^3 \cdot g^{-1}$, most of them being even smaller than 0,1 $cm^3 \cdot g^{-1}$.

Sorption behaviour of neptunium

Under the influence of organic complexing agents the R_s-values for the adsorption of neptunium from saturated salt solutions on solid NaCl are mostly very small (< 1 $cm^3 \cdot g^{-1}$). In the system NaCl/cement saturated with TBP on the other hand the R_s-value are higher than 100 $cm^3 \cdot g^{-1}$.

Sorption behaviour of plutonium

The distribution coefficients for the sorption of plutonium from salt soutions saturated with various complexing organics on solid NaCl GR deviate very much and range from 0 $cm^3 \cdot g^{-1}$ to 180 $cm^3 \cdot g^{-1}$ (cf. table 3).

Sorption behaviour of americium

The distribution coefficients obtained from the sorption of americium from NaCl/cement solutions saturated with complexing organics on NaCl GR are smaller than 1 $cm^3 \cdot g^{-1}$ (in presence of citrate and EDTA), 5 $cm^3 \cdot g^{-1}$ (in case of DBP being present), 21.5 $cm^3 \cdot g^{-1}$ (in case of TBP) and 30 $cm^3 \cdot g^{-1}$ (in case of oxalate).

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

2 D'Ans, J., "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen", Verlagsgesellschaft für Ackerbau mbH, Berlin 1933, 254

3 Final report "Solubility and Speciation of Actinides in Salt Solutions and Migration Experiments of Intermediate Level Waste in Salt Formations", FU Berlin, Institute for Inorganic and Analytical Chemistry, Department of Radiochemistry; BMFT-FKZ: KWA 5313 2; CEC Contract No.: 415-83-7 WAS D

Table 1. Solubility of NpO_2OH in various saturated salt solutions containing organic complexing agents

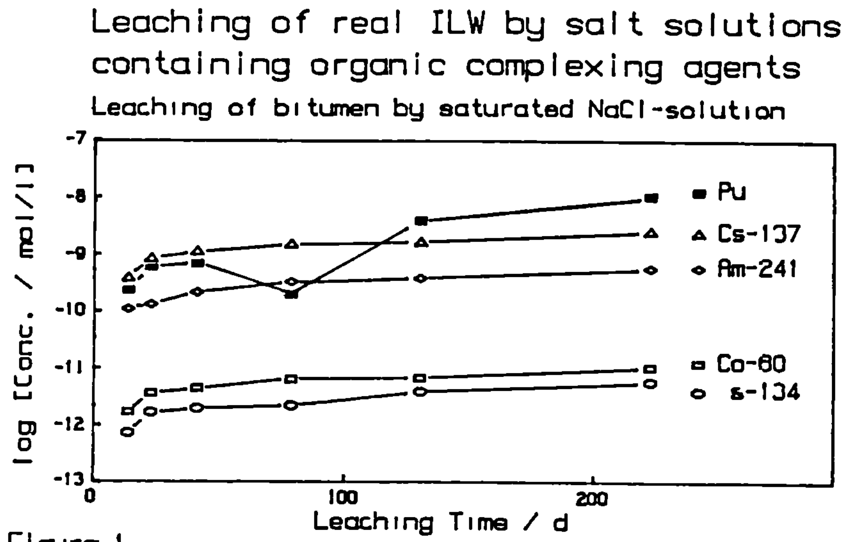
solution	org. ligand	[Np] / $mol \cdot dm^{-3}$
NaCl/Cement	without	$2.39 \cdot 10^{-4}$
	DBP	$5.46 \cdot 10^{-6}$
	TBP	$5.45 \cdot 10^{-6}$
	EDTA	$1.72 \cdot 10^{-4}$
	Citrate	$7.22 \cdot 10^{-4}$
	Oxalate	$9.94 \cdot 10^{-4}$
NaCl/Bitumen	without	$8.60 \cdot 10^{-5}$
	DBP	$2.11 \cdot 10^{-3}$
	TBP	$1.11 \cdot 10^{-5}$
	EDTA	$4.30 \cdot 10^{-3}$
	Citrate	$2.96 \cdot 10^{-3}$
	Oxalate	$1.07 \cdot 10^{-4}$
Q-Solution/Cement	without	$4.32 \cdot 10^{-5}$
	DBP	$5.15 \cdot 10^{-5}$
	TBP	$1.64 \cdot 10^{-5}$
	EDTA	$8.47 \cdot 10^{-4}$
	Citrate	$5.49 \cdot 10^{-4}$
	Oxalate	$2.66 \cdot 10^{-5}$
Q-Solution/Bitumen	without	$2.67 \cdot 10^{-4}$
	DBP	$2.32 \cdot 10^{-3}$
	TBP	$2.08 \cdot 10^{-4}$
	EDTA	$3.73 \cdot 10^{-4}$
	Citrate	$9.71 \cdot 10^{-4}$
	Oxalate	$1.36 \cdot 10^{-4}$

Table 2. Content of actinides in simulated cement waste used for leaching experiments

element	mass / mg/g cement	concentration in leachate / $mol \cdot dm^{-3}$
plutonium	3,029	$6{,}9 \cdot 10^{-9}$
americium	0,020	$6{,}5 \cdot 10^{-9}$

Table 3. Sorption of plutonium on solid NaCl under the influence of complexing organics

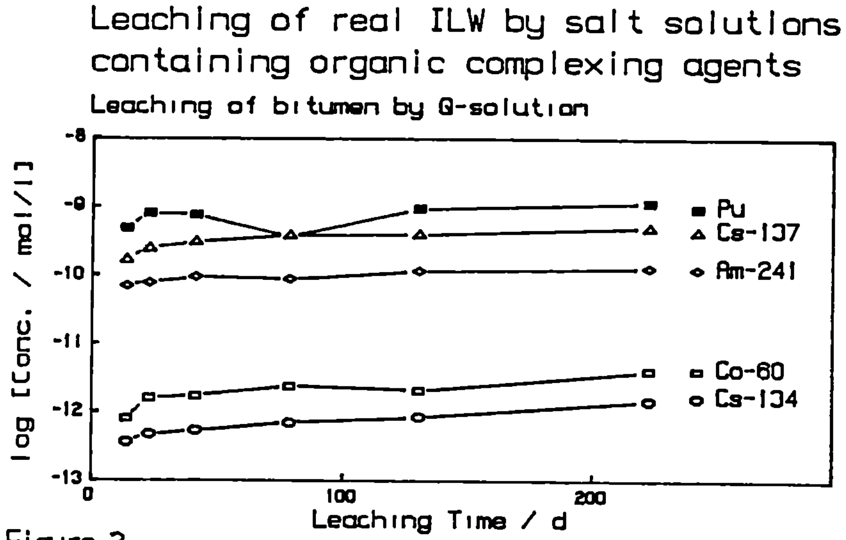
solution	org. ligand	[plutonium] / $mol\cdot dm^{-3}$	volume / cm^3	mass of NaCl / g	Rs / $cm^3\cdot g^{-1}$
NaCl/Cement	DBP	$7.0\cdot10^{-9}$	5	2.00000	3.5
	TBP	$3.8\cdot10^{-9}$	5	2.00281	0.7
	EDTA	$4.8\cdot10^{-8}$	5	2.00211	0.5
	Citrate	$5.4\cdot10^{-7}$	5	2.00284	12.2
	Oxalate	$2.1\cdot10^{-9}$	5	2.00514	0.0
NaCl/Bitumen	DBP	$1.0\cdot10^{-6}$	5	2.00388	5.0
	TBP	$3.6\cdot10^{-8}$	5	2.00102	176.6
	EDTA	$6.5\cdot10^{-6}$	5	2.00248	3.5
	Citrate	$1.2\cdot10^{-5}$	5	2.00042	1.9
	Oxalate	$2.9\cdot10^{-5}$	5	2.00326	6.1
Q-Sol./Cement	DBP	$1.9\cdot10^{-6}$	5	2.00138	0.6
	TBP	$8.5\cdot10^{-8}$	5	2.00138	24.2
	EDTA	$9.0\cdot10^{-7}$	5	2.00446	40.5
	Citrate	$1.8\cdot10^{-6}$	5	2.00073	26.8
	Oxalate	$4.2\cdot10^{-7}$	5	2.00447	50.1
Q-Sol./Bitumen	DBP	$1.6\cdot10^{-6}$	5	2.00595	30.0
	EDTA	$9.3\cdot10^{-6}$	5	2.00334	2.9
	Citrate	$7.8\cdot10^{-6}$	5	2.00185	0.5
	Oxalate	$3.3\cdot10^{-7}$	5	1.99950	48.9



Leaching of real ILW by salt solutions containing organic complexing agents

Leaching of bitumen by saturated NaCl-solution

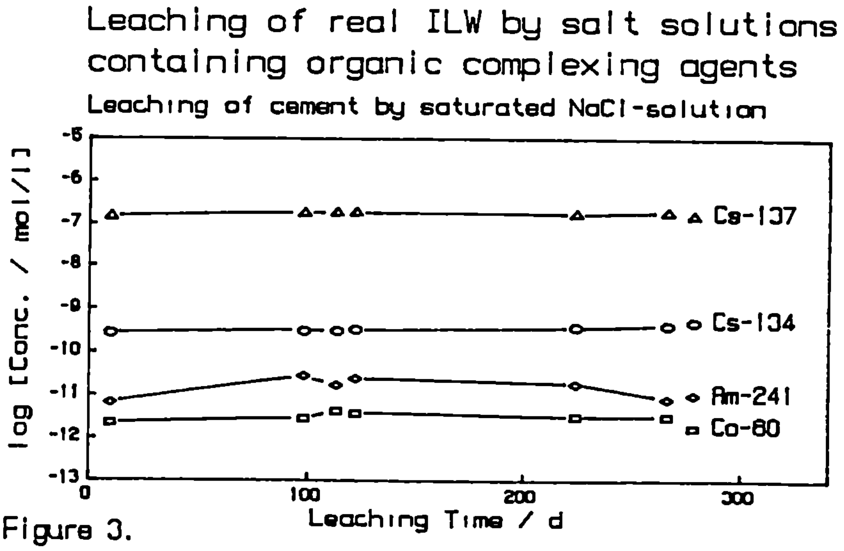
Figure 1.



Leaching of real ILW by salt solutions containing organic complexing agents

Leaching of bitumen by Q-solution

Figure 2.



Leaching of real ILW by salt solutions containing organic complexing agents

Leaching of cement by saturated NaCl-solution

Figure 3.

INVESTIGATION OF LLW AND MLW CEMENT PRODUCTS RESULTING FROM REPROCESSING

Contractor:	Kernforschungszentrum Karlsruhe GmbH Institut für Nukleare Entsorgungstechnik (INE)
Contract Nr.:	FI 1W/0092-D(B)
Duration of contract:	July 1, 1986 - December 31, 1989
Period covered:	January 1, 1988 - December 31, 1988
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 diffusion coefficients for the release from intact and corroded 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

To determine the equilibrium concentrations of relevant radionuclides for the system cemented waste form/salt solutions, laboratory experiments with U, Pu, Am and Np doped samples using Q-brine and NaCl-solution were performed. Additional, the influence of the container material (iron) on the equilibrium concentrations was investigated. To obtain more detailed information about the adsorbtion mechanismen in Q-brine, experiments with Am doped samples were performed, adding different amounts of Ce^{3+}-ions to the system cemented waste form/Q-brine. If the distribution of the radionuclides is based on a true ion exchange mechanismen, the Ce^{3+}-ions can compete with the Am ions for the exchange places and the Am concentration in solution increases. For the experiments using real samples, preparation procedures were tested to separate Pu and U from the leachants thus to be able to perform alpha-spectroscopic measurements of the radionuclides. Experiments were started, to determine the kinetic of the release of Am from cemented waste forms. The leach experiments with inactive and real full scale waste forms were continued.

Progress and results

For U dopes samples, the equilibrium concentrations in Q-brine were determined applying the same experimental procedure as for the experiments with Pu, Am and Np described in the last publications /1, 2 /. The results indicate, that the U-concentration is either determined by a distri-bution equilibrium (U content < 1.e-2 g) or by the solubility of $UO_2(OH)_2$ (U content > 1.e-2 g). The results are given in Figure 1.

To obtain more detailed information on the responsible adsorbtion mechanismen, experiments with Am doped samples were performed, adding different amounts of Ce^{3+} ions to the system cemented waste form/Q-brine. As already mentioned, Ce^{3+} ions can compete with the Am ions, if a true ion exchange mechanismus is responsible for the distribution of Am between the solid waste form and the Q-brine. For a constant Am amount, different amounts of Ce^{3+} (as $Ce(NO)_3$) were added to the system. The results, which are summarized in Table I, indicate, that the Am concentration in solution is indipendent of the added amount of Ce^{3+} ions. Therefore it is not possible, to give a more detailed description of the adsorption mechanismen.

To investigate the influence of the container material on the equilibrium concentration, experiments using Pu, Am and Np doped samples were performed. The container material (iron) can influence the equilibrium concentration by decreasing the redox potential of the system or by an additional adsorption of the radionuclides on the formed corrosion products.

The amount of iron added to the system cemented waste form/salt solution/radionuclide corresponds to the waste form/iron ratio for a real waste package (400 kg waste form, 60 kg container material).

Up to now, no influence of the iron on the equilibrium concentration of the radionuclides used was detected when the amount of the added radionuclide corresponds to the values characteristic for real samples.

To determine the equilibrium concentrations of Pu and U in experiments using real samples, the radionuclides have to be separated from the accompanying fission products and the other actinides. For this reason, separation procedures known from environmental analysis were tested under the conditions given by the saturated salt solution. In both cases it was possible to obtain samples, prepared by ion exchange or extraction technics, which could be measured by alpha-spectroscopy. Figure 2 show the obtained Pu-spectrum from a real sample. The Pu-value corresponds very well with the Pu values obtained from the experiments with doped samples.

In addition to the determination of the equilibrium concentrations experiments were performed to investigate the kinetic of the radionuclide release. Am doped cylindrical samples were leached in Q-brine and NaCl solution and the leachant was renewed daily. From the time dependence of the Am release the diffusion coefficient was calculated(2.E-17m^{2}s-1). Using this value, the Am release from full scale waste forms for the time period until the equilibrium concentration is reached, can be calculated.

The full scale leach experiments with inactive and real samples were continued. Figure 3 show the Cs release for the inactive samples. The increase of the Cs release after a experimental period of about 2 years is do to the corrosion of the samples. For the real samples, up to now, only Cs was detected in the Q brine. The results are in agreement with the results from the inactive samples.

References

/1/ P. VEJMELKA, G. Rudolph, W. Kluger
EG-Vertrag Nr. FI 1W-0092-D(B), Halbjahresbericht 1988

/2/ P. VEJMELKA, R. Köster, G. Rudolph
Source term evaluation for actinide elements in the system ILW-cemented waste form/salt brines
IAEA/CEC International Symposium on the Management of Low- and Intermediate Level Radioactive Waste
Stockholm, May 16 - 20 (1988)

Table I Am equlibrium concentrations in the system cemented waste form/Q brine with different amounts of Ce^{3+} ions (2g cemented waste form, 30 ml Q brine, RT, 1,2 E-7g Am)

Ce^{3+}-amount (g)	Am-241 concentration (Moles/l)
-	3,5 E-10
1,0 E-1	1,8 E-10
1,0 E-2	1,4 E-10
1,0 E-3	3,9 E-10
1,0 E-4	3,5 E-10

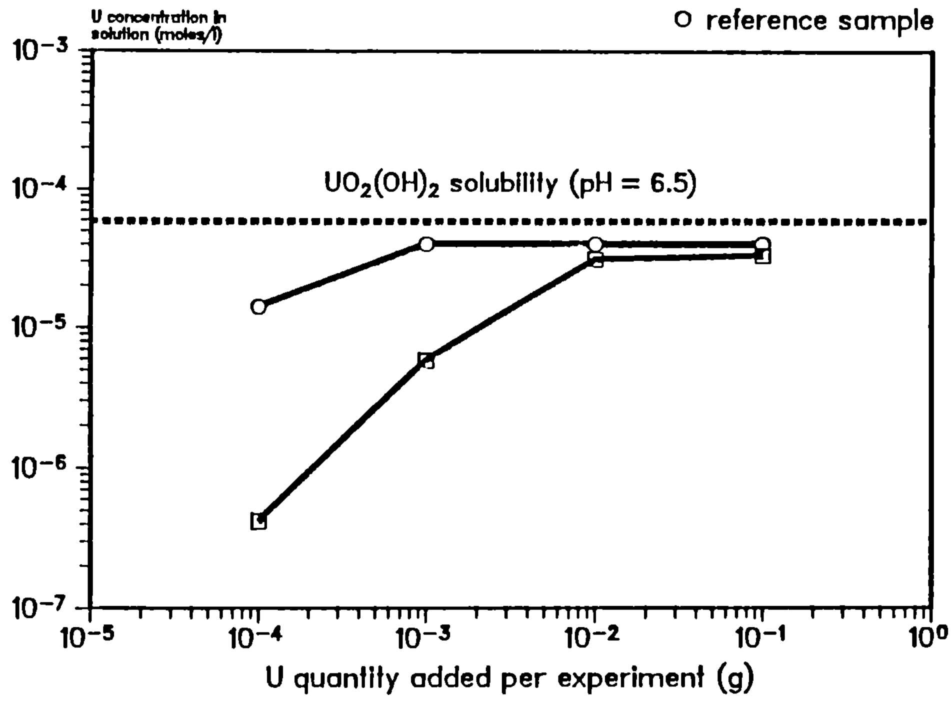


Figure 1: U equilibrium concentration in the system cemented waste form/Q brine with different amounts of U (2g cemented waste form, 30 ml Q brine, RT)

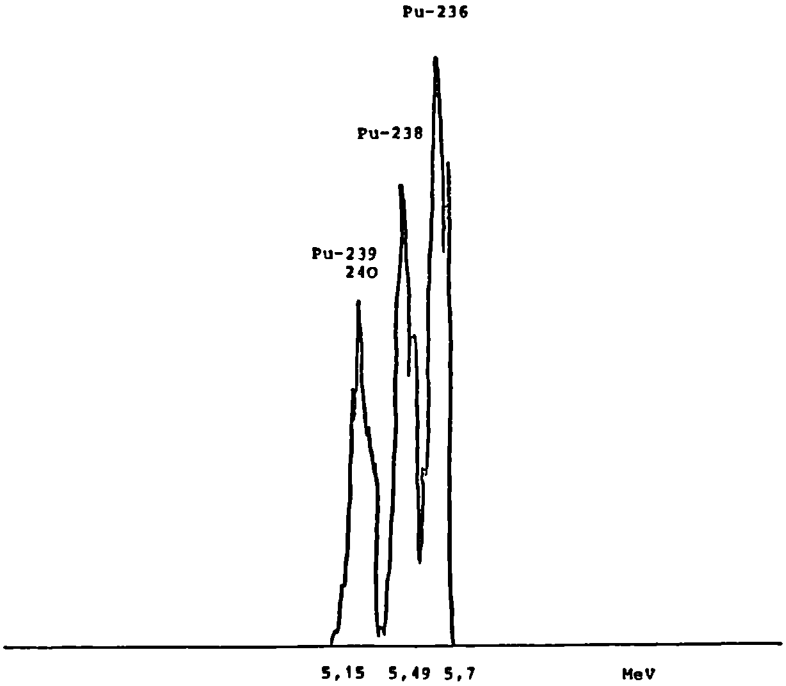


Figure 2: Typical alpha-Spectrum for Pu separated from leachants from real samples

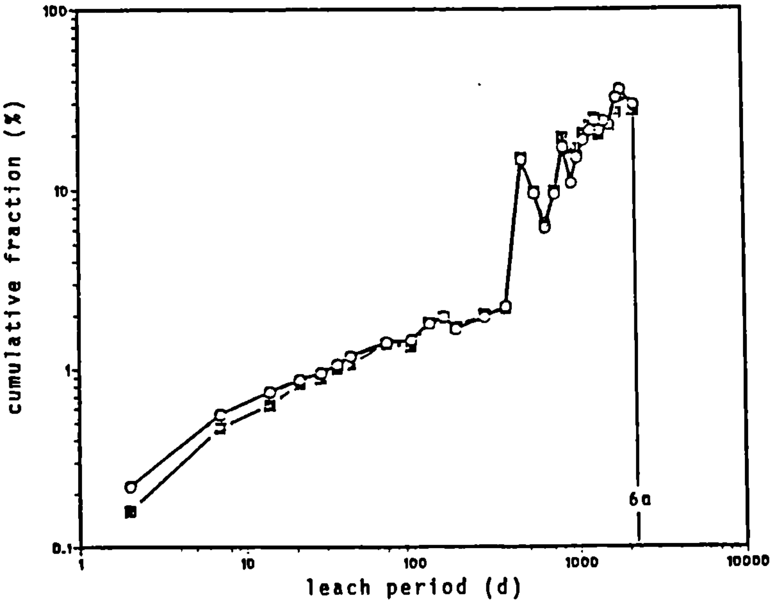


Figure 3: Cs release from inactive full scale samples during leaching with Q brine (40oC, S/V = 0,096 cm-1)

Physico-chemical characterization of bituminized Eurochemic medium level waste

Contractor: S.C.K./C.E.N. Mol, Belgium
Contract N°: FI1W/0094
Duration of Contract: 1/08/1986-31/12/1989
Period covered: 1/01/1988-31/12/1988
Project Leader: P.Ph. Van Iseghem

A. Objectives and Scope

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

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

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

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

B. Work Programme

B.1. Effect of specimen size

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

B.2. Effect of pressure

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

B.3. Ageing behaviour

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

C. Progress of work and obtained results

State of advancement

The corrosion tests on the inactive simulates are near to be finished. The data show that leaching is not affected by the specimen size; the soluble salts ($NaNO_3$, $CaSO_4$) are leached through a diffusion controlled mechanism, while the leaching of the other waste compounds is solubility limited.

The corrosion tests on the active Eurobitum samples at ambient pressure are underway since more than half a year. The first results indicate larger swelling than for the simulate samples, but the leaching of $NaNO_3$ is quite similar; the leaching of the radionuclides is very incongruent. The corrosion tests at repository like pressure are underway since November 1988; no data are available yet.

All corrosion tests will be finished within the contractual period. As foreseen, a third data point for the ageing behaviour will be analysed in the second half of 1989 (6.5 years ageing).

Effect of specimen size on the corrosion and swelling behaviour (inactive tests)

Data until one year of corrosion (the longest duration) are complete. The corrosion tests in either distilled water or a 100 gl^{-1} clay/water mixture 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:

- In both media normalized elemental mass losses (NL_i) for the soluble salts (NaO_3, $CaSO_4$) increase with time. The less soluble components (U, Fe, Zr, Mn) do also present increasing NL_i values, although they are much smaller than those for the soluble salts (suggesting incongruent leaching of the waste constituents), and for the shorter durations their concentration is often below detection limit.
- The leaching of $NaNO_3$ and $CaSO_4$ is diffusion controlled. The effective diffusion coefficient is between 2.5 and 2.7 x 10^{-9} $cm^2 sec^{-1}$, which is rather high compared with current data for bitumen waste forms.
  The dissolved thickness for $NaNO_3$ after one year corrosion, based on the NL_i data, is about 7 mm. The leaching of the less soluble compounds seems to be mainly solubility controlled.
- The leaching data are independent on the sample volume (ranging from 0.75 ml to 11 l); swelling data after one year do present some dependence on sample volume: 35 % for the smallest, 2.5 % for the largest sample.
- The presence of clay in the solution does not affect the leaching of the soluble salts, but does so for the insoluble compounds: increased leaching of U (about 10 times), decreased leaching of Fe and Mn.

To link the data from those inactive tests with the active tests (see next point), inactive tests are being performed on small (0.75 ml) and intermediate (500 ml) samples, in synthetic interstitial claywater (SIC) and a clay/SIC mixture (CCSICM); the same media are used indeed in the corrosion tests on the active bitumen samples. One year duration (the final data point) will be reached in January 89.

Effect of pressure on the corrosion and swelling behaviour (active tests)

Active Eurobitum samples of about 0.86 ml each are exposed to corrosion in either SIC or CCSICM since March 88 (ambient pressure) or November 88 (repository like pressure). Data at ambient pressure in SIC and CCSICM are available until 180 d duration. The first data at repository like pressure will be obtained in February 89 (90 d duration; the 14 and 40 d tests are to be performed yet).

The preliminary conclusions from the active test in SIC are:

- The leaching of $NaNO_3$ (the main waste constituent) proceeds almost analogous as for the inactive simulate. Ca leaches slower compared with the simulate, due to the important SO_4 content of the SIC (about 5400 mgl^{-1}).
- The activity release is strongly incongruent; the α emitters and Cs are leached for a small fraction only (< 0.1, < 0.02 % of the inventory, resp.), being constant with time. Co and Sr are further leached with time; after 180 days 0.4 % Co and 17 % Sr are dissolved. This shows that the retention capacity of Eurobitum for the radionuclides is very inhomogeneous (certainly for the well soluble βγ emitters).
- The samples do swell as much as 120 % (180 days corrosion), which is considerably more than for the simulates. This might be (partly?) due to the larger hardness of the simulates; see, e.g. for the penetration, 20 (active samples) and 13 x 10^{-1} mm (simulates). There is no evidence as yet, that this increased swelling would influence the leaching behaviour of the soluble salts (e.g., $NaNO_3$).

When adding clay to the leachant ("CCSICM"), the main conclusion is that the clay does not induce larger corrosion of the bitumen (this is in strong contrast with the corrosion of waste glass). The leaching of the radionuclides proceeds as follows, compared with the leaching in SIC: no change for the α emitters and Cs, and a reduced leaching for Sr and Co. The leaching of $NaNO_3$ is similar initially, but the increase with time is slower (compared with SIC). The swelling during the corrosion is similar to SIC.

List of publications and lectures

(1) Physico-chemical characterization of bituminized Eurochemic medium-level waste - Annual report 1987 (R2747).
Presented at the CEC progress meeting for task 3, sections 1+5 (Mol, March 1988).

(2) Physico-chemical characterization of bituminized Eurochemic medium-level waste - Semestrial progress report January-June 1988, presented at the CEC progress meeting for task 3, sections 1+5 (Harwell, September 1988).

(3) R. De Batist et al., The Belgian low- and intermediate level waste management programme, presented at the IAEA Second Research Coordination Meeting on Evaluation of Low and Intermediate Level Radioactive Solidified Waste Forms and Packages, Beijing (April 1988).

(4) P. Van Iseghem et al., Low and medium level waste forms: guidelines and related research, presented at the IAEA/CEC Int. Symp. on Management of Low and Intermediate Level Radioactive Wastes, Stockholm, may 1988.

FULL SCALE LEACHING TESTS, LYSIMETER TESTS, SCALE EFFECT

Contractor : CEA CEN CADARACHE - FRANCE
Contract N° : FI1W/0095 Task 1/5
Duration of contract : From August 86 to December 89
Period covered : January 88 - December 88
Project leader : A. SAAS
Executant of task 1 : J.C. NOMINE, CEN SACLAY

A) OBJECTIVES 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 leachiability of radioactive block.

B) WORK PROGRAMME

B1) Knowledge of the transfer of radionuclides by leaching between full, scale packages coming from the producer's facilities.

B2) Laboratory lysimetrie tests.

B3) Study of the scale effect for a cement waste form. Possibilities of extrapolation from laboratory samples to full size active packages.

C) PROGRESS OF WORK AND OBTAINED RESULTS

During the period January - December 1988, substantial results on the above mentionned objectives have been obtained, specially in the field of full size leaching tests.

Full scale leaching tests

Full scale leaching tests, using a static method with or with not leachant renewal has been performed.

- Experiments has been stopped for some blocks
- Leaching process is going on for others blocks

1.1. Cement alpha concentrates, after 455 days. The annual fractions leached, for blocks N°3 and 4 were respectively less than 1.1×10^{-4} and 3.2×10^{-5} for ^{239}Pu and less than 5×10^{-5} and 9×10^{-5} for ^{241}Am. No major degradation has been observed.

1.2. Cement alpha sludges concentrates, after 455 days. Similar conclusions can be taken on these blocks ; the average annual fractions leached for ^{239}Pu and ^{241}Am are respectively less than 1×10^{-5} and 1×10^{-4}.

1.3. Bitumen alpha, beta gamma concentrates after 455 days. The annual fraction leached, for block N°1 and 2 are respectively of :

1×10^{-5}, 3×10^{-4}, 4×10^{-3} for ^{137}Cs, ^{90}Sr, ^{60}Co ; for ^{239}Pu and ^{241}Am these values are of 4×10^{-5} and 5×10^{-5} ; a large amount of salts ($NaNO_3$) have been leached and a swelling effect corresponding to an increase of about 15% in volume has been observed.

1.4. Cement alpha beta gamma concentrate from KfK

No major change in the leachability, when the new renewal of leachant has been applied, has been observed ; but to day the 200 l drum is largely fractured.

1.5. Laboratory lysimeter tests

Progress of laboratory lysimetrer tests has not been possible during 1988, but will resume in 1989.

1.6. Scale effect

This study has been in progress during 1988 but without publishing new results ; final report after more of 1000 days of leaching is in preparation.

BITUMEN AND POLYMER CHARACTERIZATION

Contractor : CEA CEN CADARACHE - FRANCE
Contract N° : FI1W/0095 Task 2/5
Duration of contract : From August 86 to December 89
Period covered : January 88 - December 88
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

I. Biodegradation studies - Mme N. LANGOMAZINO - CEN CADARACHE

The scope of these studies is the assessement of hydrocarbons biodegradation.

The quantitative evaluation of the biodegradation is mesured by the CO_2 production.

The influence of the content of salts in the embedded waste is also studied.

II. Leaching studies - C. COURTOIS - H. VIDAL - CEN CADARACHE

The scope of these leaching studies is the :

- 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)

III. 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 PROGRAMM

I. Biodegradation studies Mme N. LANGOMAZINO
   - B1.Screening of microorganisms able to degrade hydrocarbons
   - B2.Qualitative evaluation of biodegradation of bitumen MR 90/40
   - B3.Quantitative evaluation of biodegradation of bitumen MR 90/40 and waste forms by measure of CO2
   - B4.Chemical evolution of bitumen after attack of microorganisms
   - B5.Influence of waste forms salts on the rate of biodegradation and microbial metabolism.

II. Leaching studies - C. COURTOIS - H. VIDAL
   - B1.Manufacturing of the samples (bitumen and polymer)
   - B2.Initial analysis (bitumen and polymer)
   - B3.Work survey

III. Diffusion coefficient studies - M. DE TASSIGNY

B1.Bibliography

Bibliographic state of the research in the field of ageing has been done for spectroscopic methods.

B2.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.Study of morphologic degradation

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

B4.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

I. Biodegradation studies - Mme LANGOMAZINO

The measurement of the biodegradation of a simple organic compound is made among many other parameters, by measuring the biomass formed from the substrate, and by monitoring the loss of the substrate. It has been demonstrated that bitumen is a complex compound, and its biodegradability is therefore more difficult to evaluate. The insoluble nature of the compound makes it difficult to measure the biomass, and the phenomenon of microorganism adsorption on the bitumen occurs. The presence of various highly complex hydrocarbons, many of which are known to be resistant to bacterial attack, make impossible to demonstrate any significant loss of sustrate weight.

Therefore, in order to evaluate the resistance of bitumen coated material to microorganism action, it is necessary to measure bitumen biotransformations and bioassimilation the radionuclide retention capacities of bitumen.

Degradation of hydrocarbons due to microbe attack takes place, either aerobically or anaerobically on formation of CO2 and the electron collector is oxygen and nitrate or sulfate respectively. During aerobic metabolism of complex hydrocarbons in the bitumen, a large number of intermediate or metabolites are produced (alcohols, cetones, fatty acids) which are very difficult to demonstrate and which require the use of sophisticated techniques such as chromatography coupled with mass spectrometry. Measurement of the CO2 produced only is inadequate, but is the easiest measurement that can be done to approach a quantification of the biodegradation of bitumen.

Therefore, a qualitative evaluation of these biodegradation can be perform with rapid and simple methods :

Bases on standards ASTM G21 and G22 modified in the laboratory by the introduction of microorganisms which are more appropriate to degradation of the material being tested, the resistance to biodegradation of Mexphalte R 90/40 bitumen, La hague MR 90/40 STE 3 sludge coated materials, M80/100 and La Hague MR 90/40 STE 3 sludge coated materials can be determinded.

MR 90/40 bitumen (blown bitumen) contains more saturated hydrocarbons and less polar compounds than M80/100 bitumen (directly distilled bitumen).

The results obtained are valid for the specific experimental conditions in the standard, but the restrictive nature of the standard can lead to serious errors of interpretation. Therefore the results and the conclusions obtained related to the biodegradability of the tested materials should be treated with a great deal of caution.

The modifications made to standards ASTM G21 and G22 make it possible to define the resistance to degradation by yeasts, in addition to bacteria and fungi. based on the standards, we can state that :

- Bitumen MR 90/40 is not resistant to bacterial attack. Nine strains out of eleven gave a positive response.

- On the other hand, Bitumen M 80/100 appears to be resistant to bacterial attack, since none of the strains tested lead to any significant microbe development.

- La Hague STE 3 MR90/40 sludge coated materials could be considered to be unbiodegradable to the extent that the salts present released in the environment of the culture provoke a partial inhibition of bacterial growth. M80/100 coated material is to bacterial biodegradation.

The bacteria tests selected use the bacteria which gave the highest bacterial growth rates on bitumen MR 90/40, namely :
Acinetobacter calcoaceticus, Nocardia coeliaca, Arthrobacter sp, mixed culture isolated from a bitumen site.

The modifications made to the test are very important since it can be observed that the test using the bacterial strain Pseudomonas aeruginosa, recommended by standard ASTM G22 gave a negative response on bitumen MR 90/40, and interpretation contradictory to that drawn from the other strains of bacteria used.

The fungi recommended by standard ASTM G21 all gave significant results for a material such as bitumen.

Bitumen MR 90/40 is considered to be not resistant to fungus attack, and for most fungi tested its biodegradability is equal to the maximum degree 4 in the classification given never exceeds degree 2.

MR 90/40 coated material is resistant to fungicidal invasion, as a result of migration of its salts into the culture environment.

The behavior of MR 90/40 and 80/100 bitumen and materials coated with them under yeast attack is identical to that observed for bacteria and fungi.

Inhibition of microbe growth by the salts present in the coated materials is an interesting point, but it will be necessary to carry out more detailed tests in order to confirm these results. The biodegradability response or the resistance of a bitumen to the microorganism tests must be linked to additional tests of the physical, chemical and microbiological tests, depending on the required information.

II. Leaching studies - C. COURTOIS - H. VIDAL

II.1. WASTES EMBEDDED IN BITUMEN (B.3.)

Wastes are chemical precipitation sludges issued form reprocessing plant of La Hague and embedded in blown bitumen type 90/40.

Leaching tests are conducted on cylindrical samples (⌀ 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 380 days are available and have been given last september.

Leach test is kept on and next sampling is scheduled within three months.

II.2. WASTES EMBEDDED IN POLYMERS (B.3.)

These studies are set on ion exchangers embedded in an epoxide thermosetting resin.

Leaching tests are conducted on cylindric samples (⌀ 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 year) are available and balance is being set up : Leach rate are in accordance to experted values.

Leach test is definitively stopped.

III. Diffusion coefficient studies - M. DE TASSIGNY

During 1988 the photo degradation process has been characterised by using Raman spectroscopy especially for studing the change of the organic functions C-C and C=C. This last technic is yet perfectible but cannot give the hoped results because of fluorescences which mask the interesting wavelenghts. This spectroscopic evaluation completes the two previous studies : UV-VIS spectroscopy and IR spectroscopy made in 1987.

Another method of characterization of resins has been intended in 1988 for studiing the diffusion of ions in small thickness ($< 50\ \mu$ m). If some results have been already given by laser probe or by castaing microprobe, another more sensitive method has been tried : secondary ions mass spectrometry gives the possibility of determination of diffusion of ions in the first layers of the polymer ($< 50\ \mu$ m). First examinations will be made with cesium, followed by strontium.

SPECIATION OF TRANSURANIUM ELEMENTS IN LEACHATES

Contractor : CEA CEN CADARACHE - FRANCE
Contract N° : FI1W/0095 Task 3/5
Duration of contract : From August 86 - to December 89
Period covered : January 88 - December 88
Project leader : A. SAAS
Executant of task 3 : Mme STAMMOSE - CEN FAR

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, colloides...) need a particular attention. The aim of this program is to improve speciation methods soon used in the laboratory and to set up new procedures giving more precise information (size, charge) on the different species present in the leachates.

B) WORK PROGRAM

B1) Setting up ultracentrifugation technique to compare results obtained with this method to those obtained with filtration and ultrafiltration.

B2) test a new speciation method of plutonium according to its oxydation degrees.

B3) Compare the leaching in 3 different conditions of temperature and pressure of concrete blocks doped with ^{239}Pu and ^{137}Cs.

B4) Study of the temperature influence on the distribution of plutonium between the soluble and the insoluble parts of the leachates.

C) PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

First essays of ultracentrifugation experiments have been made on concrete leachates. The valency IV of plutonium complexed by orange xylenol or arsenazo III is well separated from the solution either by ultrafiltration or exclusion chromatography with a rate around 90 %. The leaching of 3 identical blocks doped with plutonium and cesium is finished. The temperature seems to have minor importance on the leaching of plutonium while the pressure induces an enhancement of the releasing of plutonium by the block. At higher temperature, the plutonium is essentially in an insoluble form.

Progress and results

C1) The ultracentrifugation experiments allow us to isolate small insoluble forms. The size of these particles settled in the tubes depend on the viscosity of the medium, the type of rotor, the rotation speed and the duration of the experiment. The determination of the quantity of plutonium present in the 2 phases (deposed and soluble) allow us to study the distribution of the plutonium associated to particles of different size.

C2) A new speciation method founded on a selective complexation of plutonium IV is tested. Orange xylenol is a selective complexant of Pu IV, while arsenazo III reacts with all the valency states of plutonium. Then, the complexes are then separated from the solution by ultrafiltration (UF) or exclusion chromatography (GPC). the different rates of reaction for Pu IV are given in the table 1.

The results show that the two methods are quite god but the ultrafiltration technique is more easily usable. Similar experiments will be made with others oxydation degrees, first with the valence VI of plutonium.

C3) We have studied the releasing of plutonium by concrete blocks in 3 different conditions :

- 20°C : 1 atm
- 70°C : 1 atm
- 70°C : 100 atm

The different results are given in the table 2. The leaching curves are presented on the figure 1. They show that an increase of the temperature does not induce a significative enhancement of the releasing of plutonium. For a higher pressure (100 bar), the leaching of plutonium seems to be more important than for a pressure of one bar. This result should be confirmed by complementary experiment.

C4) The tables 3 and 4 present the speciation on some leachates obtained for a pressure of 1 bar.

The quantity of plutonium sorbed on the containers walls is important for the 2 series of experiments (15 % - 85 %). A study of the desorbtion of the plutonium has been made, and the results show that several rincing are necessary to reduce the activity remaining on the containers walls. The proportion of insoluble forms is more important in the solutions resulting from the leaching at 70°C than in the solutions obtained at 20°C. An increase of temperature induce probably an incresase of the kinetic of the polymerisation.

A more detailed speciation has been made on 4 leachates (3 obtained at ordinary temperature, and 1 obtained at 70°C). The results presented in the table 4 show that the majority of plutonium is on particles which size is greater than 0,22 µm.

	orange xylenol	arsenazo III
G.P.C.	91	99
UF	97	99

Table 1 : Retention of Pu-complexe in % of initial activity

sequence (days)	20°C ; 1 bar		70°C ; 1 bar		70°C ; 100 bars	
	A_1	Σ_1	A_1	Σ_1	A_1	Σ_1
1	97.3	97.3	71.9	71.9	95	95
2	12.9	110	15.4	87.3	56.3	151
7	10.8	121	4.16	91.5	35.8	187
13					19.6	207
15	7.3	128	2.6	94.1		
23	4	132	4.16	98.2		
27					12.9	220
37	1.6	134	1.5	99.7		
41					19	239
55					11	250
58	1.8	136	1.3	101		
76					7.8	258
93	2.4	138	0.9	102		
104					15.4	273
127	5.3	143	1.7	104		
153	3.9	147	0.4	104		

Table 2 : Leaching of plutonium (results in 10^{-6} μCi)

Day	Insoluble (%)	Soluble (%)	Adsorbed (%)*	Total activity ($\times 10^4$ µCi)
1	40.7	2.7	56.6	97.3
2	80.6	3.45	15.5	12.9
7	60.3	.6	39.1	10.8
15	56	2.6	41.4	7.3
23	61.3	•	38.7	4.01
37	21.3	51	27.7	1.6
58	21.7	26.4	58.2	1.7
93	21.8	30.8	47.4	2.4
127	32	25.4	41.5	5.32
153	57	10	33	3.4

Table 3 : Distribution of plutonium in leachates obtained at 20°C and 1 bar

* plutonium adsorbed on the containers walls

Day	Insoluble (%)	Soluble (%)	Adsorbed (%)	Total activity ($\times 10^4$ Ci)
1	74.4	2	23.6	71.9
2	73.4	3.5	23.1	15.4
7	33.4	4.1	62.5	4.16
15	75.5	2.6	21.9	2.6
23	15.7	0.6	83.7	4.2
37	16.4	5.2	78.4	1.5
58	39	5.1	55.9	1.3
93	17	2.6	80	0.9
127	35.6	6.4	58	1.7
153	9.9	5.9	84.9	0.4

Table 4 : Distribution of plutonium in leachates obtained at 70°C and 1 bar

	244 d - 20°C	266 d - 20°C	292 d - 20°C	279 d - 70°C
Filter 0.22μm	35	9.5	1.8	0.8
Ultrafilter XM 300	ND	0.1	ND	ND
Utrafilter XM 50	0.3	0.3	ND	ND
Ultrafilter YM 10	ND	ND	0.3	ND
Ultrafilter YC 05	1.3	0.4	0.3	ND
Sum of insoluble	36.6	10.3	2.4	0.8
Sorbed Pu	53	10.2	4.7	26
Soluble Pu	11.5	21.7	4	0.02
Total activity	101	42.2	10.1	26.8

Table 5 : Repartition of plutonium between the different species (results in 10^{-5} μCi)

ND non detectable

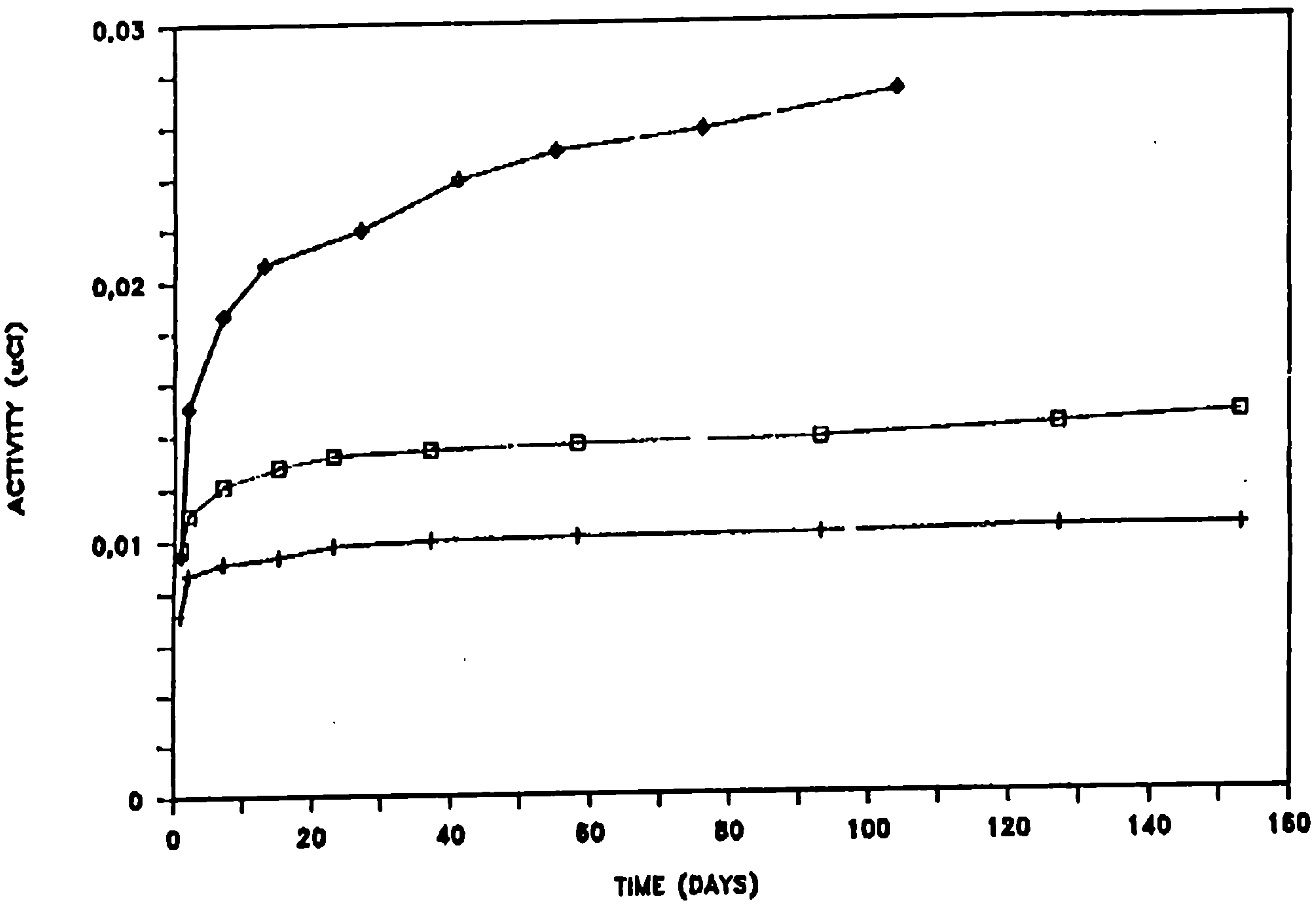


Figure 1 : Leaching of plutonium in 3 different conditions

- ⊟ 20°C - 1 bar
- + 70°C - 1 bar
- ◆ 70°C - 100 bars

EMBEDDED WASTES AND LEACHATES ANALYSIS

Contractor : CEA CEN CADARACHE - FRANCE
Contract N° : FI1W/0095 Task 4/5
Duration of contract : From August 86 - to December 89
Period covered : January 88 - December 88
Project leader : A. SAAS
Executant of task 4 : M. A. RAYMOND - 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 PROGRAM

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 solubilization 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 ABTAINED RESULTS

State of advancement

In 1988 we developed three new physicochemical procedures for the measurement of ^{99}Tc (work program B2) and we carried out the complete digestion of cement and bitumen-embedded nuclear wastes (work programs B3 and B4).

The general work progress status is as follows :

B1, B2, B3, B4, B6 are completed

B5 is reoriented towards low-level analyses in leachates and is progressing normally.

Progress and results

1. Measurement of ^{99}Tc

   ^{99}Tc is a high yield fission product with a long half life (2.1×10^5 years). As a pure beta emitter, this isotope has to be isolated before counting. Counting should be done by liquid scintillation or by beta counting with a proportional counter after electroplating.

   Because of the relatively low specific activity (630 Bq/ µg) of ^{99}Tc, we found it interesting to investigate the applicability of spectrochemical methods such as inductively coupled plasma emission spectrometry and X-ray fluorescence spectrometry.

   With a high-resolution ICP spectrometer, the first technique allowed us to reach a detection limit in pure water around 1 µg/l (630 Bq/l) without any preconcentration.

   The X-ray fluorescence technique was developed by using a preconcentration step on 46 mm disk, either by precipitation with tetraphenylarsonium chloride or by ion-exchange collection of TcO_4^- anions.

   The detection limit was found around 0.3 µ g/l (200 Bq/l).

   Both the I.C.P. and the X-ray fluorescence techniques were compared to a conventional radiochemical procedure on a synthetic effluent and no significative discrepancy of the results was observed at the 10 µg/l (6 KBq/l) level.

2. Solubilization of cement and bitumen-embedded nuclear wastes

The direct measurement of alpha and beta emitters in these matrices is not feasible so that one digestion step is required in order to operate on homogeneous liquid solutions.

2.a. Cement

The solubilization of real cement samples (5 to 10 grams) was performed by using strong acids like aqua regia and hydrofluoric acid at atmospheric pressure. The complete dissolution time was around 3-5 hours. The radiochemical measurements performed on both embedded evaporation concentrate and sludge illustrate the good reproducibility of the described procedure and the absence of significant loss of any detected radionuclide.

2.b. Bitumen

The total solubilization of samples (3 to 5 grams) from real bitumen-embedded sludges was performed at atmospheric pressure by successively using 3 strong oxidizing reagents, fuming nitric acid, perchloric acid and hydrogen peroxide. In the case where some insoluble species remained, an extra step with hydrofluoric acid was added.

The application of the procedure to a real bitumen-embedded evaporator concentrate gave results in good agreement with those obtained by direct non-destructive gamma-ray spectrometry or those derived from the analysis of the concentrate prior to embedding.

2.c. Microwave digestion

Because of the relatively long digestion times required by the developed procedures, we found it interesting to test a newly available technique, microwave solubilization.

Unfortunately, the commercial instrument we used was not found adapted to the solubilization of cement or bitumen matrices.

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 first year of activity all the contractual planned actions have been performed.

The ash selection, due to the difficulties connected with the transport of radioactive wastes, was restricted only to the Italian ashes coming from the inceneration of the real radioactive Caorso wastes.

Two ash types have been selected and they have been named Nust 1 and Nust 2. The Nust 1 ash comes from the incineration of the exhausted ion exchange resins already conditioned in the past in urea-formaldehyde. The Nust 2 ash comes from the incineration of the same materials as the Nust 1 mixed with ordinary nuclear power plant solid radwastes.

On the two ash types the following analysis have been performed:

- density
- particle size distribution
- gamma radiometric analysis
- nitric, ammoniacal and organic nitrogen
- Atomic Absorpition metal analysis
- ash cementation at 1/2,1/3,1/4 ash/cement ratios
- characterization of the obtained samples by means of:
  mechanical strength after 28 days of normal curing;
  setting time according to the Vicat method;
  thermal evolution at the sample center in adiabatic conditions;
- investigation on the swelling phenomenon and pretreatment proposal
- characterization of the pretreated cemented ash.

Progress and results

Density measurements

The density measures results are reported in the Table I. The fill density is meant here as the density obtained filling a 500 cc gratuated cylinder without any settlement and weighing the obtained ash volume. The tap density on the contrary is obtained taping the ash with the special apparatus required by the ASTM B 527-81 standard method/2/. The Nust 1 and Nust 2 ashes show quite different density values due to the different composition of the initial wastes.

Particle size distribution.

The ash particle size distribution has been determined by sieving according to the ASTM C136-82 standard method /3/. The results are shown in the Table II.

Gamma radiometric analysis.

The gamma-rays spectrometric determinations have been carried out on both ashes using a SILENA Mod. LIVIUS Multichannel Analyzer connected to a PGT Ge detector. The reference standard solution employed for the measures is produced by Amersham Company and is supplied with calibration certificate. The results are shown in the Table III.

Both ashes have very low radioactivity concentration wich in turn are 35-40 times higher than in the original waste due to the volume reduction. 90% of the radioactivity is due to the Co60 produced mostly by neutron activation in the reactor.

Nitric, ammoniacal and organic nitrogen analysis.

All these analysis have been carried out according to the sludges analysis methods established by the Italian Institute for Research on the Waters/4/.

The analysis results are shown in the Table IV. The total and ammoniacal nitrogen content in the Nust 1 ash is 7 times higher than in the Nust 2 ash: also in this case the difference can be explained observing that the Nust 1 ash comes from the Ion exchange resins incineration alone, while the Nust 2 ash was obtained from the incineration of Ion exchange resins mixed with ordinary solid wastes.

Atomic absorption metal analysis.

The AA analysis has been carried out by a IL mod. 257 instrument. The ash dissolution was performed by fusion with lithium metaborate followed by dissolution of the melt in nitric acid /5/. The concentration of the following chemical elements has been determined: Si, Al, Fe, Ca, Na, Cu, Zn, Mg, Cr, Pb, Ni, Ag, Mo, Co. As shown in the Table V Si, Al and Fe concentrations are the highest. The different concentrations of these elements found in the two ash types can be explained by the different ash origin.

Ash cementation and cemented ash characterization.

The ashes were immobilized with Pozzolanic 325 cement at 1/2, 1/3, 1/4 ash cement ratios using the minimum water amount needed to obtain a workable mixture.

In any case the water used was in the range 0.4÷0.5 water/cement ratio.

The characterization results summarized in the Table VI show very few differences between the different mixtures. The values obtained are acceptable in comparison with that obtained with the pozzolanic cement without waste shown in the same Table VI.

Investigation on the swelling phenomenon and pretreatment proposal.

In order to understand the origin of the swelling phenomenon a chromatographic analysis has been carried out on the gases collected from the cemented ashes during the setting. The analysis has shown the presence in them of remarkable H_2 concentrations. Moreover the microscopic analysis has shown the presence of small metallic pieces in the ashes. in order to demostrate 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. Only in the case of Aluminum metal powder during the cementation an important H_2 gas evolution was detected, 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.

Therefore it was established that in order to avoid the swelling effect, the ashes should be contacted, before the cementation, for more than 24 hours with a 0.01 M NaOH solution. This solution will then replace the water needed for cementation.

Some samples obtained by the cementation of the Nust 2 ash after the above-mentioned pretreatment have shown the characteristics given in Table VII.

REFERENCES.

/1/ CEN-SGK MOL Private communication.
/2/ ASTM b 527-81 "STANDARD TEST METHOD FOR TAP DENSITY..."
/3/ ASTM C 136-82 "STANDARD METHOD FOR SIEVE ANALYSIS OF FINE AND COARSE AGGREGATE".
/4/ I.R.S.A. "METODI ANALITICI PER I FANGHI", CNR. 1985. ROMA... Quaderno n. 64 Vol. 3.
/5/ B. WELZ. "SPETTROSCOPIA DI ASSORBIMENTO ATOMICO". Pag.261-62. ETAS LIBRI. 1976. MILANO

Table I The density of the Nust 1 and Nust 2 ashes.

Ash type	Fill density (gr/cc)	Tap density (gr/cc)
Nust 1/85	0.57±0.02	0.80±0.03
Nust 2/86	0.86±0.02	1.10±0.02

Table II The particle size distribution of the Nust 1 and Nust 2 ashes.

	Nust 1/85 Ash		Nust 2/86 Ash	
Particle size Mesh	Weight % in Each Fraction	Accumulated Weight %	Weight % in Each Fraction	Accumulated Weight %
<3.5	11.9	11.9	4.8	4.8
3.5-5	6.2	18.1	4.1	8.9
5-10	13.2	31.3	10.3	19.2
10-18	10.6	41.9	12.2	31.4
18-35	8.7	50.6	13.8	45.2
35-60	6.2	56.8	18.9	64.1
60-120	10.7	67.5	13.8	77.9
120-230	14.7	82.2	18.0	95.9
230-325	9.4	91.6	3.9	99.8
>325	8.4	100.0	0.2	100.0

Table III Results of gamma-ray measurements on Nust 1 and Nust 2 ashes.

	Nust 1/85 Ash		Nust 2/86 Ash	
Identified Nuclide	Specific activity (µCi/kg)	Err. %	Specific activity (µCi/kg)	Err. %
Th234	8.5	3.8	Not Detect.	
U235	0.7	1.6	Not Detect.	
Sb125	0.7	2.3	0.4	9.8
Cs134	0.2	10.1	Not Detect.	
Cs137	1.2	2.5	Not Detect.	
Zn65	6.1	32.9	Not Detect.	
Mn54	0.8	4.7	0.3	6.4
Co60	40.0	0.2	20.8	0.3

Table IV Nitrogen analysis results on the Nust 1 and Nust 2 ashes.

	Nust 1/85 Ash	Nust 2/86 Ash
Total Nitrogen	0.71%±0.05%	0.11%±0.008%
Ammoniacal Nitrogen	0.12%±0.008%	0.017%±0.001%
Nitrous-Nitric Nitrogen	<D.L.*	0.003%±0.0002%
Organic Nitrogen	0.59%±0.04%	0.093%±0.006%

*D.L.:0.001%

Table V AA metal analysis results on the Nust 1 and Nust 2 ashes.

Element	Nust 1 %	Nust 2 %
Si	4.9	13.0
Al	2.4	6.2
Fe	13.5	7.0
Ca	1.8	2.3
Na	4.7	1.8
Zn	1.0	1.6
Mg	1.3	1.4
Cu	0.6	0.8
Cr	0.2	0.2
Ni	0.06	0.08
Pb	0.06	0.05
Co	0.02	<D.L.*
Mo	<D.L.*	<D.L.*

*D.L.: Detection Limit.

Table VI Mechanical strength, setting time and exothermic temperature peak of the Nust 1 and Nust 2 cemented ashes, in comparison with the plain Pozzolanic Cement (CPZ 325) characteristics.

		CPZ 325	Nust 1			Nust 2		
Ash/Cement	p/p	----	1/4	1/3	1/2	1/4	1/3	1/2
Water/Cement	p/p	.33	.47	.50	.62	.41	.45	.50
Size	mm	100 x 100 x 100				Ø=60 h=60		
Mechanical Strength after 28 days	kN/m^2	31000	14000	13500	13500	16000	13000	14000
Exothermic Pick	°C	63	N.D.	N.D.	N.D.	58	55	35
Setting Time	h	6	N.D.	N.D.	N.D.	7	7	9

Table VII Mechanical strength, setting time and exothermic temperature peak results of the Nust 2 pretreated cemented ash, in comparison with the plain Pozzolanic Cement (CPZ 325) characteristics.

		CPZ 325	Nust 2 pretreated
Ash/Cement	p/p	----	1/2
Water/Cement	p/p	.33	0.5
Size	mm	100 x 100 x 100	
Mechanical Strength after 28 days	kN/m^2	31000	14000
Exothermic Pick	°C	63	38
Setting Time	h	6	10

EXPERIMENTAL STUDIES OF THE EDF REACTOR WASTES LEACHING (RMA4 and 5)

Contractor : CEA - CEN CADARACHE FRANCE
Contrat N° : FI 1W/0172
Duration of the contract : From August 1988 to December 1989
Period covered : August 1988 - December 1988
Project leader : A. SAAS
Executant : J. GIRARD - CEN CADARACHE

A) OBJECTIVES AND SCOPE

Qualification studies of I.E.R. coating with polymeric (PEC/SIE - Dow Method) were achieved by E.D.F. and CEA.

Very active I.E.R. 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. Four 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.

B) WORK PROGRAMME

All tests use active and inactive samples with high and low amount of ^{60}Co, ^{137}Cs, B, Li like 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 × 2 measures with active samples) - Lixiviation speed relaxed (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 × 2 measures)

B5. Ianctive sample test procedure with :

- de-ionized water
- RFS water pH8
- RFS water 5°C
- RFS water + bore

B6. Inactive sample test with 2 different volumes of leachate (1,5 and 3 liters)

B7. Inactive sample test with different V/S values

B8. Inactive sample test with different sequences

- 4 × 7 days
- 30 and 90 days

B9. Inactive sample test with agitation of water

- 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 + ^{137}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 core sample
- RFS water and impregnated sample (without mixing)
- Sample with B + Li and then sample without B + Li in the same RFS water

B12. Effect of irradiation

- 2 sample loaded with B + Li

B13. Full-scale effect

- RFS leaching of an industrial full scale package for one year.

C) PROGRESS OF WORK AND OBTAINED RESULTS

Inactive studies.

All samples for B1-B3-B5-B6-B7-B8 and B9 work program are made september 1988 (loading and coating of IER).

The leaching tests of these samples are finished and the B and Li analysis of leachate is in progress.

We have found difficulties for B1 work program. The dissolution methods seen not adapted for these samples. A new method is in progress.

Active studies.

All samples of IER are loaded with ^{60}Co and ^{137}Cs since september 1988. These samples for B1. B2-B4 and B10 work program are not coated. The laboratory was engaged about other pressing works. A new planning will be proposed in february.

Lixiviation studies scale 1. We have a problem of provisioning an active and full scale package with EDF, (EDF manufacturing plant, wastes analysis). It's necessary to know exactly the initial activity before any test and of course lixiviation.

EXPERIMENTAL ANALYSIS OF RADIOACTIVITY RELEASED BY LOW-LEVEL AND INTERMEDIATE-LEVEL RADIOACTIVE WASTE

Contractor:	Siemens AG, Erlangen, FRG
Contract no.:	FI1W-0173-D
Duration of contract:	January 88 - December 89
Period covered:	January 88 - December 88
Project leader:	H. Stöckert
Author:	K. Habeck, H. Stöckert

A. AIM AND SCOPE OF THE PROJECT

The purpose of the research project ist to determine, under simulated repository conditions, the release to air of radionuclides from cemented ion exchange resins originating from reactor coolant purification systems in pressurized water reactors. The radionuclides concerned are H3, C14, I129, Fe55, Ni63 and alpha-emitters. As radionuclides H3, C14 and I129 can form volatile compounds, they are of special concern with regard to ultimate disposal. Fe55 and Ni63, which occur in ion exchange resins in reactor coolant purification systems, are relatively long-lived and difficult to determine by radiochemical analysis techniques. The project furthermore includes analyses of the release of the above radionuclides via the water pathway.

B. PROGRESS TO DATE

2.1 Production of 5 test packages with the cementation unit installed in Gösgen nuclear power plant.

2.1.1 Manufacture of 5 drums containing ion exchange resins (originating from reactor coolant purification systems) immobilized in cement.

2.1.2 Analysis of the nuclide composition and the dose-rate of the drum contents

2.2 Preparations for the transport of the test packages

2.2.1 Determination of the acitivity concentrations in the ion exchange resins

2.2.2 Activity concentrations of the radionuclides.

2.1, 2.1.1, 2.1.2 PRODUCTION OF 5 TEST PACKAGES IN GÖSGEN NUCLEAR POWER PLANT

The test packages were produced with the permanent cementation unit in Gösgen nuclear power plant (Switzerland). The manufacture of the packages was preceded by comprehensive tests with non-active ion exchange resins, which served to establish both the suitable water : cement : resins mixture ratio and the practicability of the process using the TT cement stabilization unit.

The test packages were then produced with dried ion exchange resins from the reactor coolant purification system, on the basis of the established mixture ratio. After the visually monitored process of setting, two of the drums were closed with a non-active cast cement cover.

2.1.3 DETERMINATION OF THE NUCLIDE COMPOSITION AND THE DOSE RATE OF THE DRUM CONTENTS

The dose rates emitted by the individual drums were measured at fixed repeatable positions.

2.2, 2.2.1, 2.2.2 PREPARATIONS FOR THE TRANSPORT OF THE TEST PACKAGES

As the manufactured test packages have a high dose rate, special shielding is required for the transport and for subsequent testing. Various formalities, such as obtaining an import licence for ion exchange resins immobilized in cement, shielding for transport, etc. have to be dealt with too.

Detailed indication of the activity concentrations of the radionuclides in resins immobilized in cement is a prerequisite for shipping radioactive materials.

Following non-active preliminary tests, a resin sample was dissolved completely in an acid solvent. The subsequent activity analyses were performed to KWU specifications.

The activity concentrations of the analyzed radionuclides are shown in table 3.

Table 1: **Measurements for single drums at fixed repeatable positions, in mSv/h**

Drum no.	Contact dose rate			Dose rate at a distance of 1 m		
	Top	Side	Bottom	Top	Side	Bottom
1	100	160	140	30	15	10
2	100	140	140	20	10	8
3	90	130	130	10	8	7
4	15	100	100	3	9	8
5	15	100	100	3	10	8

Table 2: **Breakdown of the activity concentration in ion exchange resins**

40 %	Co60
40 %	Cs137
5,19 %	Cs134
Remainder:	Co58, Mn54, Sb124

Table 3: **Activity concentration in ion exchange resins, in Bq/g of resins; date: August 2nd, 1988**

Co60	$1,4 \cdot 10^7$
Cs137	$5,8 \cdot 10^6$
Cs134	$3,0 \cdot 10^6$
Ni63	$3,6 \cdot 10^6$
Fe55	$1,8 \cdot 10^6$
Mn54	$8,2 \cdot 10^4$
Ni59	$2,0 \cdot 10^4$
Sr90	$8,0 \cdot 10^4$

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 1988 - December 31 1988

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 exchangers in modified vinylester polymer) and RMA10 (incinerated PCM materials in cement) maintain their integrity during irradiation but samples of RMA3 (organic ion exchangers in cement) and RMA11.1 (mixed PCM materials in cement) swell and eventually disintegrate under some γ irradiation conditions. Disintegration of RMA3 samples occurred when samples were γ irradiated whilst immersed in water. Samples of RMA11.1 which cannot rapidly dry out swell, sometimes substantially, during γ irradiation. The principal gases of interest in gas evolution experiments are hydrogen and oxygen. Hydrogen is evolved under all circumstances but oxygen evolution does not always occur. Samples of RMA10 evolve oxygen when α irradiated in an inert atmosphere but oxygen concentration initially falls during α irradiation in air atmosphere. Samples of RMA11.1 absorb oxygen from an air atmosphere during both α and γ irradiation. A comparison has been carried out of the effects of γ and α irradiation on identical cement grouts using BFS/OPC mixes produced under high shear mixing conditions. In contrast to earlier results on such systems, no γ irradiated samples showed physical deterioration after irradiation to 9 MGy but the α irradiated samples all showed surface cracks after about 1 MGy. The gas evolution measurements showed that during α irradiation oxygen evolution commenced after a dose of ∿ 1 MGy whereas oxygen was completely removed from the atmosphere during γ irradiation. Hydrogen was evolved under all conditions and the rate of production was found to be dependent upon the dose rate. More hydrogen was evolved during α irradiations than during γ irradiation. A technique for the measurement of hydrogen permeability through cement systems has been further developed and such measurements can now be performed on a routine basis. More work is however required to obtain reliable data for cement systems which are completely saturated with water. γ irradiation has started on a waste form simulate of RMA11.1 which more closely resembles the real waste form. The waste material is enclosed in a steel mesh basket which is totally encased in cement grout. Samples of fully active dissolver residues have been obtained from the dissolver of the fast reactor reprocessing plant at Dounreay and transported to Harwell. The fuel hull samples were from fuels that had achieved 8 and 16% burn-up in PFR. Characterisation analyses have begun at Dounreay and Harwell prior to the preparation of immobilised samples at Harwell.

Progress and results

1. Gas evolution/absorption during γ irradiation (B2)

The gas evolution and absorption behaviour of several types of specimen has been studied. Results are available for cement matrix materials and for waste form simulates of RMA11.1. Hydrogen gas was evolved from all these materials, the amount of gas produced from OPC alone and from mixtures of BFS and OPC was similar but mixtures of PFA and OPC gave a lower gas yield. Hydrogen evolution was increased for samples of RMA11.1 waste form simulate compared to that from a PFA/OPC cement mix used as the matrix material, this increase was due to the rapid evolution of hydrogen from PVC and cellulose materials present in the waste. BFS/OPC cement mixtures absorb oxygen in the absence of irradiation but the rate of absorption was enhanced during γ irradiation. Oyxgen was also absorbed by the waste form simulates of RMA11.1 and by samples containing individual components of this waste encapsulated separately. The rate of oxygen loss was influenced by the γ dose rate whereas the rate of hydrogen evolution was found to be independent of dose rate. There was some evidence of the evolution of small amounts of HCl during γ irradiation of samples of RMA11.1 in closed containers. The amount of HCl in the gas mixture was influenced by the sample dimensions and the surface area exposed to the atmosphere.

2. Gas evolution/absorption during α irradiation (B3)

A similar range of samples has been studied to those described in the previous section with the addition of samples containing a waste simulate of RMA10. Hydrogen gas was evolved from all samples but for α irradiation the rate of hydrogen production was found to be influenced by the α dose rate. The amounts of gas produced during α irradiation were significantly higher than during γ irradiation of similar samples, this may indicate that during α irradiation there is a sufficiently high population of free radicals in the system for recombination reactions to become significant in reducing the observed yield of molecular hydrogen. This would explain the observed dependence of $G(H_2)$ values on dose rate. For samples containing mixtures of BFS and OPC cement materials the rate of hydrogen evolution was not influenced by the sample compositions but was dose rate dependent. During irradiation in an air atmosphere oxygen was initially absorbed but evolution of oxygen was observed after α irradiation to a dose of about 1 MGy regardless of dose rate. Samples containing RMA10 simulate behaved similarly to the cement matrix samples. Oxygen was evolved during α irradiation under nitrogen atmosphere and the rate of gas production was again found to be strongly dependent upon the dose rate. During α irradiation in an air atmosphere oxygen was initially absorbed until an equilibrium concentration was established. Samples containing RMA11.1 simulate evolved hydrogen at a steady rate independent of α dose and the gas pressure in the system. The values obtained for $G(H_2)$ were however strongly influenced by the dose rate. These samples absorbed oxygen from an air atmosphere until the oxygen was totally removed from the gas around the samples. There were traces of other gases in the system including carbon monoxide, methane and ethane.

3. Dimensional stability, etc. (B4)

Work on matrix materials has concentrated on a comparative study of the effects of α and γ irradiations on BFS/OPC cement systems using grouts mixed at a high shear rate. Previous work /1/ has shown that some BFS/OPC cements crack and disintegrate during γ irradiation but these samples were γ irradiated to 12 MGy without showing any signs of physical deterioration. No significant changes in weight or dimensions were measured and compression strength remained unchanged after irradiation. There has been no previous experience of cracking in BFS/OPC systems during α irradiation but samples mixed at high shear rate and maintained at high humidity all showed surface cracks after α irradiation to a dose of about 1 MGy. No significant dimensional changes or weight changes were measured. Several waste form simulates have also been studied, RMA3, 5, 10 and 11.1. During γ irradiation samples of RMA3 in vented containers and decanned lost weight due to the evaporation of water but dimensional changes were small. Similar results were obtained for unirradiated controls. However, samples which were maintained wet by immersion in water increased in weight and showed considerable swelling during γ irradiation, the samples began to disintegrate after a dose of between 900 and 1300 kGy. Identical control samples increased slightly in weight due to water absorption but the dimensions remained virtually unchanged. Compression strength of decanned samples was slightly decreased after irradiation to 1300 kGy compared to that of identical controls and samples from vented containers. Samples of RMA5 in vented containers and decanned lost weight, samples maintained wet increased slightly in weight but all dimensional changes were small and there were no signs of physical deterioration after γ irradiation to 1 MGy. There were no significant dimensional changes measured for samples of RMA10 during α irradiation. The compression strength of α active samples was however much lower than that of inactive controls possibly due to the influence of radiolysis gases evolved during setting of the cement matrix. Compression strength of α active samples decreased with increasing α dose up to a dose of 20 MGy then remained constant at higher α doses. Earlier results on samples of RMA11.1 showed that samples which do not dry out rapidly can swell during γ irradiation sufficiently to rupture the seams of the container. This swelling was thought to be a result of the presence of pockets of radiolysis gas trapped within the matrix though no direct evidence of this has emerged. Samples containing some of the individual materials present in this waste encapsulated in cement also crack during γ irradiation; most notably those containing PVC which totally disintegrated after 9 MGy at 3 Gy s^{-1}, and also those containing the rubber compounds Hypalon and neoprene which cracked during curing, these experiments were abandoned after a dose of 6 MGy because the samples could no longer be measured. Samples containing powdered materials have however been α irradiated to doses in excess of 20 MGy without any signs of physical deterioration. The compression strength of irradiated samples of RMA11.1 was decreased compared to that of identical controls. Experiments are currently underway on samples which resemble the real waste form more closely than the samples used previously. As in the real waste form the waste materials are enclosed within a steel mesh basket which is totally surrounded by a layer of pure cement grout. The measurements are in the early stages but it has become clear that all samples, both the controls and those being γ irradiated, have a tendency to fracture across the interface between the mesh basket and the lower layer of pure cement grout.

4. Additional measurements (B5)

During γ irradiation of samples containing PVC the chemistry of the cement pore water was altered, a sample of 10 $^{w}/o$ PVC contained chloride ion at a concentration of approximately 1M after irradiation to 9 MGy. The pH of the pore solution had also decreased significantly to 9.8. Samples containing mixed RMA11.1 waste simulate which included PVC also show increased chloride ion concentration in the pore water after irradiation but no significant pH reduction has been measured for these samples. The behaviour of BFS/OPC cement samples which exhibited cracking during irradiation may have been caused by radiolysis gas, mainly hydrogen, becoming trapped in the closed pore network of the cement matrix. If this is the case then the rate at which hydrogen can escape from the cement is an important factor in determining whether or not a sample will crack. A technique for measuring hydrogen permeation rates on a routine basis has now been developed and results are promising. The total porosity and the hydrogen permeability of cements decrease as the sample ages but are increased if the cement dries out and as the water to cement ratio is increased. More data are still required for samples saturated with water as the detection technique used is only just capable of measuring the gas concentrations obtained. If a sufficient data base can be generated then it may be possible to predict any changes in gas permeability which occur during long term storage and disposal of cemented wastes.

5. Procurement of wastes (B6)

Samples have been obtained of hull residues remaining from the dissolution of irradiated uranium-plutonium oxide fuels in the fast reactor fuel reprocessing plant at Dounreay. The fuels had achieved 8 and 16% burn-up in PFR. The hull samples have been transported from Dounreay to Harwell. The two batches are being characterised prior to being used in the radiation stability experiments. 160 g portions of the hulls have been dissolved in nitric-hydrofluoric acid mixtures at Dounreay and the solutions are being analysed for the actinide materials, fission products and activation products that were associated with the hull samples.

6. Manufacture of waste forms (B7)

Stainless steel vessels with a diameter of 75 mm have been built and leak tested. These will be used for the measurement of gases released or absorbed by radiolysis of the waste form. Inactive simulant fuel hulls have been immobilised in a 3:1 BFS cement grout to test the procedures to be used for the active experiments.

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/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 waste forms, 1987 Annual Report, AERE-R13019 (1988).

/2/ WILDING, C.R., PHILLIPS, D.C., LYON, C.E., The effects of radiation on intermediate level waste forms, Presented at the 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 December 1989
Period covered : July - December 1988
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

Four waste forms have been selected for study from the range of UK intermediate level wastes. Each waste form is to be used as an example of its general type. The waste forms are: Magnox sludge in a 3:1 BFS/OPC matrix, steel fuel hulls in 3:1 BFS/OPC, organic PCM in 3:1 PFA/OPC and ion exchange materials in a vinyl ester resin. Samples of the fully active waste materials required have been obtained.

Data are being obtained for temperatures of up to 1000°C and for fire duration of 2 hours so that an appreciation is gained of the behaviour of wastes under these conditions.

Small scale inactive heating experiments have been carried out to obtain preliminary information and to develop techniques to be used in the active experiments. Preparations for the active experiments are underway.

A one-dimensional heat conduction model has been developed. The model incorporates such temperature dependent properties as are available and makes allowance for heat loss due to evaporation of water from the immobilising matrix.

PROGRESS AND RESULTS

2.2 PROCUREMENT OF WASTES

Samples of Magnox sludge waste and fast reactor hulls have been obtained for use in the small-scale active experimental programme. Samples of organic PCM will be prepared to a reference composition by controlled contamination (with plutonium oxide containing americium) of mixed shredded organic materials originally in sheet form. Samples of ion exchange materials will be prepared by loading the ion exchangers with caesium-137 and strontium-85. A blend of the ion exchange materials used to date in the clean up of pond waters is being used and samples have been obtained from the CEGB. Samples of inactive ion exchangers immobilised in vinyl ester and components for the manufacture of the vinyl ester polymer have been obtained from the CEGB.

2.3 MANUFACTURE OF WASTE FORMS

Samples of inactive Magnox sludge simulant (magnesium hydroxide powder slurried in water to give 20 weight % solids) have been immobilised by adding an equal weight of 3:1 BFS/OPC cement powder to the stirred slurry. The mixture was then poured into the stainless steel cans to be used in the thermal test experiments. Can diameters of 12 and 15cm have been used in the preliminary inactive trials. A thermocouple array is fitted in the can before pouring in the cemented waste slurry so that temperatures can be measured at various positions along a radius on the mid-plane of the cylinder of waste.

The waste form was cured by heating at 55°C for 20 hours, initially beginning within 2 hours of casting but later experiments were allowed to cure at 20°C for 2 days before curing at 55°C for 20 hours.

Samples of inactive fast reactor hulls simulant (stainless steel tubing, 6.35mm OD x 15mm long) were immobilised by adding them to a cement grout prepared from a 3:1 mixture of BFS/OPC with a water to cement ratio of 0.35. The cement grout was mixed with a high shear Silverson stirrer to give a low viscosity. The immobilised waste in its stainless steel can was cured by heating at 55°C for 20 hours.

Two types of can were used. One had a loose fitting lid and was used suspended from a balance in heating trials. The other had a sealed lid fitted with an exit pipe to be used for the collection of particulate material and volatile components.

2.4 HEATING OF WASTES AND WASTE FORMS

Samples of waste form in 12cm diameter stainless steel cans have been heated by suspending them from a balance in a preheated furnace at 300°C or

1000°C. The temperature profiles through the waste form were measured as a function of time. The centre temperature of a 12cm cylinder of Magnox sludge simulant waste form did not exceed 100°C for 2 hours of heating at 1000°C whereas for a similar sample of stainless steel hulls waste form the centre temperature exceeded 100°C in 40 minutes.

2.5, 2.6 MEASUREMENT OF MATERIALS RELEASED FROM HEATED WASTE FORM SAMPLES

The measured rates of steam production (via weight loss measurements) were 0.004 and 0.03 g/cm^2/minute for Magnox sludge simulant samples placed in furnaces at 300°C and 1000°C, respectively. The stainless steel hulls waste gave a steam production rate of 0.03g per minute per square centimetre of outer surface area of waste form when heated at 1000°C.

From experiments with smaller scale, non-packaged samples of Magnox sludge waste form, the size distribution of the solid particles carried forward in the steam produced was found to be in the range 0.1 - 1µm. Similar experiments with ion exchange materials immobilised in vinyl ester resin have shown that 63 weight % of the waste form is volatilised during heating at 1000°C. The products were condensed as organic liquid (22% of initial sample weight), as aqueous liquid (31% weight %) or remained as a gas (10 weight %, 88 litres per kg waste form).

2.7 EXAMINATION OF RESIDUES

The residue from heating Magnox sludge waste form at 1000°C was essentially a monolithic block comprised of a friable powdery material. SEM examination showed that the solid contained very fine particles, $<$ 1µm in size, formed into agglomerates.

The residue from heating the stainless steel hulls waste form was monolithic with fine cracks present in the surface.

The residue from heating ion exchange materials in vinyl ester resin was a porous coke block.

2.8 THEORETICAL ASSESSMENT OF BEHAVIOUR OF WASTE FORMS ON HEATING

The theoretical assessment has begun by development of a mathematical model to calculate the temperature distribution through a 500 litre drum of ILW following a fire accident. A one-dimensional heat conduction model has been developed which incorporates such temperature-dependent properties as are available and makes allowance for heat loss due to dryout of the ILW matrix. The model has been used to calculate temperatures within drums, either as a bare drum or within a 285 mm thick transport flask, exposed to temperature of 1000°C for 2 hours. These calculations predict that in the transport flask 80% of the waste form can exceed 100°C with a peak temperature of 300°C. For the bare drum case 70% of the waste can exceed 100°C with a peak outer temperature of 800°C.

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 - April 1989
Period Covered:	April 1988 to December 1988
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-dependant 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 generators, mobility of soluable 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

The work has proceeded well in 1988, and significant progress has been made. The likely contents of low level waste streams have been considered, and waste formulations have been prepared that are typical of various 'average' types of waste. Formulations comprising single materials have also been considered where these may occur in actual waste streams. A test programme has been devised that allocates compacted drums to tests on the basis of likely significance of the results, ie. not all drums are subjected to all tests. A variety of test rigs have been designed. Most significant is that for force development in a restrained compacted drum stored either in air or immersed. A rig to permit vacuum saturation has also been prepared, together with rigs to capture gases produced by corroding drums, and to allow sampling of the water in which the drums are immersed.

A total of thirty 200 litre drums were prepared, shipped to Hansa Projekt, and compacted. Monitoring of dimensions has continued since that time and an ancilliary project has assessed the usefulness of X-raying compacted drums as a method of quality control. Immersion of a number of the drums has been undertaken with interesting results.

Due to the fact that the design and fabrication of the restraining test rigs has taken longer than anticipated, it is likely that a 'time only' extension to the contract will be requested.

Progress and Results

1. Selection of Simulated Waste Streams for Test (B.1., B.2.)

The drum compositions selected are shown in Table I. Certain materials are of specific interest, for example, paper which forms the basis of disposable clothing for use in active areas, for clear up operations and for filters. Compacted paper/cellulose will respond to wetting more markedly than most other materials with the exception of vermiculite (used in clearing up of spillages) which has been included in the programme to represent an extreme case.

Plastics are likely to give time dependant expansions, and three materials have been included in the programme. These were polyvinylchloride, polythene (extensively used in sheet form and as bottles) and synthetic rubber (neoprene) used for rubber gloves.

Drums containing two types of mixed waste were also prepared. The most potentially interesting waste stream is a mixture of plastic and paper. Perhaps more typical of laboratory arisings is a mixture of 'soft and hard' - plastic, paper, laboratory apparatus, tubing, wiring, glass and building materials. The extent to which the 'hard' items reduce the efficiency of the supercompaction process and make the compacts dimensionally stable was considered worthy of investigation.

2. Definition of Test Programme (B.3.)

After dimensional monitoring of all compacted drums, each drum will be subjected to one or more of the following test regimes:-

a) Stress development in air (Drums W10 - W14)

The stresses exerted by a compacted drum restrained against axial expansion will be measured,

b) Expansion in water/leaching/off gases (Drums W15 - W18)

These specimens will be drilled (to facilitate water ingress) and vacuum saturated. Each specimen will then be stored in a chamber that will collect any gases generated. Dimensions of the specimens will be recorded periodically, and the water analysed for the presence of a dye incorporated into the centre of each specimen as a simulated leachate. Gases given off (if significant) will be analysed.

c) Stress development in water

Specimens will be first vacuum saturated ((b) above) and then treated as in (a) above except that additional facilities will be incorported into the rig to maintain specimen saturation.

d) Expansion in air

Long term monitoring of some of the compacted drums will be undertaken.

e) Unrestrained water immersion

Four compacted samples have been prepared using fibre board drums in place of metal drums. Immersion of these specimens (which has already been undertaken) will enable the response of the drum materials to water to be assessed when not constrained by the presence of a metal drum.

Preparation and Compaction of drums

Drum contents were largely obtained from the U.K.A.E.A. Winfrith stores, thus ensuring virisimilitude with real waste arisings. Compaction at Hansa Projekt in Hamburg proceeded well; the total time for compaction of thirty drums was about 3½ hours. Due to the mode of the operation of the Hansa Supercompaction it was not possible to obtain load/deflection data from the wastes used, although typical data is available from Hansa for similar materials.

An important result from the actual compaction exercise is that certain waste streams comprising single materials may not be suitable for the supercompaction process. Drums containing neoprene exhibited time-delayed bursting of the seams of the metal drums. Although no major additional movements have occured, the achieved non-symetrical shape of the damaged compacted drum much diminishes the advantages of the supercompaction process.

(B6) Dimensional Monitoring

Table II attached gives an indication of the degree of compaction achieved, and of the extent of delayed movements. More data will be available in later reports.

Table I Drum Compositions and Schedule of Tests

No.	Drum Type	Waste	Type
W5	N	PVC	Expansion in Air
W6	N	Neo	" "
W7	N	Poly	" "
W8	N	P+P	" "
W9	N	S+H	" "
W10	N	PVC	Stress dev. in air
W11	N	Neo	" "
W12	N	Poly	" "
W13	N	P+P	" "
W14	N	S+H	" "
W15	N	V	Wet expansion/leaching/off gas
W16	N	Pap	" " "
W17	N	P+P	" " "
W18	N	S+H	" " "
W19	N	V	Stress dev. in Water
W20	N	Pap	" " "
W21	N	P+P	" " "
W22	N	S+H	" " "
W23	N	Pap	Expansion in Air
W24	N	Pap	SPARE
W25	N	V	Expansion in Air
W26	N	V	SPARE
W27	R	P+P	SPARE
W28	R	S+H	"
W29	R	Pap	"
W30	R	V+H	"
W31	F	V	Soaking & Visual Inspection
W32	F	Pap	" " "
W33	F	P+P	" " "
W34	F	S+H	" " "

KEY

Drum Type	N	New metal drum
	R	Reconditioned metal drum
	F	Fibre Board drum
Waste Type	PVC	Polyvinylchloride
	Neo	Neoprene
	Poly	Polythene
	P+P	Plastic & Paper 50%/50%
	S+H	Soft & Hard 80%/20%
	V	Vermiculite
	V+H	Vermiculite & Hard Material

Table II Compacted drums - compaction and delayed movements

Drum No	Contents	Compaction Factor	Central Expansion after 10 days
W5	PVC	5.36	NIL
W6	Neopreme	5.46	NIL
W7	Polythene	6.4	1.5 mm
W8	Paper/Plastic	20.43	0.5 mm
W9	Soft/Hard	7.33	1.2 mm
W10	PVC	5.33	NIL
W11	Neopreme		
W12	Polythene	6.36	NIL
W13	Paper/Plastic	19.07	1.5 mm
W14	Soft/Hard	7.33	0.5 mm
W15	Vermiculite	17.88	NIL
W16	Paper	15.6	1.0 mm
W17	Paper/Plastic	18.65	1.25 mm
W18	Soft/Hard	7.66	0.65 mm
W19	Vermiculite	13.62	1.0 mm
W20	Paper	13.62	0.6 mm
W21	Paper/Plastic	19.5	0.6 mm
W22	Soft/Hard	7.8	0.75 mm
W23	Paper	21.45	1.0 mm
W24	Paper		
W25	Vermiculite	16.50	NIL
W26	Vermiculite		
W27	Paper/Plastic	19.38	1.4 mm
W28	Soft/Hard		

FIRE EXPOSURE TESTING OF ENCAPSULATED SIMULANT RADIOACTIVE WASTES

Contractor : UKAEA - AEE Winfrith, UK
Contract No : FI 1W 0198
Duration of Contract: July 1988 - December 1989
Period covered : July 1988 - December 1988
Project leaders : D. J. Holman, 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.

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 to be 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).

Once the packages have been prepared 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.

One of each of these packaged wastes will be subjected to a pool fire test as a repository fire (bare drum) and one to heating in an electric furnace as a transport fire (drum in an overpack). Measurements will be made during all of the tests to identify the activity release mechanisms, the activity release fraction and the consequences for subsequent package disposal.

C. PROGRESS OF WORK AND OBTAINED RESULTS

This contract was agreed in July 1988 and work commenced immediately. As soon as the waste types to be studied were finalised, orders were placed for the appropriate quantities of simulants and simulant raw materials. These have now all been received. After consultation with the modelling experts at Harwell, modifications to the design package instrumentation were carried out to provide the input data required for development of the theoretical model. The required modifications to the design of the thermal facilities at Winfrith to measure both gaseous and particulate release during fire exposure testing have been completed. Equipment to facilitate these modifications has been ordered. Drums, thermocouples and remaining materials for instrumented package production have been procured and specimen manufacture is underway, with immobilisation of waste to commence in the new year.

Experimental measurements can be divided into two categories:

(a) On-line Measurements (during test)

Provision has been made in the design of the apparatus to be used in each of the tests (both fire and furnace tests) for several on-line measurements to be taken.

(i) Temperature - an array of thermocouples is accurately positioned within each monolith. Also, thermocouples are located to measure the drum internal/external surface temperature as well as the temperature of the fire/furnace conditions that the package is being subjected to.

(ii) Off Gas Analysis Circuit. Figure 1 shows a schematic "diagram" of the equipment proposed to measure both gaseous and particulate release. Incorporated into this are:

- an inert gas feed to purge the ullage space within the package,
- a filter unit, using replaceable 0.2 µm capacity cartridges. Changing these cartridges, and weighing/retrieving the solids accumulated, at intervals during the test should give values for the rate of particulate release from the package. The retrieval material will undergo size analysis. The pressure gauges on the inlet and outlet of the

filter will indicate changes in pressure as solids build up on the filter cartridge,

- a heat exchanger to condense steam released from the monolith. A collection vessel, equipped with a sight glass, enables the rate of steam release to be measured and correlated with package temperature profiles,
- a cold trap to collect any volatile material (particularly organics) not retained in the condensate trap,
- a gas chromatograph to make on-line analysis of samples of gaseous release from the package at intervals during the test.

(b) Off-Line Analysis (post test)

(i) Data collected from the thermocouples will produce temperature/time profiles and build an accurate picture of the thermal performance of the package.

(ii) Particle size analysis of material collected on the filter cartridges will be carried out.

(iii) Condensate and cold trap contents will be analysed.

(iv) When the specimen is removed from the test facility the following work will be performed:

- package integrity assessment.
- specimen decanning leading to an assessment of monolith integrity, surface inspection and crack quantification. Core samples of the monolith will enable strength measurements and thermal analysis (Thermo Gravimetric and Differential Scanning Calorimetry).

These measurements will be used to identify critical temperatures at which dehydration or phase changes occur. Also, to quantify the materials released from the waste and the encapsulants and assess the degradation of the wasteform.

At present specimen and facility instrumentation is being fabricated. After this, specimen preparation ie. filling drums with waste/encapsulant followed by the appropriate curing periods will take place. The fire test facilities at Winfrith are being modified to accommodate the experimental requirements of this programme, each incorporating the analytical equipment described above - which is under construction. Fire testing will commence shortly after this equipment has been fully commissioned.

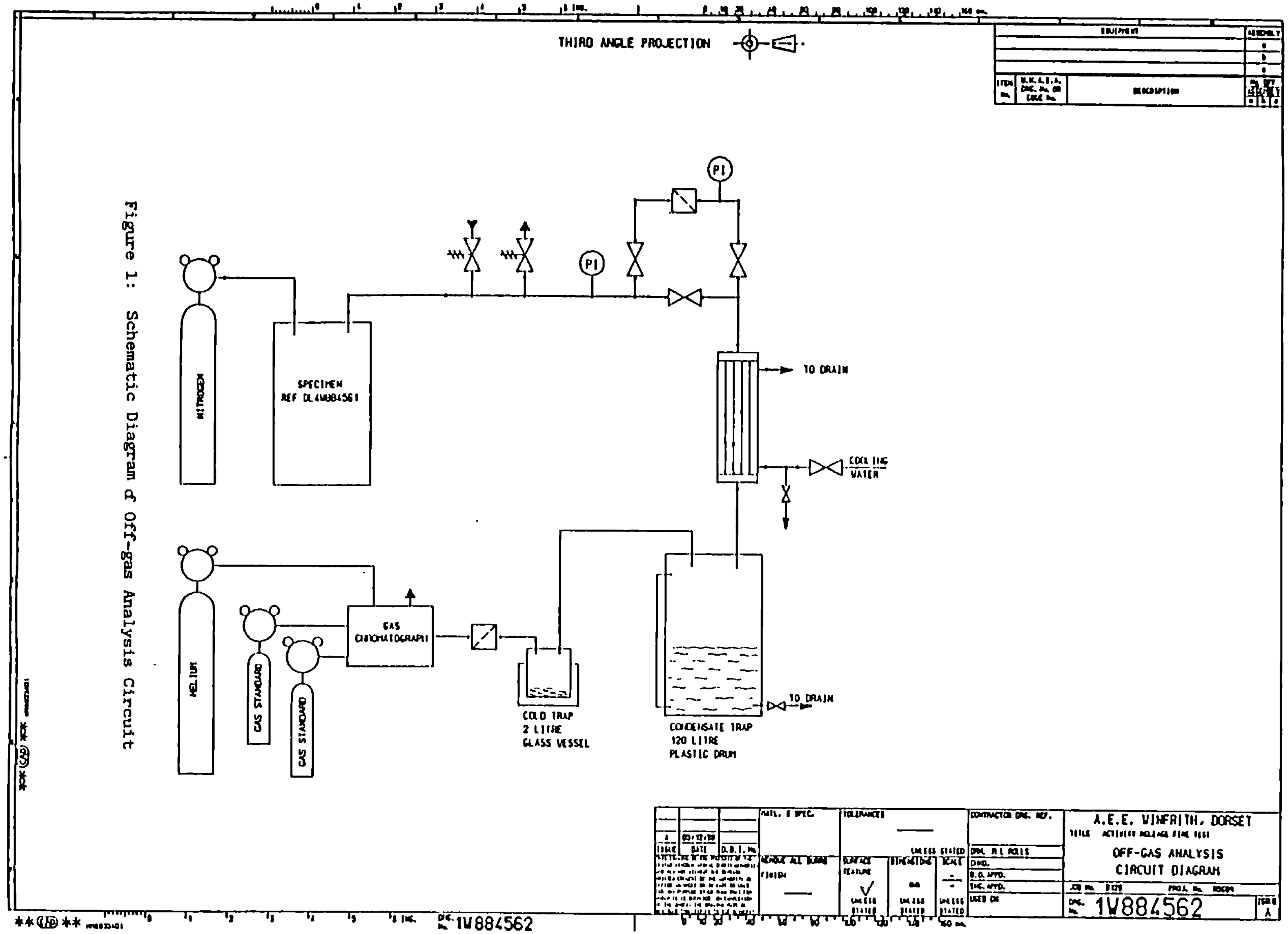

Figure 1: Schematic Diagram of Off-gas Analysis Circuit

3.2. High Active and Alpha Waste Form Characterisation

Investigation of the Long Term Behaviour of HLW Glass Under Conditions Relevant to Final Storage

Contractor: Fraunhofer-Institut für Silicatforschung (FhG-ISC),
Würzburg, F.R.G.
Contract No.: FI1W/0028
Working period: May 1986 - April 1989
Project leader: H. Roggendorf

A. Objectives and Scope

Borosilicate glasses are proposed as waste form for the final disposal of High Level Waste (HLW) by the Federal Republic of Germany. Between 1980 and 1985 extensive studies on the corrosion mechanisms of the inactive HLW glass type SM 58 in a salt brine were performed by the contractor (contract nos. WAS-232-81-53 D (B) and WAS-323-83-53 D (B)). In 1988 the long time corrosion tests with the HLW glass SM 58 were finished (test durations up to 5 years in solution 1 (Table II) at temperatures up to 200 °C /1/); a short summary of these results is included in this report.

A theoretical study /2/ on reported corrosion data (for different glasses and different corrosion conditions) showed that most HLW glasses corrode according to a very similar pattern. The main mechanisms are:

- network dissolution,
- formation of reaction product layers on top of the glass, and
- ion exchange.

The following model was developed from these results: In fresh leachants the corrosion starts with an initial rate r_o linearly depending on t. Due to the accumulation of reaction products in the leachate, this initial rate slows down and reaches finally a long term rate r_∞, which is typical of corrosion in leachates saturated with respect to silica. The rate r_∞ should depend linearly on t.

At the start of the investigations presented here, only few data were available for this long term corrosion of HLW glass in salt solutions. Therefore, the corrosion of the HLW glass type SON 68 (or R7T7) in salt brines was investigated under the conditions of silica saturation. Silica saturation was achieved in the laboratory by enlarging the ratio of sample surface area to solution volume (S/V). The interest was focused on the composition of the surface of the residual glass as well as on the composition of the leachate and on the investigation of their influences on the corrosion process. The corrosion tests were performed in cooperation with the Hahn-Meitner-Institut (HMI), Berlin.

B. Work Programme

B.1. Corrosion pre-tests for the optimization of analytical techniques.
B.2. Supplementary corrosion tests.
B.3. Optimization of analytical techniques (X-ray photoelectron spectroscopy (XPS), acid etching).
B.4. Optimization of preparation methods.
B.5. Preparation and measurement of standard samples with XPS.
B.6. Surface analysis of corroded glass samples.
B.7. Preparation and sampling of saturated leachates at test temperature with subsequent chemical analysis.
B.8. Evaluation of test results.

C. Progress of work and obtained results

Summary

During 1988 nearly all test series have been completed. Additionally, a new test series was performed for the corrosion of SON 68 in solution 3 at 190 °C. The results give an overview on the corrosion behaviour of SON 68 in a concentrated NaCl solution in the short and medium term range. Furthermore, long time corrosion experiments with another glass type (SM 58) have been completed after corrosion times of up to 5 years.

The quantification of the XPS method (combined with Ar ion milling) with external standards was completed. A good calibration was obtained for the elements Si, B, Na, Ca, Nd, and Cs.

The investigated ion exchange profiles (and hence the measuring times) were in most cases by a factor of 10 larger than expected compared to earlier results obtained for the HLW glass SM 58. Furthermore, hydrofluoric acid etching with subsequent analysis of the dissolved glass, which was proposed as analytical technique to analyze deep ion exchange profiles, failed due to pit formation in the glass surface under the conditions of long term corrosion. Nevertheless, it was possible to analyze the surface of 8 out of 12 corroded test samples with XPS.

The sampling of the leachates at test temperature was performed for all three leachates at 190 °C.

The evaluation of the experiments is not yet completed.

The general work progress is as follows:

B.1. to B.5.: are completed,
B.6. : partly completed (8 out of 12 samples), cannot be completed due to the lack of experimental capacity,
B.7. : completed,
B.8. : partly completed.

Progress and results

1. Supplementary corrosion tests (B.2.)

Previously reported results concerning the corrosion of the HLW glass SON 68 (composition in Table I) in salt solutions (Table II) stated that:

- the long term corrosion process depends linearly on (S/V)•t in the solutions 1 and 2
- and seems to follow a square root time law in solution 3.

To investigate the different finding for solution 3 further, a set of additional corrosion test was performed. SON 68 glass chips of different sizes were corroded up to 1 year at 190 °C in solution 3. The S/V ratio was varied by applying different chip sizes and leachant volumes, but not by the addition of glass powder. The measured mass losses (after removing the reaction product layer) of the glass chips are presented in Figure 1 as mass loss per leachant volume versus (S/V)•t. After 1000 d•m^{-1} the normalized mass losses reached a constant level. This was not observed in our previous tests with powder addition. In the meantime, Lutze et al. reported /3/ a linear time dependance for the corrosion of SON 68 in solution 3 for the long term range. One interpretation is, that the diffusion of dissolved glass reaction products in the interstitial solution within in the glass powder was responsible for the measured square root time law. This diffusion was avoided by Lutze et al. by rotating the autoclaves and in our new test series by omitting the glass powder.

Another way to investigate the long term behaviour of corroding glasses (besides increasing the S/V ratio) are real long time experiments. The HLW glass SM 58 (composition in Table I) was corroded up to 5 years at temperatures between 80 and 200 °C in solution 1. The results are presented in Figure 2. After about 120 d a linear time dependance of the corrosion process was observed for all four test temperatures.

2. Optimization of analytical techniques (B.3.)

One aim of the investigations was to analyze quantitatively the surface composition of corroded HLW glasses. To acchieve this, XPS in combination with Ar ion milling was applied. For the calibration of the XPS method a set of 15 external standards was prepared and analyzed. These external standards had a general composition similar to SON 68. Their specific composition was varied to cover the expected range of surface compositions. For Si, B, Na, Ca, Nd, and Cs a linear relation between the concentration of an element and the counting rate of a XPS signal of the respective element was observed. In most cases the peak area of the respective XPS signal was evaluated. The calibration was improved by relating the XPS counting rate of the respective element to the counting rate of the oxygen signal. The calibration for Al, Zn, Ba, Li, and Fe was not precise enough to be used for quantitative surface analysis. The reasons are their low concentrations in SON 68 and overlapping peak areas.

To analyze deep ion excange profiles (depth > 1 µm) another, faster technique was proposed: chemical etching of the glass surface with hydrofluoric acid and subsequent chemical analysis of the dissolved glass. The etching technique was improved by applying low temperatures and ultrasonic agitation of the acid. It was possible to reproducibly etch off layers of uncorroded SON 68 glass with a thickness of 100 nm. It was not possible to analyze glass samples which were corroded under the conditions of silica saturation by this method, because the respective surfaces had a porous structure. Within a short time (< 30 s) the whole ion exchange zone (depth > 1,5 µm) was etched off. Therefore, this technique was given up.

3. Surface analysis of corroded glass samples

At the Hahn-Meitner-Institut (HMI), Berlin, 12 SON 68 glass chips were corroded for the surface analysis. An evaluation of the leachate analysis data obtained by the HMI showed that in each case the leachates were saturated with respect to silica. The surfaces of 8 of these samples were analyzed with XPS (the reaction product layer was mechanically removed before the analysis). In Table III the depths of the Na concentration profiles are given. The depths measured for the samples W2 and W4, ("long term" corrosion in solutions 1 and 2 at 190 °C; $(S/V)\cdot t > 100000\ d\cdot m^{-1}$), respectively, are rather large compared with the depths measured for W1 and W3 ("short term" corrosion; $(S/V)\cdot t < 1000\ d\cdot m^{-1}$). Surprisingly, Mg was found in the surface of W2 and W4 up to a depth of 1.5 and 2.0 µm, respectively. SON 68 does not contain Mg, but the solutions 1 and 2 contain abundant amounts of Mg. From this observation (combined with the experience of hydrofluoric etching; see above) it was concluded that the surface of both samples is porous. This was proven by scanning electron microscopy for W2. The difference between the depth of the Mg penetration and the depth of the Na profile seems to be similar for W1 and W2 as well as for W3 and W4. As this differenc can be regarded as the real ion exchange zone in the glass, one can conclude that the depth of this zone remains constant under the conditions of silica saturation. This conclusion should be regarded as being preliminary, since it is based on two data pairs only. The Na concentration profiles for W5 and W6 (corroded in solution 3) are only 1.1 µm deep. The respective depths do not increase with higher $(S/V)\cdot t$ values. In the case of W6, Mg was found up to a depth of 0.5 µm, which is rather surprising, since solution 3 contains only minute amounts of Mg. An explanation might be that the surface of the corroded glass adsorbs preferentially Mg. At lower corrosion temperatures

(W10 and W12) smaller Na concentration profiles are found. Again a slight penetration of Mg into the glass is observed. A part of this measured Mg penetration might be due to the sample preparation: a thin layer of precipitated silica (which could not be removed mechanically) seems to cover the glass surface. These layers are between 0.1 and 0.25 µm thick. The results are not yet fully evaluated.

References

/1/ ROGGENDORF, H. and SCHMIDT, H., Long term corrosion of glasses in salt brines, paper to be presented at the 15th Intern. Congr. on Glass, July 2 - 7, 1989, Leningrad, USSR.

/2/ CONRADT, R., ROGGENDORF, H., and OSTERTAG, R., Report of the Comission of the European Communities, Report EUR 10680 EN (1986).

/3/ LUTZE, W., MÜLLER, R., and MONTSERRAT, W. Chemical corrosion of COGEMA glass R7T7 in high saline brines - Part II, Mater. Res. Soc. Symp. Proc. 127 (1989) (in print).

Table I. Composition of the HLW glasses SON 68 and SM 58 in wt.-%

glass	SiO_2	B_2O_3	Na_2O	Li_2O	Al_2O_3	CaO	MgO	Fe_2O_3	rest
SON 68	45.5	14.0	9.9	2.0	4.9	4.0	0	2.9	16.8
SM 58	56.8	12.3	8.0	3.7	2.1	3.8	2.1	1.7	9.5

Table II. Composition of the leachants in wt.-%

solution	NaCl	KCl	$MgCl_2$	$MgSO_4$	$CaSO_4$	$CaCl_2$	K_2SO_4
1	1.45	4.73	26.80	1.40	0	0	0
2	0.31	0.11	33.03	0	0.005	2.25	0
3	25.90	0	0	0.16	0.21	0	0.23

Table III. Depths of the Na concentration profile and of the Mg penetration in SON 68 corroded in salt brines

sample	sol.	Θ in °C	$(S/V)\cdot t$ in $d\cdot m^{-1}$	depth of (in µm) Na profile	Mg penetration
W1	1	190	820	1.4	n.d.
W2	1	190	120000	2.5	1.5
W3	2	190	820	1.5	0.2
W4	2	190	159000	3.8	2.0
W5	3	190	8200	1.1	n.d.
W6	3	190	1300000	1.1	0.5
W10	1	110	242000	0.5	0.2
W12	3	110	2500000	0.4	0.1

n.d.: not determined

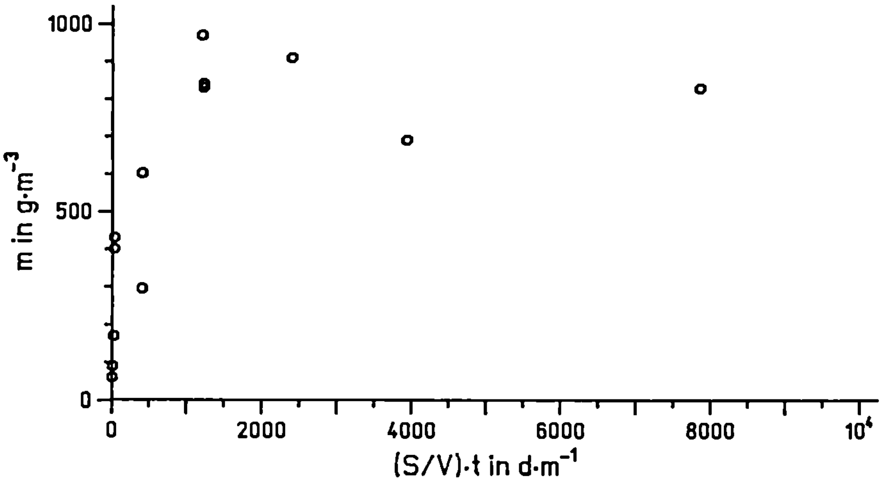

Figure 1. Amount of reacted glass per leachant volume m as a function of (S/V)•t; SON 68 corroded in solution 3 at 190 °C; S: surface area of the glass; V: leachant volume; t: corrosion time

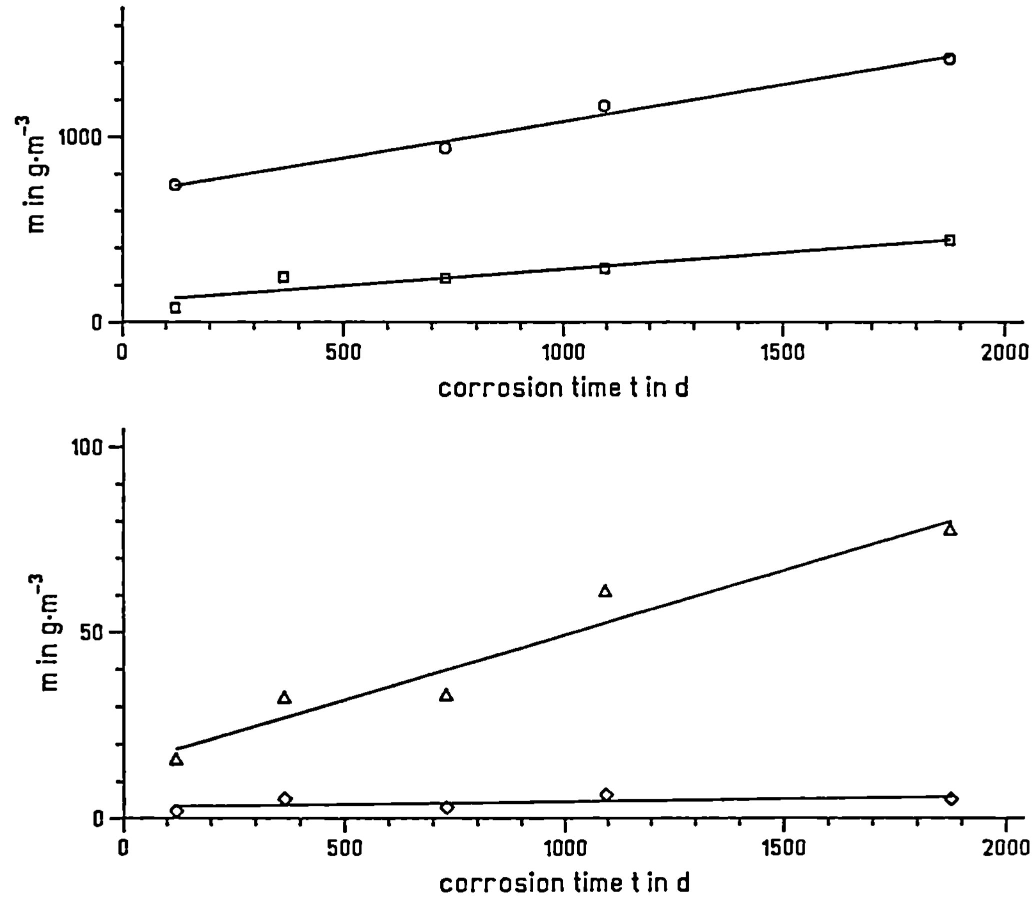

Figure 2. Mass of reacted glass per leachant volume m as a function of the corrosion time t; SM 58 corroded in solution 1 at 190 °C and 130 bar; corrosion temperature:
: 80 °C; : 120 °C; : 160 °C; o : 200 °C

BASIC MECHANISMS OF AQUEOUS CORROSION OF WASTE GLASSES

Contractor:	CEA, CEN-Valrhô, SDHA, F
Contract No:	FI1W-0030
Duration of Contract:	August 1986 - July 1989
Period Covered:	January 1988 - December 1988
Project Leader:	N. Jacquet-Francillon

A. OBJECTIVES AND SCOPE

Although a major research effort has been undertaken during the last decade on aqueous corrosion of nuclear glasses [1,2] our understanding of the basic corrosion mechanisms is essentially phenomenological and many important questions remain unanswered. This understanding is 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

2.1 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?)

2.2 Hydrothermal leaching and analysis of the crystalline phases formed between 50°C and 250°C.

2.3 Examination of the interface or ionization layer between the surface layers and the sound underlying glass.

2.4 Determination of the concentration profiles in the surface layers for the principal actinides.

2.5 Filtration study of the physicochemical form in which plutonium is found in the leachates.

2.6 Investigation of technetium behavior.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

2.1 Solubility: About one hundred experiments have been analyzed as part of a thorough investigation of the R7T7 glass solubility limit and corrosion rate under saturation conditions. The actual work accomplished has largely exceeded the scope of this contract.

2.2 Hydrothermal Leaching: This task has been completed:
- ICP analysis of the leachate and determination of the corrosion rate at each temperature.
- electron microprobe analysis of the specimen surfaces
- determination of new crystalline phases by X-ray diffraction.

2.3 Corrosion Front: The STEM examinations have been completed, although (pending the availability of nuclear resonance methods specified in the work program to investigate the Na^+ and H^+ diffusion profiles) a number of SIMS analyses are now in progress.

2.4 Actinide Concentration Profiles: These studies involving the Np, Pu and Am distribution profiles in the surface layers developed during Soxhlet tests were terminated at the end of 1987.

2.5 Plutonium Filtration Study: These experiments have only just begun.

2.6 Technetium Leaching: All of these experiments lasting up to 1 year have now been completed in *Volvic* water and in double distilled water. All of the analysis results are now available. SIMS will be implemented in 1989 to obtain a Tc distribution profile in the interface layer.

Progress and Results

2.1 Solubility

Various apparent silicon solubility limits (C*) were found depending on the SA/V ratio: 50 ppm (400 m^{-1}), 100 ppm (2000 m^{-1}) and 200 ppm (8000 m^{-1}). These differences were clearly related to pH variations as a function of the SA/V ratio, demonstrating that interdiffusion phenomena cannot be disregarded in a closed system.

The evolution of the Si and B concentrations is shown in Figure 1 for the three SA/V ratios. The rise in the boron concentration between 3 months and 1 year allowed the very low corrosion rates obtained under saturation conditions to be measured. The low corrosion rates depend on the SA/V ratio and thus do not appear to be representative of a "residual affinity" of the glass [3].

The rise in the boron concentration in solution also appears to correspond to a slight rise in the silicon concentration. This may be due to two phenomena:
- a slight pH increase during the test resulting in a slight increase in solubility over the duration of the test;
- formation of colloids causing renewed corrosion as silicon was consumed by the colloids.

2.2 Hydrothermal Leaching

During 1988 the work focused on optimizing X-ray diffraction methods to identify new mineral phases formed at the surface of the specimens (this work was done in collaboration with the University of Poitiers).

a) 50°C

No crystallized phases could be identified despite the use of a very sensitive linear localization detector [4].

b) 150°C

Although mineralization was very limited, several minerals were identified. The X-ray diffraction diagrams for a specimen leached for 84 days at 150°C showed lines at 20.1 Å, 11.6 Å and 3.02 Å characteristic of hydrated calcium silicates such as gyrolite ($4CaO$, $6SiO_2$, $4H_2O$) or okenite (CaO, $2SiO_2$, $2H_2O$). Spectral reflections at 14 Å (related to the 11.5 Å peak), at 7.1 Å and 1.54 Å were unchanged with a glycolated specimen. These reflections are characteristic of a trioctahedral chlorite (line 060 at 1.54 Å); this chlorite is structurally similar to the zinc-bearing berthierines found by Noguès at 90°C [1]. The characteristic reflections of minerals from the analcime-pollucite series were no longer visible in the spectrum, although they had been observed earlier after shorter leaching durations.

c) 250°C

Intense mineralization was observed at 250°C. Crystals were visible under a binocular microscope after only 14 days of leaching. They grew regularly thereafter on the specimen surface, forming aggregates 1000-1500 µm wide. The initially twinned crystal forms were modified during their growth, but no clear variation in composition could be detected between minerals of different sizes. Three types of minerals were clearly identified:

- Minerals from the analcime-pollucite series. Two types of pollucite compositions were noted: a common one (Si, Al, Na, Cs) and another containing Si, Al, Ca, Zr, Na, Cs in which Zr and Ca enrichment was accompanied by Na and Cs depletion.
- Smectites. The 1.520 Å line is characteristic of a trioctahedral smectite.
- Calcium silicates. Okenite predominated in the 14-day sample, while gyrolite was more common in the longer duration experiments.

2.3 Corrosion Front

Only a few preliminary secondary ion mass spectrometry (SIMS) experiments were conducted in 1988. The thickness of the corrosion front can be estimated from the shape of the sodium interdiffusion profile. After 28 days at 50°C this thickness was estimated at 0.15 µm, corresponding to an interdiffusion coefficient of about 10^{-16} $cm^2 \cdot s^{-1}$ at that temperature. This estimate is subject to caution, however, because of surface roughness which was observed to be enhanced after ion abrasion, and which could have artificially enlarged the diffusion profiles.

A nuclear resonance method will be used to obtain some H^+ and Na^+ profiles in 1989.

2.6 Technetium Leaching

The leach curves were similar to those previously obtained [2] with nonradioactive SON 68 glass, both in *Volvic* mineral water and in double distilled water. The final corrosion rate after one year for an SA/V ratio of 50 m-1 (approx 10^{-6} $g{\cdot}m^{-2}d^{-1}$) was substantially higher than at higher SA/V ratios (approx 6 × 10^{-8} $g{\cdot}m^{-2}d^{-1}$ for 8000 m-1).

The technetium leach rates under oxidizing conditions were only 10-20% lower than the boron leach rates.

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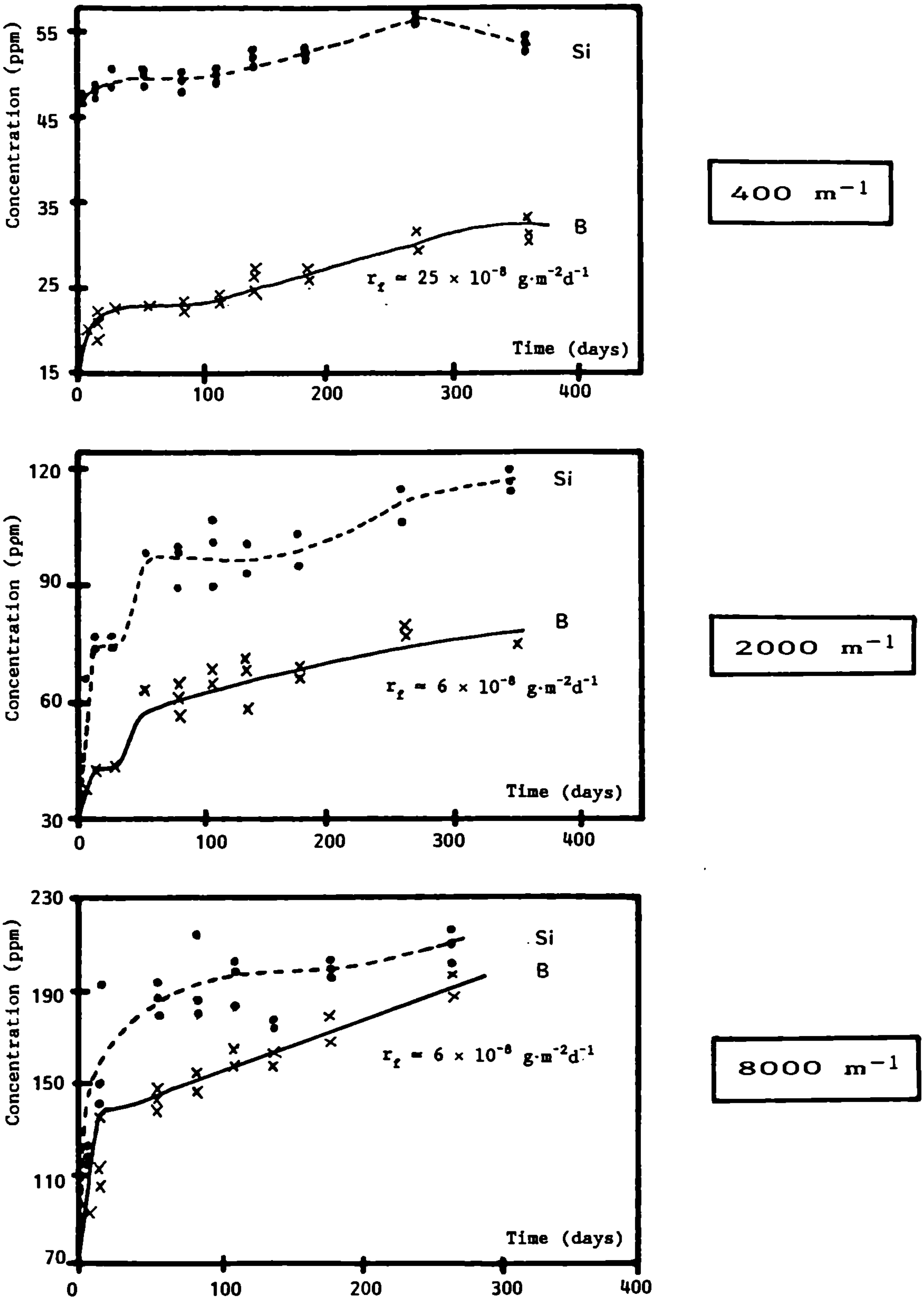

Figure 1 - Boron and Silicon Concentrations versus Time during the "Solubility" Experiments

TESTING THE ALTERATION OF WASTE GLASSES UNDER GEOLOGICAL STORAGE CONDITIONS

Contractor:	CEA, CEN-Valrhô, SDHA, F
Contract No:	FI1D-0096
Duration of Contract:	September 1986 - August 1988
Period Covered:	January 1988 - December 1988
Project Leader:	N. Jacquet-Francillon

A. OBJECTIVES AND SCOPE

A large number of parameters must be taken into account to predict glass alteration behavior in a geological repository: flow rate, temperature, pressure, pH, Eh, CO_2 content, radiolysis, water composition, nature of the surrounding rock, backfill material, possible corrosion products, etc. Laboratory parameter studies have been conducted for many years and are indispensable to an understanding of the glass alteration mechanisms and the effects of each parameter. However, none of the parameters is independent of the others and although investigating them separately is not sufficient, a systematic study of all possible combinations would be prohibitive. Under these circumstances parameter experiments must be completed by integral tests which simulate all of the parameters of a granitic repository as realistically as possible.

The objective of this program is to conduct a series of integral leaching experiments meeting this criterion. The program is expected to provide information in the following areas:

- equilibrium concentrations which tend to occur when all of the environmental materials are present;
- glass alteration rate under steady-state conditions;
- effect of smectite (considered for storage in France) on glass alteration: previous experiments showed the determining effect of the nature of the clay used as a backfill material;
- identification of newly formed compounds under integral test conditions;
- actinide behavior in a complex geological medium: leaching rate and physicochemical form.

B. WORK PROGRAM

2.1 Two nonradioactive experiments with simulated SON 68 glass using monolithic and fractured blocks to simulate an industrial glass block.

2.2 Four experiments with alpha-doped glasses: the glass samples will be spiked with uranium-thorium, neptunium, plutonium and americium, respectively.

2.3 Four mini-experiments with moist clay on nonradioactive glass and on plutonium-doped glass.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

All the experiments covered by this contract have now been completed and the related investigations have been carried out. Test TAV 9, which has been in progress for 32 months, will continue as part of the "long duration" test under contract FI1W2-0180 and will not be terminated until July 1989.

Progress and Results

2.1 TAV Experiments: Nonradioactive Glass in Granite

Three experiments were undertaken according to a procedure designed to take account of the parameters imposed by storage in a granitic environment in which the glass was leached in contact with environmental materials (NS 24, granite, sand + 5% smectite). Test TAV 7 was conducted with a monolithic glass specimen; TAV 9 and TAV 11 used fractured glass specimens with an estimated 10:1 or 12:1 increase in glass surface area due to fracturation.

Results:

Although the glass surface area exposed to leaching in a fractured glass block was 10 to 12 times greater than for a monolithic glass block, the glass quantity effectively leached increased only by 1.4 times. Observations showed that glass corrosion was not limited by water access into the block, by probably by the concentration of the species in solution (Figure 1).

A small amount of clay was observed to result in much more significant glass alteration, although the steady-state silicon concentrations were higher than those observed in pure water at the same pH. The environmental materials may affect the C* ("solubility limit") of the glass surface.

Under the test conditions (low clay mass and large glass surface area) the corrosion rate diminished sharply between 3 and 12 months. At the end of the test the glass corrosion rate under pseudo steady-state conditions remained between 3.5 and 10 times higher than for the same SA/V ratio in pure water. Newly formed phases on the glass surface were too poorly crystallized or were present in insufficient quantities to be identified.

2.2 TAV Experiments: Radioactive Glass in Granite

Three tests were carried out with radioactive glass specimens under the same conditions as above: the specimens were doped with ^{237}Np, ^{238}Pu and ^{241}Am, respectively.

Results:

The experiments showed that the glass activity did not modify the corrosion behavior of the glass matrix (Figure 2). However, the presence of clay significantly affected the actinide behavior, notably actinide retention in the alteration film. The radioactivity released by leaching was quickly trapped by the clay (and sand) and did not diffuse to a large extent in the leaching pot: 75% of the neptunium, 90% of the americium and 99% of the plutonium remained trapped within the first few centimeters around the glass block. The actinide retention factors in the alteration film were lower than those measured during experiments in pure water: $RF_{(B)}Np \simeq 2$; $RF_{(B)}Pu \simeq 80\text{-}240$; $RF_{(B)}Am \simeq 8$ (Table I).

2.3 Tests in Moist Clay

These tests were conducted with nonradioactive glass specimens and with ^{239}Pu-doped glass.

Results:

With both active and inactive glass specimens, the presence of moist smectite 4a resulted in severe glass alteration even within the closed system imposed by the test conditions. The glass corrosion rate corresponded to the value expected for a Soxhlet system at 90°C: the R7T7 glass dissolution activation energy is about 75 kJ/mole, and the corrosion rate virtually doubles between 90°C and 100°C (Figure 3). It should be noted that no drop in the corrosion rate was observed after 6 months under nonradioactive conditions.

Moreover, in presence of moist smectite 4a the ^{239}Pu retention factor was even lower than for the TAV tests ($RF_{(M)}Pu = 6$) while in double distilled water a retention factor of 400 was measured for ^{239}Pu. Plutonium becomes a mobile element in the alteration film in the presence of large amounts of clay. As in the TAV tests, the ^{241}Am retention factor in the alteration film was very low ($RF_{(M)}Am = 3\text{-}5$).

Conclusion

This investigation highlights the need for careful attention to the selection of environmental materials, notably clays (if they are used) since they have a decisive influence on the degree of glass alteration and on actinide retention by the alteration film.

Clay, by consuming glass corrosion products (Si, Na, Al, Zn, etc.) prevents or retards the accumulation of a high silicon concentration in the leachate that slows glass corrosion, and probably affects the C* at the surface.

The most important factor that must be taken into consideration with respect to glass alteration in the presence of clay appears to be the C/SA ratio (clay mass to glass surface area). This factor seems to regulate the time during which high corrosion rates are maintained (Figure 4) since clay does not have an unlimited capacity to consume glass corrosion products.

Activity	^{237}Np		^{239}Pu Glass				^{241}Am	
			$^{239/40}$Pu	^{241}Am	$^{239/40}$Pu	^{241}Am		
	10^3 Bq	%	10^3 Bq	10^3 Bq	%	%	10^3 Bq	%
Leachate	0.3	0.2	0.2		0.1	0	0.7	0
Solution Samples	0.3	0.2	3		1	0	1.9	0
Sand + Smectite								
Sample	16		15/29	204	5.4	7.3	29038	
+ Remainder	178/338		218/768	8333/13875	84	89.8	$(299/474)\times10^3$	
Total	194/354	92	233/797	8597/14079	89.4	97.1	$(328/503)\times10^3$	99
Granite	4	1.9	9	46	3.5	1.6	-	-
NS 24	12	5.7	15.5	32	6	1.1	2204	1
Total (22 months)	211/371	100	261/825	8618/14160	100	100	$(330/505)\times10^3$	100

Table I - Measured Leached Activity Balance (Minimum/Maximum Hypothesis) after 22 Months for TAV tests with ^{237}Np, ^{239}Pu and ^{241}Am

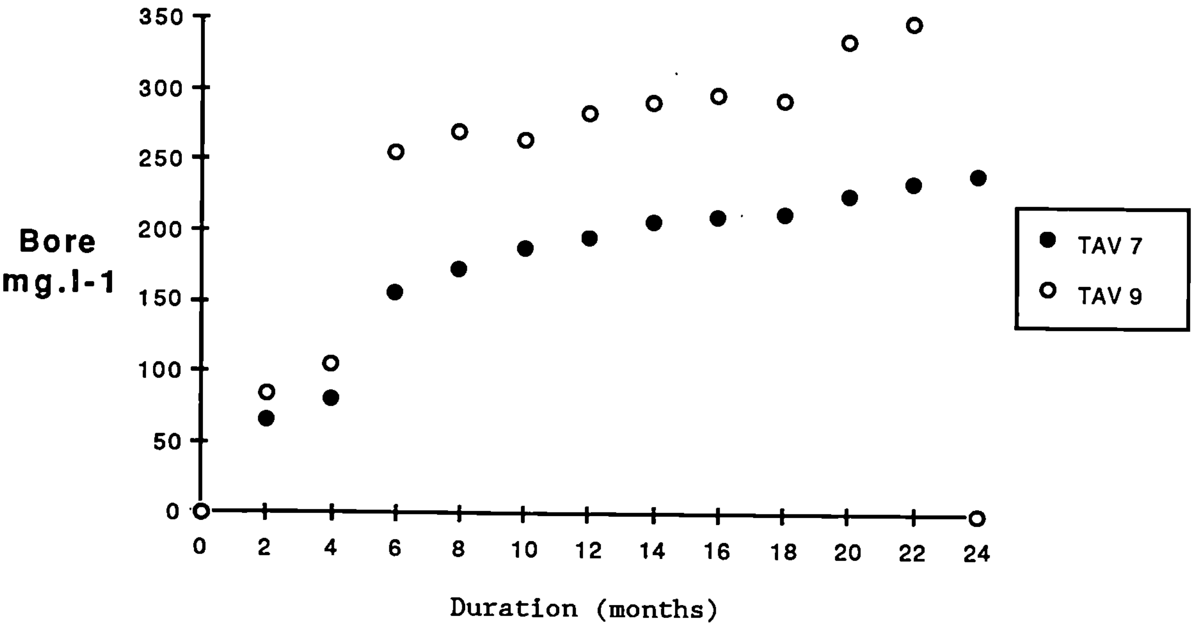

Figure 1 - Comparative Evolution of Boron Concentrations in Solutions of Leaching Vessels TAV 7 (monolithic) and TAV 9 (fractured)

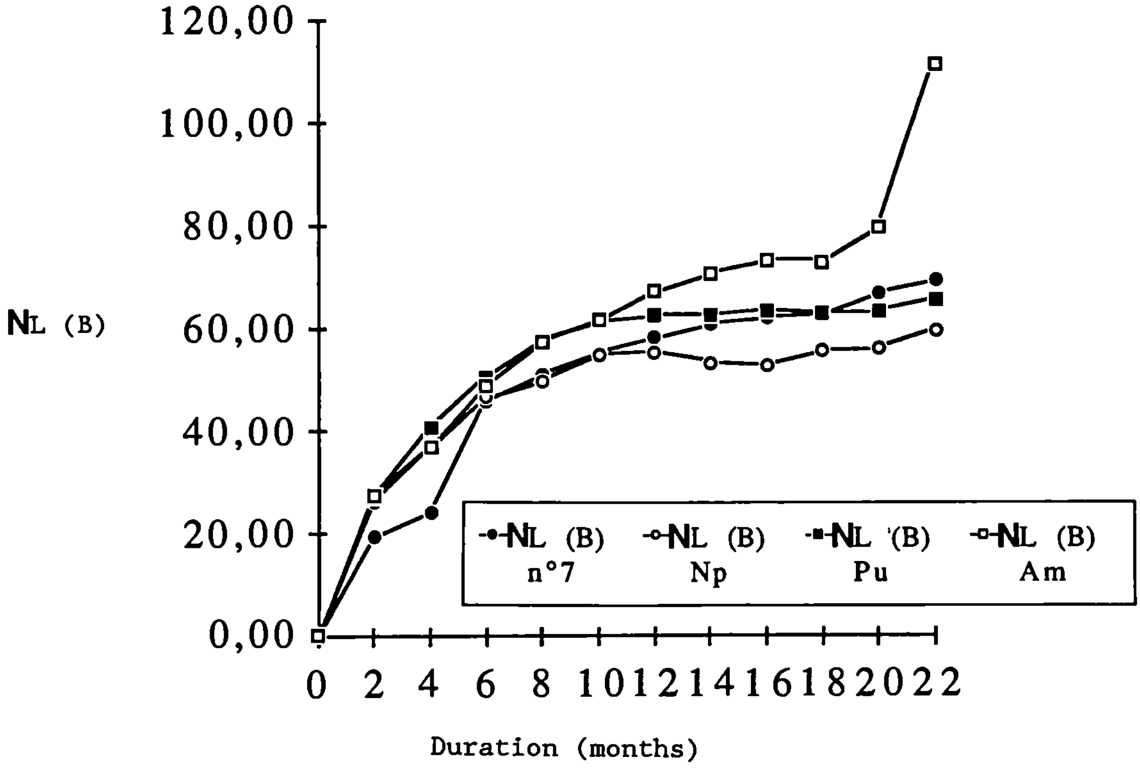

Figure 2 - Comparative Evolution of Normalized Boron Loss(g·cm^{-2}) for TAV 7, ^{237}Np, ^{239}Pu and ^{241}Am

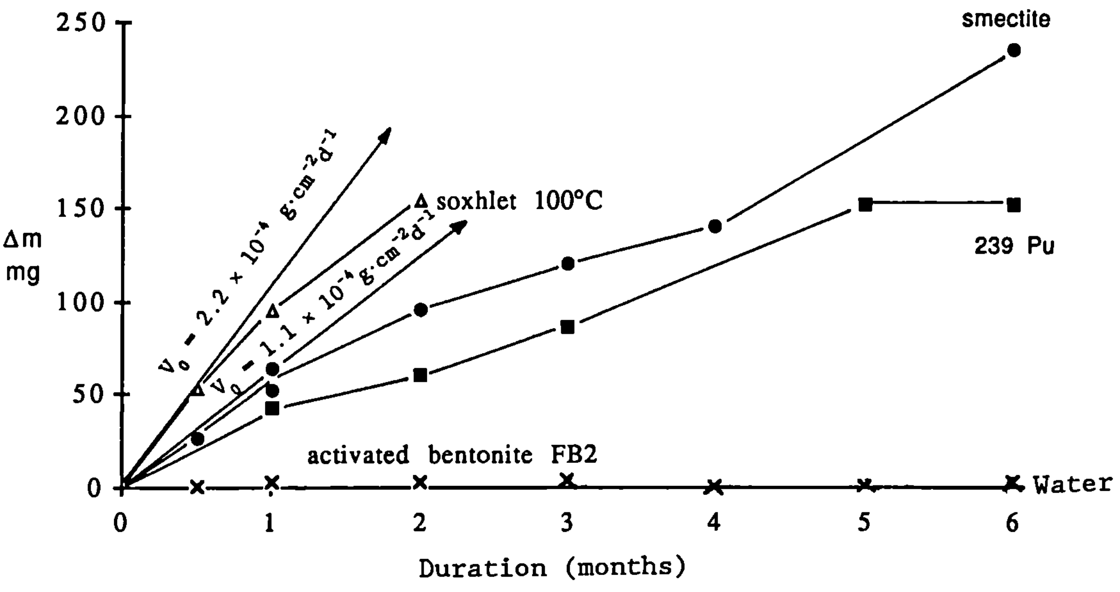

Figure 3 - Mass Loss (mg) versus Time:
Results in Moist Clay at 90°C Compared with Soxhlet Test Results at 100°C and Pure Water Tests under Static Conditions

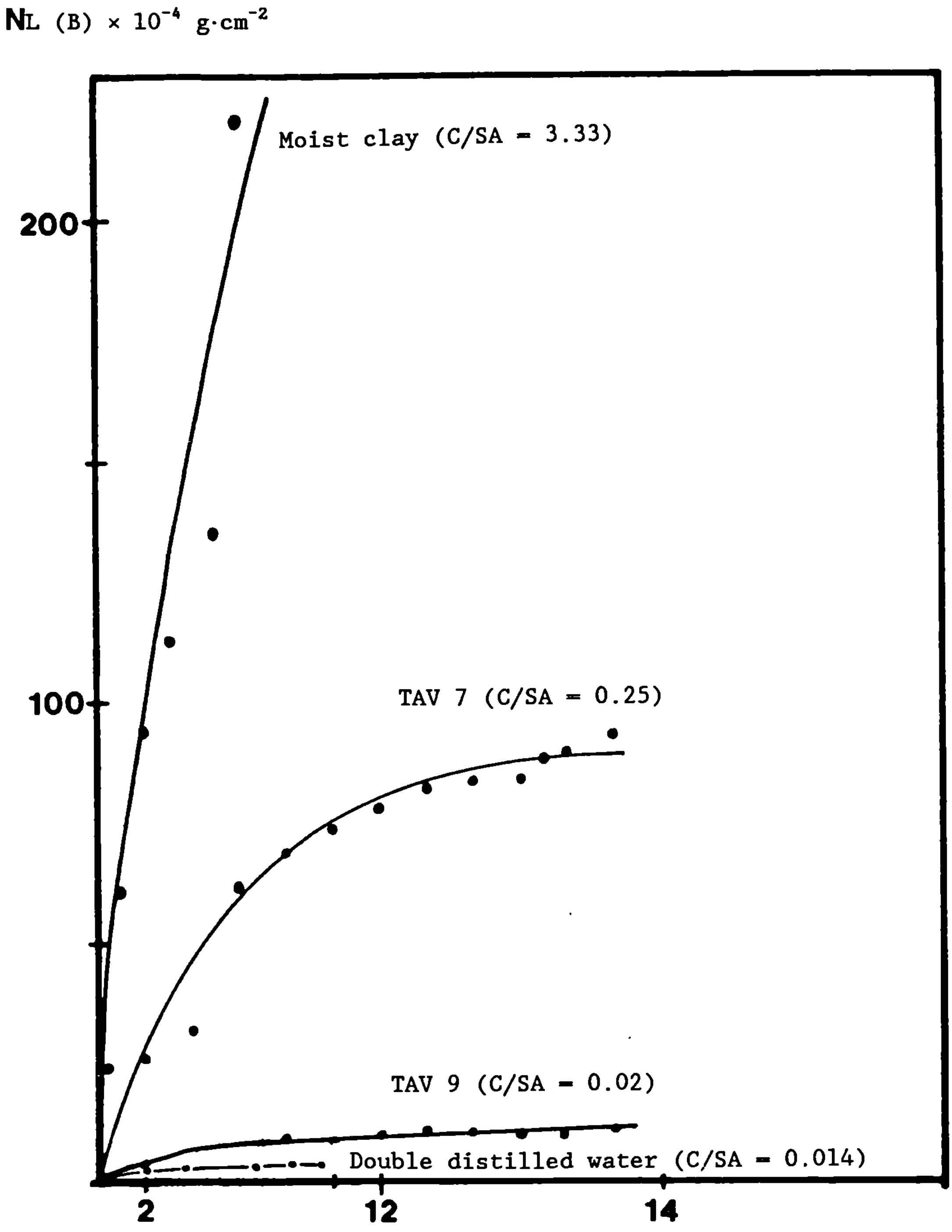

Figure 4 - Effect of C/SA Ratio (Clay mass/glass Surface Area) on Corrosion Rate

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 glasses which had 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 general progress of the work is as follows:

. B.1. and B.2 are progressing normally.

. B.3. The product quality of the vitrified waste was found not to affect the leach rate and was therefore unlikely to affect the equilibrium concentrations that will determine the release rate. This section was therefore considered not to be technically necessary.

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.

Previous work /1,2/ had shown that under reducing conditions and in the presence of a backfill containing 1 part of Ordinary Portland Cement to 3 parts Pulverised Fuel Ash (OPC(1)/PFA(3)) the steady state concentrations of Tc, Np, Pu and Am were respectively 0.1, 4, 1 and 45 times their Limiting Concentrations. Further capsules were set up with the variables as specified in Table I to investigate whether any of these variables caused significant increases in the steady-state concentrations. Capsules were opened after 1, 3, 6, 12 and 13 months. The results for the 12 months capsules are given in Tables II to V. For many of these, the oxidation potential (Eh) had risen above the lowest values reached but this did not seem to affect the observed concentrations.

The concentration of Tc in the only capsule that did not contain Fe or Ti metal was much higher than the others, presumably due to the formation of soluble Tc[IV]. The capsule containing Ti + stainless steel had a significantly higher concentrations than the others and the concentration in the capsule containing metallic iron but with an air atmosphere was also above the limiting concentration.

The concentration of Np was highest in the capsule containing Boom clay, where it was about two orders of magnitude greater than those containing OPC/PFA. The concentrations of Pu and Am were also highest with this backfill but the differences were not so great as with Np.

Coupons of glass contained in the capsules enabled weight loss leach-rates to be measured and these are given in Table VI. The value obtained in the clay containing capsule was $2.4 \times 10^{-6} g.m^{-2}.sec^{-1}$, about the same as would be found in an MCC-1 test. In the capsules containing OPC/PFA the leach rates were about one hundred times less than this.

In all these experiments, the results for SON68 were similar to those for MW.

Steady state concentration measurements were also made in systems containing samples of two fully active MW glasses with activity levels of 20 $GBq.g^{-1}$. Because of the high activity, the system was different from the doped glass experiments. A sealed steel vessel was sampled at intervals rather than separate glass capsules being opened after a given time period had elapsed. The water to solids ratio had therefore to be higher in these experiments than for the doped glass ones in order to have sufficient leachant for several analyses.

The results are also given in Tables II to V. The concentrations for Tc, Np, Pu and Am are factors of 7, 10, 10^3-10^4 and 1-10 higher respectively than for the doped glass experiments. The differences for Tc, Np and Am may be due to the different conditions but this seems improbable for Pu. A possible explanation is that it is due to the relatively higher Pu inventory in the fully active experiments.

2. Radiation stability of the glasses

The density of the UK reference glass MW, doped with 2.5wt.% Pu-238, has continued to decrease with radiation dose giving a predicted linear expansion at saturation of 0.16%. A sample of SON68 which has received a lower dose is behaving similarly but it is too early to predict the saturation expansion.

3. References

/1/ BOULT, K.A., DALTON, J.T., HOUGH, A., MARPLES, J.A.C., ROBERTSON, G.P., and WILKINS, R.I., in CEC annual report for 1987, EUR 11482

/2/ HOUGH, A., and MARPLES, J.A.C., International Conference on the Scientific Basis for Nuclear Waste Management XII, Berlin 1988. To be published by MRS 1989.

4. Conference attended

MRS conference in Berlin, October 1988 as reference /2/ above.

TABLE I: WEIGHTS OF COMPONENTS USED IN THE CAPSULES(/GRAMS)

Component	Ref	Oxidising Conditions (g)	90°C	SON68	Ti Overpack	Clay	Humic acid	Fe_2O_3 (g)
Glass (a)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Iron (b)	5.0	5.0	5.0	5.0		5.0	5.0	
Fe_2O_3								7.15
Titanium (c)					0.10			
Stainless (d) Steel					0.12			
OPC(1)/PFA(10)	10.0	10.0	10.0	10.0	10.0		10.0	10.0
Clay(e)						10.0		
Humic Acid (f)							0.005	
Water	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0

(a) MW except for set 4 (SON68)
(b) Commercial purity Fe filings
(c) Ti - 0.2wt.%.Pd
(d) 316 Stainless steel
(e) Boom clay from Mol in Belgium
(f) Commercial purity
(g) Air atmosphere (otherwise $Ar-5\%H_2$)

TABLE II: Tc CONCENTRATIONS AT 12 MONTHS (MOLES.$m^{-3}/10^{-5}$)
(LIMITING CONCENTRATION: 6.7)

Component	Eh(mV)	pH	Filter	
			0.45µm	1.8nm
OPC(1)/PFA(3) (Previous work /1,2/)	+60	11.4	0.7	0.35
OPC(1)/PFA(10)	-70	10.5	2	2
Oxidising (Fe)	+165	10.4	10	10
Oxidising (Fe_2O_3)	+240	10.3	11000	10000
90°C	+240	9.2	4.5	4.5
SON68	+135	10.5	2	3
Ti/SS	+105	10.5	130	130
Clay	-420	7.7	6	7
Humic Acid	+45	10.5	3	3
Fully Active				
(a) Magnox waste	+100	9.7	<50	
(b) THORP waste (1 month)	+110	10.2	15	

TABLE III: Np CONCENTRATIONS AT 12 MONTHS (MOLES.m^{-3}/10^{-7})
(LIMITING CONCENTRATION: 2.1)

Component	Eh(mV)	pH	Filter	
			0.45µm	1.8nm
OPC(1)/PFA(3) (Previous work /1,2/)	-20	11.4	7	9
OPC(1)/PFA(10)	+50	10.5	6	1
Oxidising (Fe)	+250	10.5	15	2
Oxidising (Fe$_2$O$_3$)	+220	10.3	12	30
90°C	+180	9.4	20	10
SON68	+165	10.6	85	40
Ti/SS	+105	10.5	7	10
Clay	-150	7.8	1200	1700
Humic Acid	+105	10.5	30	30
Fully Active				
(a) Magnox waste	+100	9.7	60	
(b) THORP waste (6 months)	+110	10.2	60	

TABLE IV: Pu CONCENTRATIONS AT 12 MONTHS (MOLES.m^{-3}/10^{-10})
(LIMITING CONCENTRATION: Pu-239: 20% Pu-240.23)

Component	Eh(mV)	pH	Filter	
			0.45µm	1.8nm
OPC(1)/PFA(3) (Previous work /1,2/)	-60	12.5	20	4
OPC(1)/PFA(10)	+40	10.4	0.1	0.1
Oxidising (Fe)	+60	10.8	0.3	0.2
Oxidising (Fe$_2$O$_3$)	+240	10.1	0.1	0.03
90°C	+120	9.7	0.1	0.05
SON68	+170	10.8	0.05	0.03
Ti/SS	-170	10.6	0.05	0.1
Clay	-410	7.8	3	2.5
Humic Acid	+165	10.7	0.02	0.02
Fully Active				
(a) Magnox waste	+100	9.7	100	
(b) THORP waste (6 months)	+110	10.2	1200	

TABLE V: Am CONCENTRATIONS AT 12 MONTHS (MOLES.$m^{-3}/10^{-9}$)
(LIMITING CONCENTRATION: 0.047)

Component	Eh(mV)	pH	Filter	
			0.45µm	1.8nm
OPC(1)/PFA(3) (Previous work /1,2/)	+10	10.6	2	2
OPC(1)/PFA(10)	+50	10.5	0.2	0.4
Oxidising (Fe)	+250	10.5	0.4	0.3
Oxidising (Fe_2O_3)	+210	10.3	0.5	0.3
90°C	+180	9.4	0.2	0.3
SON68	+165	10.6	1	0.2
Ti/SS	+105	10.5	0.3	0.2
Clay	-150	7.8	2.0	2.0
Humic Acid	+105	10.5	0.5	0.1
Fully Active				
(a) Magnox waste	+100	9.7	9	
(b) THORP waste (6 months)	+110	10.2	0.3	

TABLE VI: WEIGHT-LOSS LEACH RATES AFTER 12 MONTHS AT 60°C
($g.m^{-2}.sec^{-1}/10^{-8}$)

Components	Leach rate
OPC(1)/PFA(3) (Previous work/1,2/)	<1
OPC(1)/PFA(10)	1.8
Oxidising (Fe)	2.2
90°C	2.3
SON68	3.6
Ti/SS	2.2
Clay	240
Humic acid	3.0

LONGTERM BEHAVIOUR OF TRU-WASTE BEARING CERAMICS

Contractor : Kernforschungszentrum Karlsruhe GmbH / FRG
Institut für Nukleare Entsorgungstechnik (INE)
Contract N° : FI1W/0098-D (B)
Working Period. : January 1988 - December 1988
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 10^{-8} and 10^{-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 α-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 α-emitting radionuclide, so the desired high α-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 (α-dosis).

B.3 : Leaching of these samples at elevated temperature in Q-brine.

B.4 : Characterization of these samples after the leaching experiments and after reaching the α-dosis required.

C. PROGRESS OF WORK AND RESULTS OBTAINED

1. Synthesis and Preparation of Samples (B.1, B.1.1)

Due to its availability, Plutonium(-238)O_2 with an amount of 20 wt.-% has been incorporated into the ceramic matrix, which consisted of a mixture of 66 wt.-% reactive corundum, 17 wt.-% kaolinite, and 17 wt.-% bentonite. Another series of specimens for comparing investigations consisting of the same type of matrix, loaded with 30 wt.-% of dissolver residues from the reprocessing of fast breeder reactor fuel has been prepared 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 (Al_2O_3), mullite ($Al_6Si_2O_{13}$) and PuO_2, considering the ceramic KAB 78 containing 20 wt.-% Pu(238)O_2,
- corundum (Al_2O_3), traces of mullite ($Al_6Si_2O_{13}$), (U,Pu)O_2, ε-phase and RuO_2 with respect to the KAB 78 ceramics containing 30 wt.-% of original dissolver residues.

During the first two years the internal absorbed α-dose of the Pu(238) ceramics reached 5.6 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.

By means of electron microscopy well selected regions of the "time-lapse" sample have been recorded twice 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 α-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/cm^2d 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 started and are still running.

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)O_2.

CHARACTERIZATION OF HLW GLASS SAMPLES

Contractor: HMI, Berlin, FRG
Contract No: FI1WK-0099D(B)
Duration of contract: October 1986 - December 1989
Period covered: January 1988- December 1988
Project Leader: G. Malow

A. OBJECTIVES AND SCOPE

In the frame of the two preceding European joint programmes on "Testing and Evaluation of the Properties of Various Potential Materials for Immobilizing Highly Radioactive Waste" starting in 1975 a large amount of data on the characterization of simulated solidified high level waste forms has been acquired. Thermal, mechanical and radiation stability and the chemical stability under the attack by various aqueous media were tested. The experiments have been performed under waste repository relevant conditions and under simplified laboratory conditions selected to investigate the corrosion mechanism. In the present research programme, the fully radioactive Cogema glass R7T7, proposed as a reference glass, will be investigated in a hot cell facility. The results will be compared with those obtained for non-radioactive glass samples in order to find out whether there are significant differences due to radiation and/or different way of glass manufacturing. Due to a delay in the melting of the highly radioactive glass, the experiments could not be started. Therefore, a short term post-investigation of the highly radioactive glass from the PAMELA plant has been proposed. The aim is a check-up of the active LEWC glass SM513LW11.

B. WORK PROGRAMME

1 HAW glass R7T7 or SON68.18.17.L1C2A2Z1 will be produced in Valrho,France, sent to the contractants with nominal composition and production conditions.
2 Preparation of imbedded, polished samples for investigations listed under 3.1, 3.2 and 4.
3 Quality control outside the hot cells.
3.1 Chemical composition of the bulk glass by EPMA measurements and comparison with nominal composition.
3.2 Investigation of homogeneity of the glass and unsoluble phases in the glass melt by EPMA and SEM.
4 Crystallization and devitrification at the temperature of maximuum crystallization velocity.
5 Leaching experiments.
5.1 Preparation of samples: chips and possibly powder.
5.2 Experiments in autoclaves between 110° and 190°C in saturated salt brines.
5.3 Short- and long-term leaching experiments, i.e. between ≤30 d and ~1000 d.
6. Analyses of the leachates by ICP atomic emission spectroscopy.
7. Investigation of HAW glass after leaching.
7.1 Mass loss measurements of leached glass samples.
7.2 SEM and EPMA investigation of the surface layers and identification of crystalline phases.

C. PROGRESS OF WORK AND OBTAINED RESULTS

1. COGEMA GLASS SON68.18.17.L1C2A2Z1

Due to the delay in the production of the highly radioactive glass in Valrho, France, the beginning of the investigations on the radioactive glass R7T7 has been scheduled for 1989. Therefore, results cannot yet be presented at this time.

The research programme was started with the installation and testing of new equipment for the hot cell facility used when performing the experiments listed in the work programme.

The quality control of the glass will be executed by using scanning electron microscopy to check the homogeneity of the glass and insoluble phases. Electron microprobe will be used for analysing the chemical composition of the glass and crystal phases formed during annealing at the temperature of maximum crystallization velocity.

Corrosion experiments will be carried out at 150 and 190°C under static conditions in saturated NaCl-$CaSO_4$ and KCl-$MgCl_2$-Na_2SO_4 brines and with container material present. The leachates will be analysed by ICP for the elements Sr, Zr, Mo, Ba, La, Ce, Nd, Cr, Fe, Mn, Ni and the glass formers Si and B. The surface will be investigated by SEM and EPMA and enrichments and depletions of elements in the surface layer will be reported. The question of long-term extrapolation of corrosion rates will be addressed.

2. PAMELA glass SM513LW11

Specification

Samples of the highly active PAMELA glass SM513LW11 have been shipped from the PAMELA plant in Mol, Belgium to HMI. Sample preparation for optical and scanning microscopy and annealing experiments have been started. Some properties of the inactive glass described in /1/ will be used to compare the results on radioactive and inactive glasses. The crystallization experiments with the highly active glass have been completed. The detected crystal phases are much the same as in the inactive simulated glass.

The γ-spectrum of the PAMELA glass is shown in figure 1, identified peaks are labelled (energy range being 30 keV to ~1,8 MeV, 4096 channels). Most of the γ-lines belong to europium and cesium. The line at 1,332 MeV belongs to Co-60, the one at 59 keV to Am-241. Figure 1b demonstrates the high energy resolution of the Ge-detector (1,74 keV at 1,332 MeV (Co-60)), emphazising the high potential to analyse complex γ-spectra in great detail. The specific γ-activities were measured and compared with the data from the PAMELA plant (table 1). These values are in a good agreement. Standard deviations are given in parentheses. Only the values for Eu-154 and Am-241 are just outside the error limits.

In order to estimate the specific activity of Sr-90, a glass sample was fused and separation of Sr-90/Y-90 performed.The fusion process was performed with a piece of glass instead of glass powder. Therefore a high excess of sodium carbonate had to be used. For the following separation process the pH-value of the fusion solution was set to 5.3±0.1. Under this pH condition, the fusion solution is unstable and has to be processed immediately. The quantitative separation of Sr-90/Y-90 was demonstrated by using the chelating resin CHELEX 100®. A detailed description of the separation procedure will be given in /2/.

Leaching

Mass Losses

Leaching experiments were performed according to MCC-1 /3/ with the PAMELA glass SM513LW11. For reasons of easier handling in the hot cells the ratio between the sample surface area and the volume of the leachant (SA/V) was $\sim 2m^{-1}$ instead of $10m^{-1}$ as in MCC-1. Leaching was performed for 10, 30 and 100 days at temperatures of 90 and 150°C. The mass losses calculated from activity measurements and from weighings are shown in figure 2. Figure 2 additionally shows normalized mass loss values for the simulated inactive glass. The agreement of the normalized mass losses of the inactive glass and the calculated mass losses from the Cs-activity measurements is good.

Surface layers

The glass surface layers were investigated by γ-spectoscopy and microprobe analysis. Figure 3 shows a γ-spectrum of the surface layer after leaching 30 days at 150°C. A number of Eu-154 peaks were detected, but also Cs-137 and Co-60. Most of the Cs-activity was detected in the leachate whereas Eu-154 could not be detected in the leachate. SEM investigations have revealed that there at least two separate surface layers on the glass. The qualitative analysis by microprobe revealed no differences in the composition of the two layers. A quantitative evaluation of these findings, (leachate and surface layer composition) is in progress.

REFERENCES

/1/ Schiewer, E., "The Borosilicate Glass for 'Pamela'", Radioactive Waste Management and the Nuclear Fuel Cycle, Vol7 (2),April 1986, pp. 121-138.

/2/ Strachan, D.M., Schubert, P.,Kingston, H.M., "PRECONCENTRATION OF TRACE TRANSITION METAL AND RARE EARTH ELEMENTS FROM HIGHLY SALINE SOLUTIONS",Analytica Chimica Acta, to be published 1989

/3/ MCC-1P Static Leach Test Method, Nuclear Waste Materials Handbook (US Department of Energy, DOE/TIC-114s00, 1981)

TABLE I: SPECIFIC ACTIVITIES OF THE PAMELA GLASS SM513LW11

Nuclide/ Radiation	Specific Activities after Plant Operator		measured (decay corrected)	
	[Bq/g]	[mCi/g]	[Bq/g]	[mCi/g]
Cs-137	1,4 E09	37,8	1,3 E09	35,1 (±8%)
Cs-134	1,2 E07	0,32	1,2 E07	0,32 (±13%)
Eu-154	2,7 E07	0,73	2,4 E07	0,65 (±4%)
Am-241	1,2 E07	0,32	8,7 E06	0,23 (±25%)
Alpha	2,1 E07	0,57		
Beta	3,7 E09	100		

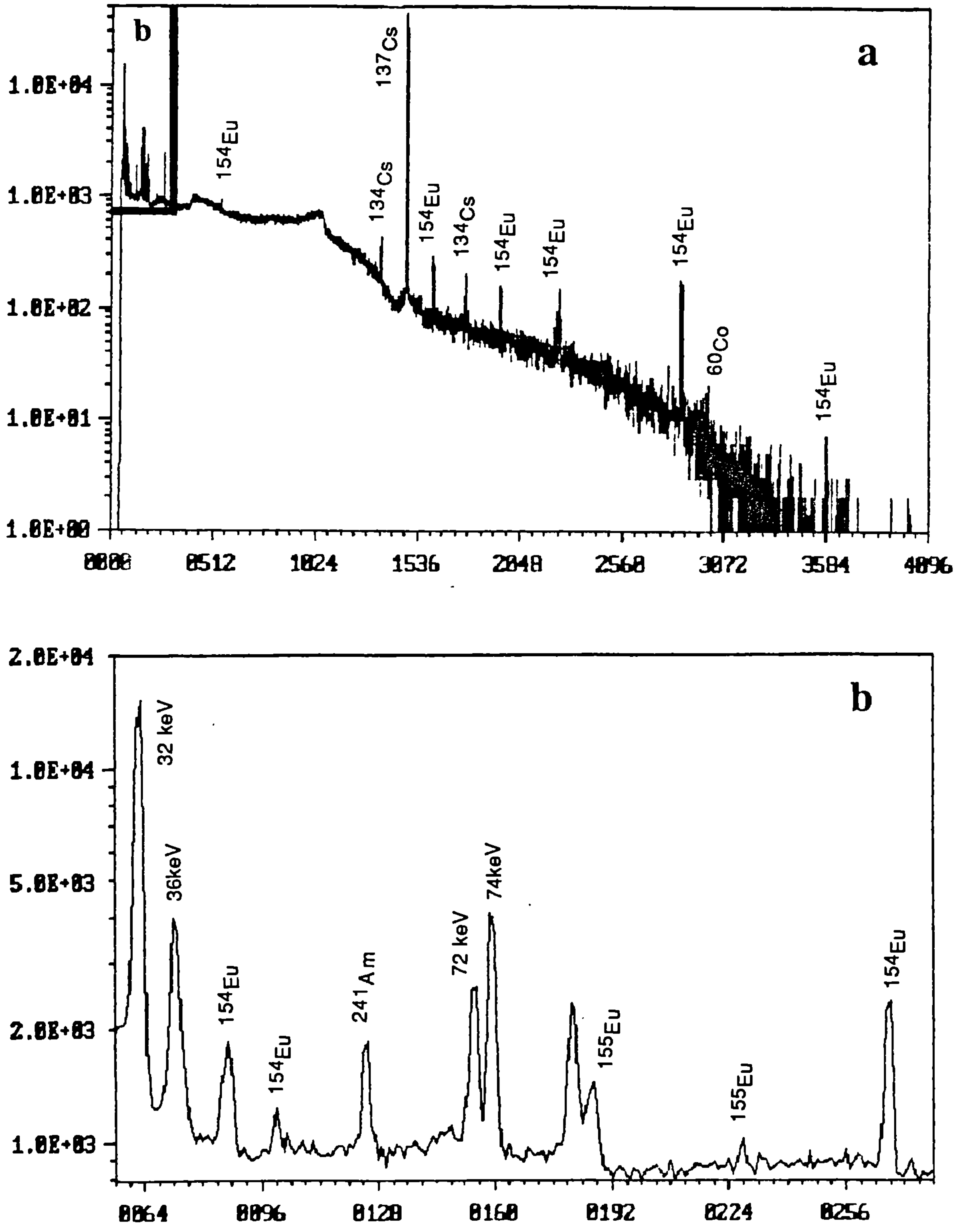

Figure 1: γ-spectrum of the PAMELA glass SM513LW11
a) in the energy region from ~30 keV to 1,8 MeV
b) in the low energy region from ~30 to 130 keV

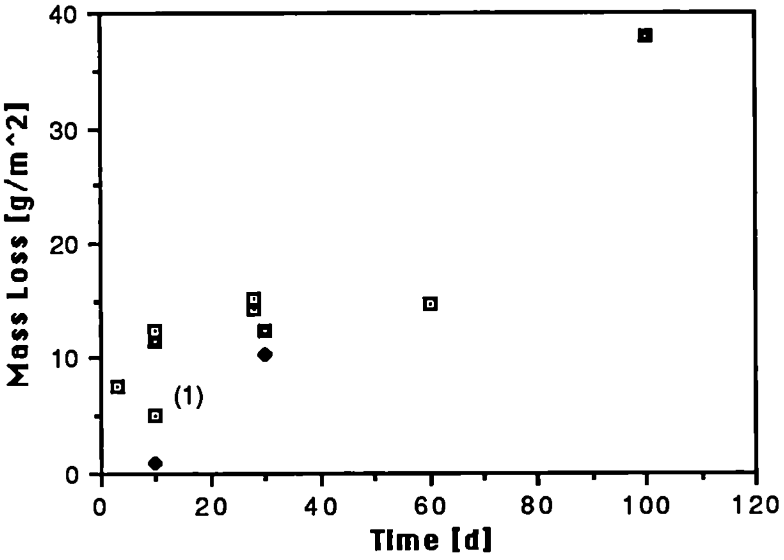

Fig. 2a

- ▫ 90°/Δm from normalzied mass losses of B,Na,Li and Mo (inactive glass)
- ◆ 90°/Δm* from weighing of the active glass
- ▪ 90°/Δm*Cs from activity measurements of Cs-137

(1): simulated inactive sample 30d at 600°C annealed

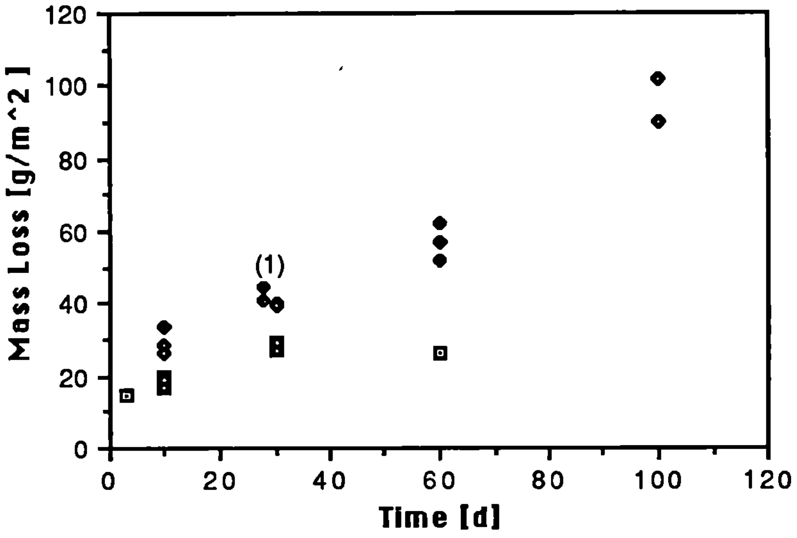

Fig. 2b

- ▫ 120°/Δm
- ◆ 150°/Δm from normalized mass losses of B,Na,Li and Mo (inactive glass)
- ▪ 150°/Δm* from weighing of the active glass
- ◈ 150°/Δm*Cs from activity measurements of Cs-137

(1) : Sample from the inactive Pilot Plant

Figure 2: Mass loss of the PAMELA glass SM513LW11 in deionized water measured and calculated by various methods.
a) at 90°C
b) at 120°C and 150°C

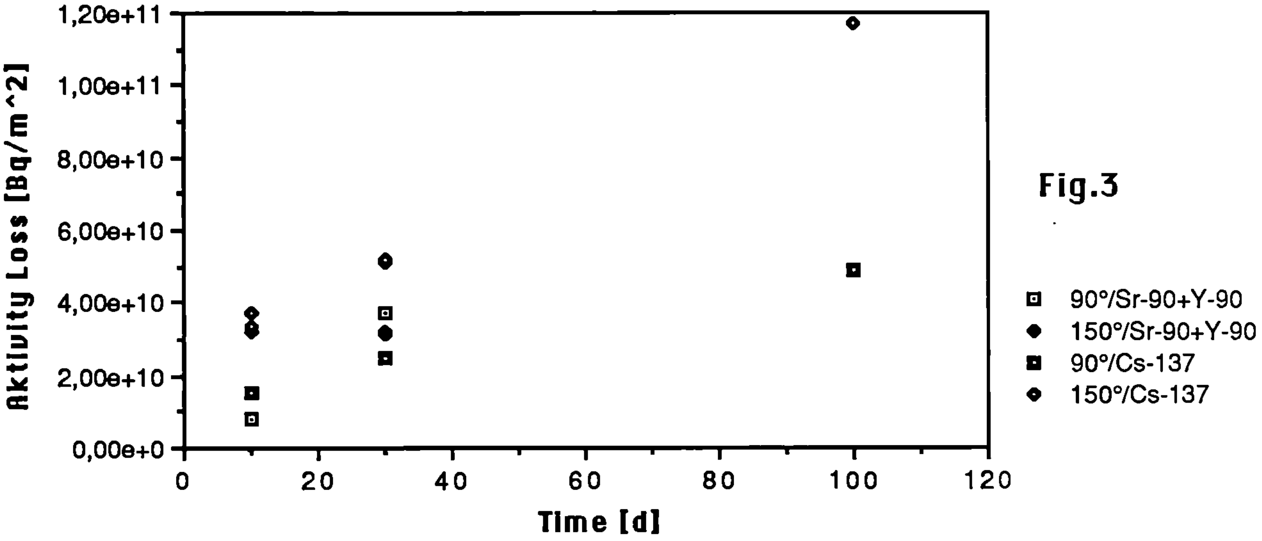

Fig.3

Figure 3: Activity losses of Sr-90+Y-90 and Cs-137 of the PAMELA glass SM513LW11 in deionized water at 90°C and 150°C.

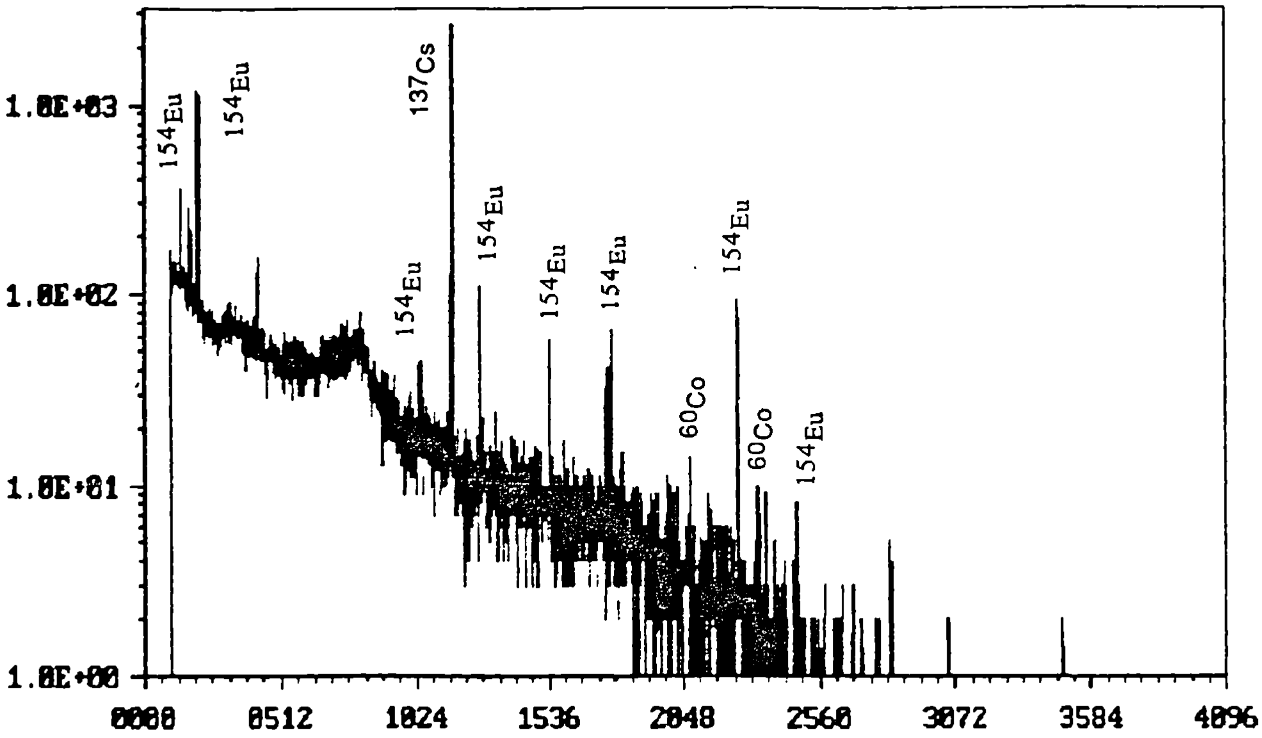

Figure 4: γ-spectrum of the PAMELA glass SM513LW11 after leaching in water (30 days at 150°C).

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 1988
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 no 302-83-15 WASB, 324-83-55 WASB, FI1W0100). Important progress was realised on the lucidation 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 and Pu-Cs-Sr doped glasses from the 86-87 programme are underway since more than 1.5 year. The influence of the surface layer (86-87 programme) has been evaluated. Further data and interpretations will continue to be produced. Preparations were done to start the "solubility" corrosion tests on Pu-Cs-Sr doped glasses, using powdered glass (86-87 programme). The other tests on inactive and tracered glasses from the 86-89 programme are to be started. These include, a.o. all tests on Np-Tc-Fe tracered glasses. This delay will necessitate an extension of the programme until 1990.

The corrosion experiments in an external γ irradiation field were continued in 1988, with an irradiation time of max. 90 d (dose rate $\cong 0.60 \times 10^5$ rad h^{-1}).

No corrosion tests on fully active glass samples were carried out yet, due to the actual unavailability.

Significant progress was realised for the in-situ experiments. The tests in the humid clay atmosphere were started at once, after improving the technical operation mode. During the second half of 1988 the first in-situ experiment (two years at 90°C, in direct contact with clay) was retrieved; the experimental data showed that the in-situ test could indeed provide significant and valuable data.

Progress and results

I. Corrosion mechanisms in clay media

I.1. Inactive experiments (glasses SON68, SM513, SM527, WG124)

The experiments started during the 86-87 contract were continued and further interpreted. The tests relate to either corrosion at 90°C in two clay media (mixtures of 10 or 500 g Boom clay per liter synthetic interstitial claywater, SIC), where durations of 1.5 year were reached, and an investigation of the influence of the surface layer formed during corrosion. For these latter tests a new test schedule was elaborated.

* Corrosion at 90°C in two clay/SIC media.
The trends observed during the first half year are confirmed: in the concentrated clay medium ("CCSICM") the glasses are corroded into a larger extent (about 10 times) than in the diluted clay medium ("DCSICM"). In the CCSICM, the corrosion rate continues to drop with further duration, and Si concentration in solution remains constant over the whole test duration. Boron continues to leach (case of the HLW glasses), whereas Mo stops leaching (case of LLW glass WG124). In the DCSICM data show an apparent saturation in solution for boron. Electron microprobe cross section analysis reveals that subsurface zones (e.g. enriched in Al and Na in case of SON68) form in the diluted clay medium, which are believed to be more indicative for the glass corrosion than the upper surface layer.
* Blank tests (only clay/SIC solutions) at 90°C show that the concentrations in solution of elements such as Si, Fe and Al decrease after some three months of interaction.
* Experiments performed at various temperatures (40, 90, 170°C) have shown that the surface layers formed during corrosion in general are not protecting towards corrosion.

I.2. Radioactive (tracer) experiments (glasses SON68, SM513, SM527)

During 1988 results were obtained on the leaching of Pu, Cs and Sr from glass SM527 at 90°C in CCSICM, until 240 d. The leaching of these isotopes proceeds with a slowly decreasing rate (approximately congruent with the glass matrix). The total inventory, and the mobile inventory (with molecular weight < 10^5 MW units) of Pu and Cs leached are of the same order of magnitude as for glasses SON68 and SM513. The data for Sr are not conclusive. The distribution coefficient, K_d, for Pu is about 10 times larger than for the other glasses, suggesting that Pu is relatively more sorbed on the clay in case of SM527. Analysis of the two year data for SON68 and SM513 is in progress.

Preparations were made for the following corrosion tests:
- Evaluation of the influence of the redox potential, E_h (using monolithic specimens of SON68, SM527 and WG124).
- Investigation of the solubility of the radionuclides in SIC, by using glass powder (125 - 250 µm particle size).

II. Influence of an external γ radiation field

A second irradiation campaign was finished, consisting of three irradiation tests (14, 42, 90 days) with a dose rate of about 10^{-5} rad h^{-1}. Compared with the first campaign (86-87), the clay to water ratio was increased (500 instead of 100 gl^{-1}), and SIC was used instead of pure water; also a few tests without clay were performed, using SIC or real interstitial claywater ("IC"). Conditions were either anoxic or oxic. The conclusions ralate to gas formation and glass corrosion;

(1) The generation of hydrogen increases with increasing dose; when clay is present, H_2 formation is smaller, however, and even decreases for the longer irradiation. This shows that H_2 is incorporated in some way in the clay. The H_2 generation in real claywater is larger than in the synthetic claywater. Other radiolysis products are CO_2, CH_4 and O_2.

(2) Glass corrosion in the clay/SIC solution is almost not influenced by the γ irradiation (90 days test). No further details are known so far. The decreased glass corrosion upon γ irradiation found before, in the more diluted clay medium, may be correlated with a larger dissolution of the clay in the irradiation field (resulting in larger Ca and Na concentration in solution).

III. In-situ experiments

III.1. Experiments in a humid clay atmosphere

As mentioned in the annual report for 1987, the ongoing experiments were seriously disturbed by excessive water accumulation within the tubes. During the first half of 1988 the experiments were stopped, and a suitable pumping system installed. The four inner teflon tubes including the waste glass samples were removed, repared, installed in the underground laboratory again (loaded with new specimens) and heated.

Investigation of the glass samples included in the first test sequence was limited, as they were subjected alternatively to humid atmosphere and water in a non-systematic way. The SAN60 (precursor for SM527) glass is strongly corroded, and at the same crystallized.

III.2. Experiments in direct contact with clay

In August 1988 the first retrieval of a test tube was realised. The test was carried out at 90°C during two years. The tube was overcored, retrieved, and dismantled in the laboratory, without major problems. The 64 waste form samples were cleaned and carefully weighed. The relevance of the test was proved by the following considerations:

- the clay surrounding the tube was in a perfect condition (contact with tube, humidity, E_h);
- no mutual interaction between the waste form samples occurred;
- moreover, the data for mass loss and surface morphology (composition, thickness of the layer) were comparable with those obtained in lab simulation tests.

The results show that the thickness of glass dissolved per year ranges between 180 and 20 µm, depending on the glass composition. Small changes in the glass composition, e.g. replacing part of the Fe_2O_3 by Al_2O_3 results in a significant improvement of the corrosion stability.

Publications and Lectures

(1) Laboratory and in-situ interaction between simulated waste glasses and clay - Annual report 1987
Presented at the CEC pogress meeting for task 3, sections 2 + 3 (Wurzburg, April 1988)

(2) Laboratory and in-situ interaction between simulated waste glasses and clay - Semestrial progress report January-June 1988
Presented at the CEC progress meeting for task 3, sections 2 + 3 (Harwell, September 1988)

(3) P. Van Iseghem, Glass-clay comparibility studies in Belgium
Nuclear Europe no 8-9, 54 (1988)

(4) P. Van Iseghem, W. Timmermans and B. Neerdael
In-situ testing of nuclear waste glasses in a clay laboratory - results after two years corrosion, Poster presentation at the XIIth Int. Symp. on the Scientific Basis for Nuclear Waste Management, October 88, Berlin

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 1988 - December 1988
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

Eleven tests have been undertaken to investigate the effect of environmental materials on leaching of transuranium nuclides. The 3-month and 6-month tests with ^{237}Np and ^{239}Pu have been completed, but the solution analysis results are not yet available. The 9- and 12-month tests with ^{237}Np and ^{239}Pu are still in progress; this part of the program is scheduled to end in June 1989.

The status of the integral tests is now as follows:

- Long-duration test (TAV 9): to be completed in July 1989.
- Clay tests: initiated in mid-January 1989.
- Salt tests: feasibility study now in progress (major difficulties have been encountered, including corrosion of experimental devices, spurious crystallization, etc.)
- Radioactive tests: these experiments have been seriously delayed; they depend on the fabrication of radioactive glass samples in the Vulcain cell and on publication of the safety report authorizing leach tests in the Clovis cell.

Part B - Thermoluminescence Investigation of Irradiation Damage in Glass

Investigation of TL mechanisms in simple glass compounds constituting the R7T7 nuclear waste glass has begun at the University of Bordeaux. At the same time, a prototype glove-box thermoluminescence analyzer has been designed and is now being built at Marcoule to investigate actinide-doped R7T7 glass samples.

Progress and Results

Part A - Radioactive Glass Interaction with Environmental Materials

2.2 Effect of environmental materials on leaching of transuranium nuclides

The results of the longer duration tests must be in before any conclusions can be drawn. It can already be affirmed, however, from mass loss measurements on the ^{237}Np and ^{239}Pu samples after leaching, that the degree of alterability is independent of the actinide contained in the glass but varies 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:

$$\text{sand} \leq \text{granite} < \text{bentonite} < \text{salt} < \text{illite} \leq \text{smectite} < \text{Boom clay}$$

^{237}Np Tests: Analysis results of activity released from the glass showed that under oxidizing conditions neptunium is a mobile element only weakly retained in the alteration film (Table I and Figure 1). The ^{237}Np retention factor in the alteration film was about 1 for all of the tests, with a maximum of 2 in presence of sand. The normalized neptunium mass loss between 3 and 6 months increased in all of the tests except with sand and granite.

^{239}Pu Tests: These tests were conducted on glass pellets containing ^{239}Pu together with ^{238}Pu and ^{241}Am. The leach rates for ^{239}Pu were lower than for ^{237}Np, but the combined leach rates for ^{238}Pu/^{241}Am were lower still. This probably indicates that in the media investigated (except for Boom clay) americium is more strongly retained than plutonium in the alteration film (Table II). The retention factors calculated from the mass loss from the glass samples were higher than for ^{237}Np. Low retention factors were found with granite, bentonite and salt. These figures are only indicative, however, given the uncertainty on the actual mass loss. More accurate retention factors can only provided relative to the boron leach rate.

Part B - Thermoluminescence Investigation of Irradiation Damage in Glass

The first objective was to understand thermoluminescence mechanisms in simple glass subsets of R7T7 glass. An investigation of TL mechanisms in vitreous silica and in a sodium borosilicate corresponding to the basic R7T7 glass composition involving combined use of TL, electron spin resonance (ESR) and cathodoluminescence (CL) revealed the role of oxygen holes as electron centers and of unbonded oxygen atoms as hole centers. The luminescent center could be due in part to the presence of trace amounts of titanium.

The results obtained with a quaternary (sodium alumino-borosilicate) glass sample were similar to those already observed with simpler glasses. They confirm the dominant role of oxygen as a hole center, and of oxygen vacancies as electron centers. Since the boron-oxygen hole center (BOHC) was the only paramagnetic center, the other centers involved must have captured an even number of charge carriers. As with the simpler glass specimens, this was attributed to the presence of B^{2-} centers (oxygen vacancies having captured 2 electrons) and Q^{2+} centers (oxygen atoms having lost two electrons) after irradiation. In either event, the glow curve thus appears to reveal oxygen defects in the material. Pending a more thorough demonstration, we feel that these results can be extended to R7T7 glass.

Table I - Normalized Mass Loss and Retention Factors for Neptunium

Material	Test No	3 Months		6 Months	
		NL(Np) 10^{-4} g·cm^{-2}	RF(Np)	NL(Np) 10^{-4} g·cm^{-2}	RF(Np)
Smectite	1 2	10.25 10.26	2.1 2.5	15.1 14.8	1.4 1.4
Bentonite	1 2	1.02 1.11	8.3 8.5	1.6 1.3	1.3 1.5
Illite	1 2	15.38 12.2	1.4 1.4	21.2 21.8	0.7 0.8
Boom Clay	1 2	19.55 22.45	1.5 1.4	42 54.8	1 0.9
Sand	1 2	3.55 3.3	1.9 1.7	1.1 1.3	2.1 1.8
Granite	1 2	4.53 3.9	1.8 1.4	1.5 1.6	- -
Salt	1 2	3.73 3.83	3.2 2.2	6.2 6.7	0.7 0.6

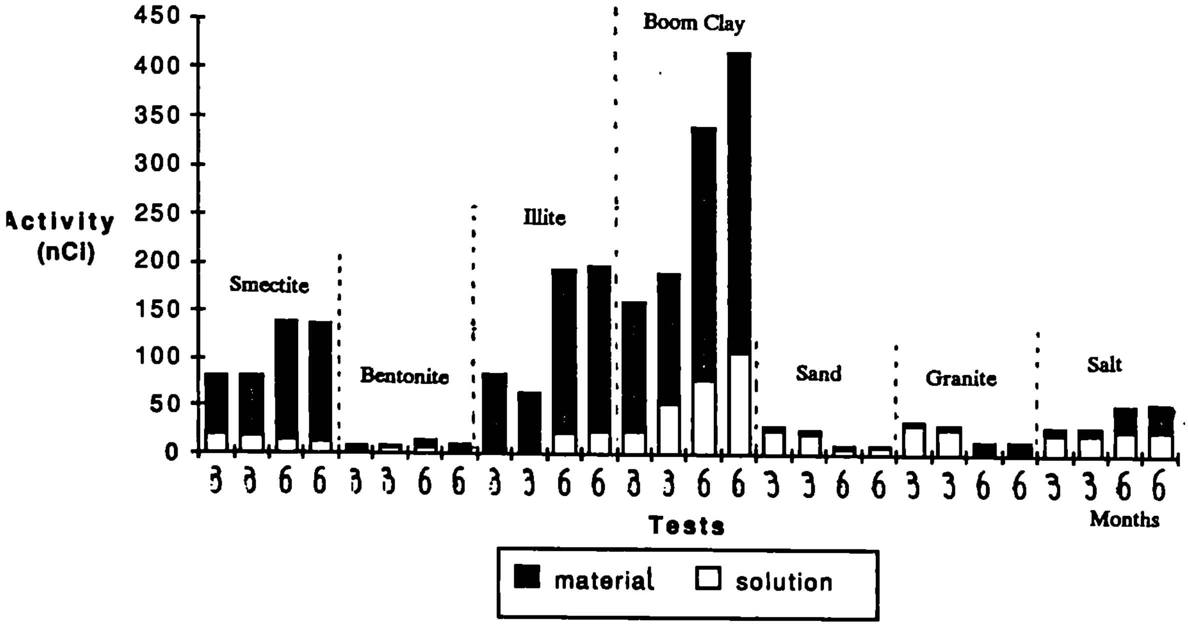

Figure 1 - Activity (in nCi) in Solutions and Environmental Materials for 3- and 6-Month Tests with ^{237}Np-Doped Glass

Table II - Normalized Mass Loss and Retention Factors for Actinides in the Alteration Film Based on α Spectrometry Data: ^{239}Pu-Doped Glass after 3 Months

Material	Test No	Normalized Mass Loss 10^{-4} g·cm^{-2}		Retention Factor	
		NL(^{239}Pu)	NL(^{238}Pu/^{241}Am)	RF(^{239}Pu)	RF(^{238}Pu/^{241}Am)
Smectite	1	1.02	0.75	22	30
	2	0.64	0.58	47.5	52.4
Bentonite	1	0.5	0.46	4.4	4.8
	2	0.52	0.49	6.3	6.7
Illite	1	1.16	0.5	19.7	45.8
	2	1.24	0.96	22	28
Boom Clay	1	1.54	2.6	10.5	12.1
	2	1.9	4.39	20.2	8.7
Sand	1	0.13	0.09	21.5	31.1
	2	0.19	0.11	13.7	23.6
Granite	1	0.4	0.22	2.5	4.5
	2	0.43	0.26	1.4	2.3
Salt	1	0.28	0.19	11.4	16.8
	2	0.4	0.26	7.5	11.5

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 1988 - December 1988
Project leader : 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 the 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.FI1WI/192 and FI1W2/00029).

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 Preparation and characterization of the glass in the cold IVET pilot plant (full scale).

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Some glass compositions have been prepared and tested. The glass composition named ENEA 8 has been selected and preliminarly characterized.

B.2.1 item has been cancelled, due to the constraints in the waste/glass ratio arising from the "ULISSE" process.

According to the research programme, the ENEA 8 glass has been prepared in condition as well as possible simulating the plant procedure. It has shown a bad thermal behaviour when slowly cooled. Then, another promising glass named BAZ has been chosen and characterized.

The physico-chemical characterization has been completed, while the mechanical and the chemical characterization is in progress.

MCC-1 static leach tests are going on at 90 °C, both at SA/V = 10 m^{-1} and 100 m^{-1}. Distilled water (DW), synthetic interstitial claywater (SIC) and other clay related leaching systems are foreseen.

The general work progress status is as follows:

- B.1 and B.2.2 are completed.
- B.2.3 and B.3 are processing normally.

Progress and results

B.1 Glass Composition Selection

The glass selection procedure has been carried out taking into account the plant operation needs and characteristics.

The chemical composition of the HLW stream to be vitrified is an input coming from the "ULISSE" programme for the conditioning of the MCE waste. It consists of two different fractions:

- a sludge containing all the fission products (less than Cesium) and Actinides;
- the zeolites loaded by Cesium.

The waste/glass ratio has been fixed by the same programme at 57.12 % w/w, according to a total reduction volume factor of about 70.

The prepared glasses have been tested by means of a visual examination and a qualitative evaluation of the preparation semplicity, homogeneity and mechanical properties of the product.Moreover, a preliminary examination of the divitrification behaviour by Differential Thermal Analysis (DTA) and a short Soxhlet leaching test have been carried out as a preliminary characterization to select the best glasses.

The composition of the selected glasses is shown in TABLE I. In TABLE II the results obtained from the preliminary characterization of these glasses are summarized. All the above studies have been carried out using simulated and simplified chemical solutions and preparing procedures.

A better simulation has been carried out for further studies on the ENEA 8 selected glass.

B.2.2 Preparation of the selected glass in more realistic conditions

Actual loaded zeolites coming from the cold SERSE plant and laboratory simulated sludges have been used at closer plant conditions, particularly with reference to the glass cooling rate after the melting. The glass preparation feasibility has been unaffected by the use of the zeolites. The very slow cooling rate, on the contrary, produced a large devitrification in the glass samples, pointing out a poor thermal stability of the glass.

The same test has been performed using the BAZ glass composition. As no devitrification effects have been observed, this glass composition has been adopted and characterized.

B.2.3 The selected glass characterization

The viscosity curve, the thermal behaviour, the mechanical properties according to the Vickers microindentation method, the density, the transformation temperature (Tg) and other physico-chemical parameters and properties have been measured. The MCC-1 (Materials Characterization Center) standard test, matrix D (maximum duration 91 days) has been used to characterize the chemical stability in distilled water (DW), synthetic interstitial claywater (SIC), clay-water mixture (CWM) and leached clay solution (CW).

The test temperature is 90 °C. Two SA/V ratios have been planned:

- 10 m^{-1} with DW and SIC as leachates,
- 100 m^{-1} with all the four leaching systems.

The already available data refers to SA/V = 10 m^{-1}.

The Mass Losses in DW up to 28 days duration suggest that no saturation effect arises until this time. The values are comparable with those obtained with the BEL 15 Italian reference glass in the same conditions. The test performed using SIC as leachant shows the usual glass weight increase in the time. The combined effect of the glass leaching and of the salts precipitation, as expressed by the apparent Mass Loss, is less than in the case of the BEL 15 glass in the same conditions. Surface analyses are in progress to define the morphology and the nature of the precipitates. A better understanding of the corrosion behaviour should be obtained when the Elemental Mass Loss data will be available. In TABLE III the results obtained from the characterization of the BAZ glass are summarized. In Fig. 1 the available results for the Mass Losses in DW and SIC at 90 °C and SA/V = 10 m^{-1} up to 28 days, are shown.

TABLE I : CHEMICAL COMPOSITION OF THE SELECTED GLASSES.

	SiO_2	Na_2O	Al_2O_3	B_2O_3	CaO	Li_2O	TiO_2	Fe_2O_3	ZnO
ENEA 8	42	19.5	16	6	0.5	6	6.5	3.5	-
DEC 1	43.5	14	12	17	4	4	2	3.5	-
DEC 1.3	43	14	12	18	4	-	1.5	3.5	4
DEC 1.4	42	14	14	18	3	-	1.3	3.7	4
IVET 2	46.4	15	14	15	3	2	1	3.6	-
BAZ	47.4	16.5	13.5	10	3	5	-	4.6	-

TABLE II : PRELIMINARY RESULTS OF SOME GLASS CHARACTERIZATION.

	ENEA 8	DEC 1	DEC1.3	DEC1.4	IVET 2	BAZ
Density (g/cm^3)	2.57	-	-	-	-	2.54
Tg (°C)	425	460	520	500	480	435
Leaching* ($gm^{-2}t^{-1}$)	2.7	12	9.4	8.1	7.3	6.7
Thermal Expansion Coefficient* ($°C^{-1}$)	135E-7	-	-	-	-	133E-7
Pouring properties***	++	+	-	-	++	+
Homogeneity***	+	+	+	+	+	+
Mechanical properties***	++	+	+	++	+	++

* Mass Loss as measured by Soxhlet leaching test: 72 h, 110 °C, 12 ± 2 min filling cycles.

** Range 140-350 °C

*** Qualitative remarks collected during the preparation of the glasses as expressed in terms of relative units.

TABLE III : SOME REPRESENTATIVE DATA CONCERNING THE BAZ GLASS CHARACTERIZATION.

Density (g/cm^3)	2.57 ± 0.02
Transformation Temperature	430 °C
Thermal Expansion Coefficient*	117 E-7 °C^{-1}
H_V**	6.7 ± 0.3 GPa
Elastic Modulus***	86 ± 9 GPa
K_{IC}****	0.86 ± 0.04 MPam$^{1/2}$
Thermal behaviour*****	hardly detectable devitrification after 60 h at 700 °C

*	range 140 - 350 °C
**	Vickers microhardness
***	according to the Knoop indentation method
****	Critical stress intensity factor, according to Evans and Charles eq.
*****	Heat treatments followed by X-rays analyses: 60 h at 500, 700 and 1000 °C.

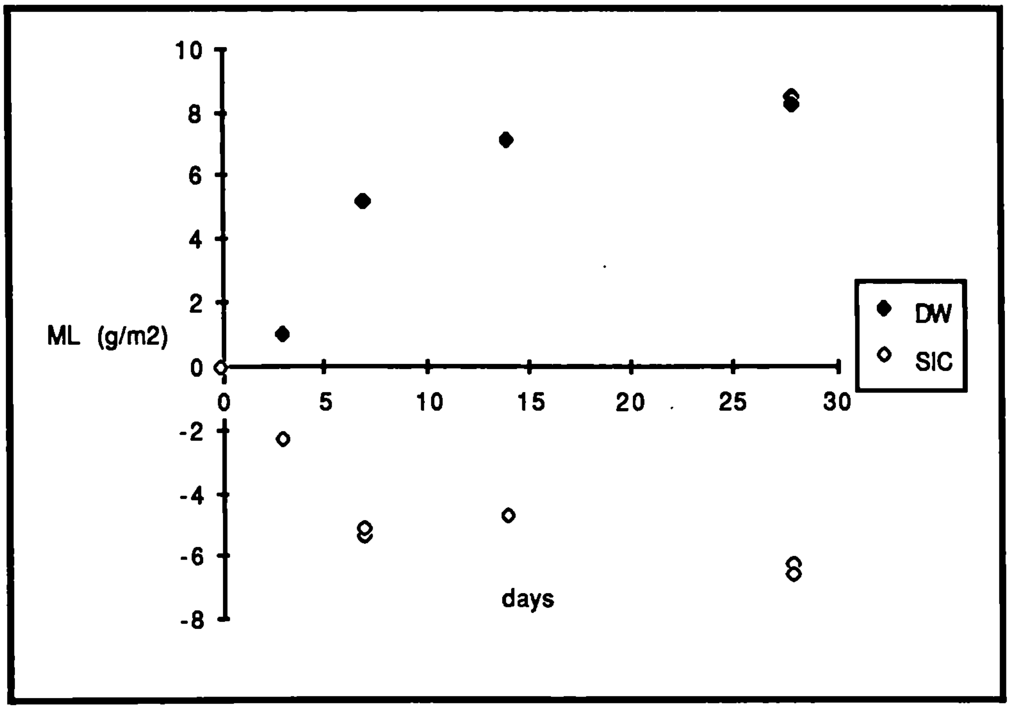

Fig.1 Mass Losses of the BAZ glass in Distilled Water and in Synthetic Interstitial Claywater.

INVESTIGATION OF FULL SCALE HIGH LEVEL WASTE CONTAINMENT GLASS BLOCKS

Contractor: CEA, CEN-Valrhô, SDHA (France)
Contract N°: FI1W-0182
Working Period: January 1988 - December 1989
Period Covered: January 1988 - December 1988
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 phenomena was undertaken, and the CASTEM code system was implemented to model the stress distribution fields.

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 leach testing in order to measure the degree of fracturation. Tomography examinations have begun and will continue in 1989. Leach tests have been completed for the 400 kg blocks, and will continue during 1989 on the 200 kg blocks.

Progress and Results

B.1 Theoretical Investigation

Developing a mathematical formulation for the phenomena affecting glass cooling is difficult because of the number and nature of the phenomena involved, and the mathematical complexity of the relation between creep and stress relief phenomena.

A simple description of tempering in glass (a viscoelastic material) would involve imposing a temperature gradient resulting in thermal stresses that are partially relieved by viscous flow. The permanent residual stresses are thus roughly equal and of opposite sign to the thermoelastic stresses relieved during the cooling process. In fact, however, other phenomena are involved, and must be taken into account: temperature equalization stresses, solidification stresses or structure effects.

The modeling work undertaken consists in calculating the thermal stresses sustained by a glass block subjected to known cooling conditions. Initially the glass is tempered: the molten glass surface is suddenly cooled and contracts, while the still molten core flows to adapt to the new conditions. When the core solidifies in turn, its contraction is hindered by the already solidified outer layers which are submitted to compression forces; the core itself is submitted to tensile loading by reaction.

Cooling of the block does not occur instantaneously, however, and the high internal temperatures result in partial relaxation of these stresses by viscous flow, even for temperatures at which the glass is solid.

After the glass block has completely solidified and the temperatures have dropped to a point at which stress relaxation can be considered negligible, the presence of a temperature gradient will result in stress loading that can be calculated according to elasticity theory.

These considerations show that an analytical solution is impossible, even if the temperature profile and stresses in the glass blocks are known at all times, as this would imply calculating the stress relaxation at every point as a function of both the temperature and the stresses themselves.

Codes from the CASTEM system will be used: a glass block mesh code, a transient heat transfer analysis code, a mechanical analysis code and a post processor.

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 full scale industrial prototype and cooled according to the thermal reference scenario adopted for the La Hague vitrification facilities. The block intended for tomographic examination was cast in a special experimental metal canister designed to be dismantled. The first tomography has been carried out on the container as cast, and will be followed in 1989 by a second examination of the partly disassembled container to assess the effects on the glass itself of relieving the canister stresses.

B.2.3 - B.2.4

Two types of industrial glass blocks cast into detachable cylindrical canisters 420 mm in diameter were used to determine the degree of glass fracturation from the water leaching behavior:

- 400 kg blocks (containing two successive 200 kg melts) subjected to various cooling scenarios and intended for static leach tests in water at 100°C;
- 200 kg blocks (from the first or second melt in a 400 kg industrial waste package) used for dynamic leach tests in water at 100°C.

Surface area values determined by chemical analysis of the leachate indicated a fracturation factor of 5 to 8 for the 400 kg blocks. The results for the 200 kg blocks will be available in 1989.

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 1988 - December 1988
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, peability, 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 progressing normally
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 ($\leqslant 2\ \mu m$), 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 swelling properties of the clay which are investigated using swelling pressure cells and oedometers. In the last case, the experimental procedure consists of subjecting the clay powder to loading and unloading cycles in the range of 0.1 to 40 MPa. For the study of fully saturated material, clay is first saturated with distilled water under 0.1 MPa during 10 days. According to the classic Terzaghi theory /1/, the void ratio "e" is presented as a function of the decimal logarithm of the total vertical load $\log_{10}(\sigma)$. The results shown in Figure 1 indicate that the material behaves as a soil: plastic deformation and effect of the stress history are observed with a) a normal consolidation curve (loading cycles), b) "swelling" curves (unloading cycles) which characterize the material behavior under over consolidated state. One immediate consequence of this is that the stress history of saturated material must be taken into account /2/. The strongest effective stress undergone by the material must be known to determine the "swelling pressure", since there is no one to one relation between the void ratio and the material stress state. In practice, this involves the knowledge of the mechanical state of the pre-compacted clay and of the saturation conditions. The same soil behavior is found when temperature is increased. But for a given effective stress, the material settles more and more quickly at 80°C than at room temperature ; the oedometric curve is shifted down by 0.1 unit of void radio.

3. Temperature effect on clay material properties

It is demonstrated that Fo-Ca clay is able to rehydrate after heating (up to 250°C) under dry conditions. New experiments will start to investigate H_2O vapor effect on clay properties (COUTURE effect) (/3/,/4/).

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 (Figure 2). When potassium is present, illite formation is observed but this formation is inhibited by calcium ; the CEC is maintained constant. The following reactions are likely to occur:

* with H_2O and $H_2O + CaCl_2$

H.C. smectites + kaolinite + H_4SiO_4 ==> L.C. smectites

* with $H_2O + KCl$

H.C. smectites + K^+ ===> illite + Ca^{2+} + Na^+ (undifferentiated mixed layer of illite/smectite/kaolinite)

* with $H_2O + KCl + CaCl_2$

H.C. smectites+kaolinite+H_4SiO_4+K^+ ==> L.C. smectite+illite+Ca^{2+}+Na^+

It appears that smectite formation requires silica, coming from quartz present as secondary mineral. In practice, in the case of vitrified waste disposal, additives will be used in the engineered barrier to prevent glass dissolution.

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. The main following conclusions can be drawn :

- pH is the starting parameter of degradation reactions. For example, figure 3 presents pH effect on total porosity for the studied cements. Ion nature and concentration are secondary factors which only act on kinetics,
- at high pH (13), no important degradation is observed, except for the higher salt concentration in the case of OPC,
- at pH = 11.5, OPC is very sensitive to chloride and sulfate ; blended cement, due to very fine porosity, offers stronger resistance to salt attack.

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 the effect 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. Experiments are now carried out to understand if this pore water is aggressive towards cement paste.

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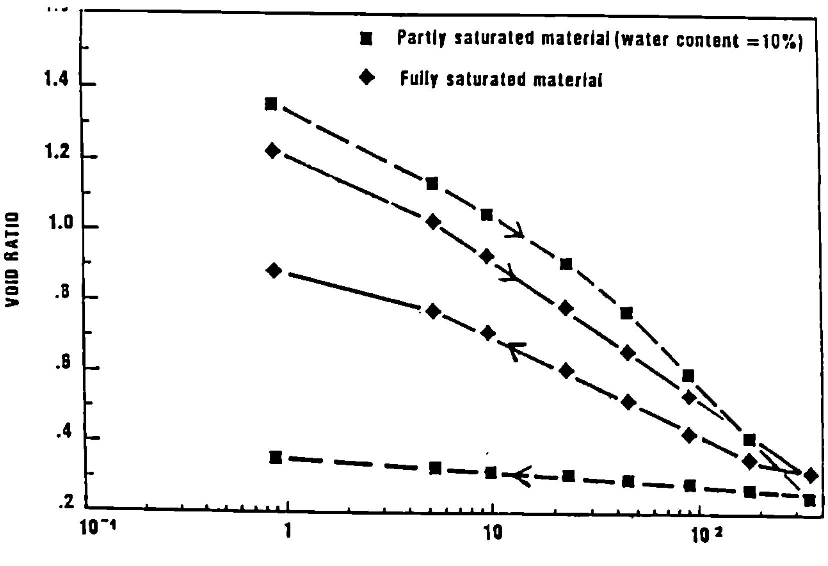

Figure 1 : One dimensional consolidation test on fully and partly saturated materials (reference 4a)

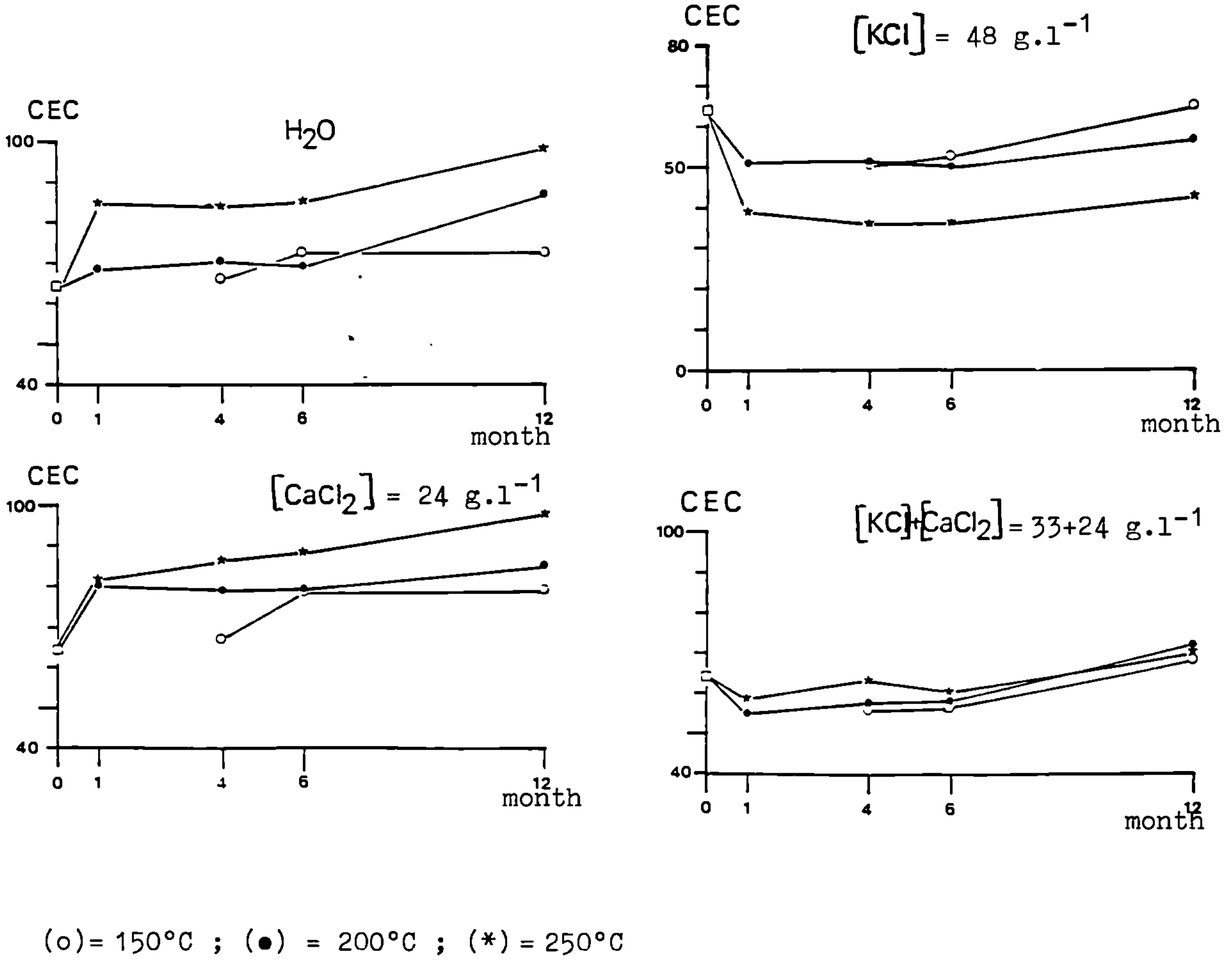

Figure 2 : Hydrothermal degradation of reference 4a clay. Cation exchange capacities as a function of time and temperature.

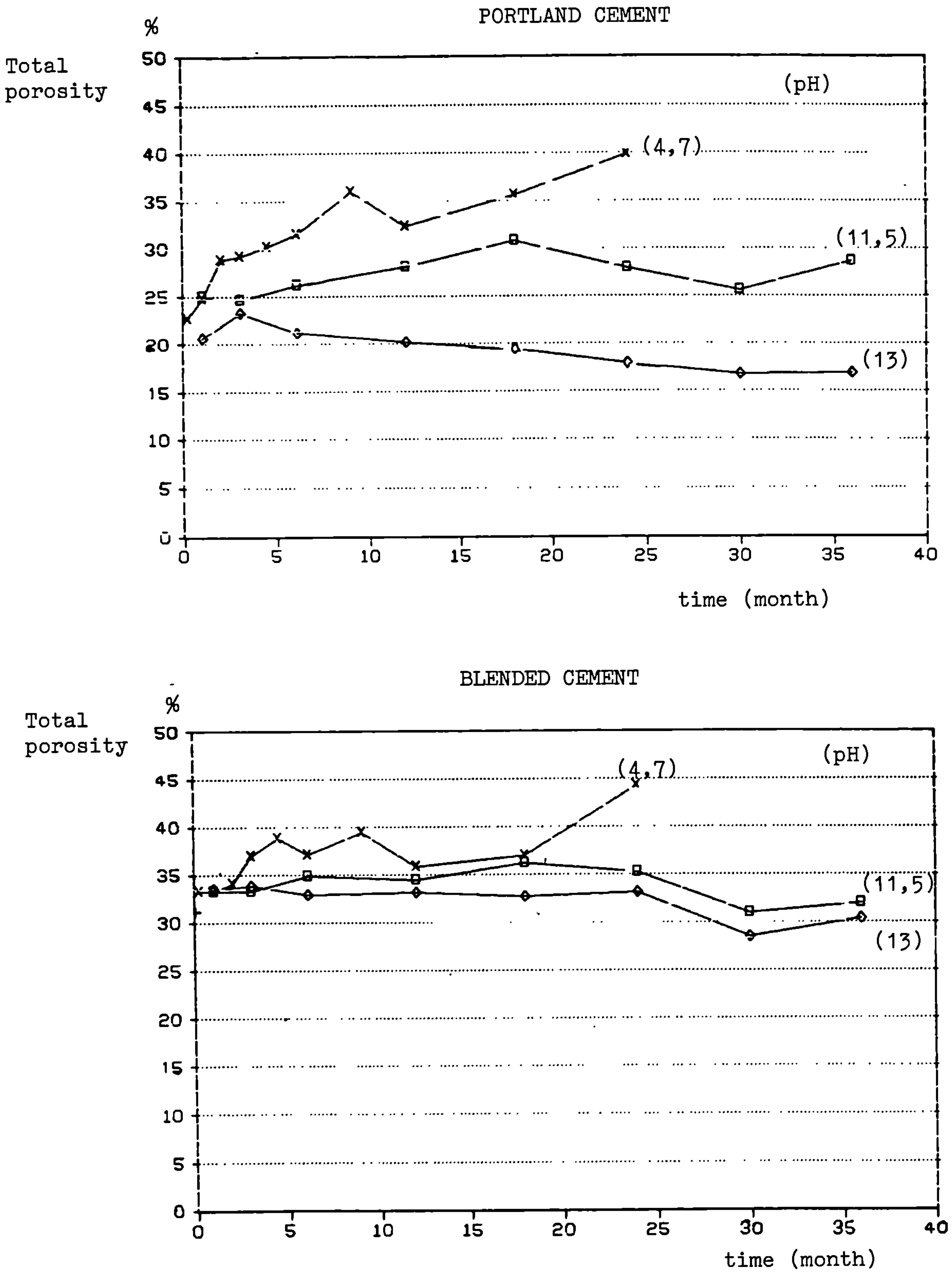

Figure 3 : Evolution of the total porosity as a function of pH
(Mercury porosimetry measurement)

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

The object of this contract is to study the clay/granite mixtures as probable backfilling and sealing materials for the storage of high level radioactive wastes.

For this purpose, the characterization of thirty types of Spanish commercial clays and two types of granites has been carried out.

According to the results of the general characterization of the above mentioned materials, eight types of clays have been selected based on the following criteria: high content of smectite and/or illite; low content of organic C, carbonates and principal complexing agents of radionuclides; high plasticity, specific area and cation exchange capacity.

The mineralogical composition of the eight selected clays has been exhaustively studied by chemical analysis and X.R. diffraction of the total sample and the <2 µm fraction. Thus, a more precise content of the clay minerals of the total sample has been determined, as well as the definition of the structural formula, provided the mineral composition of the <2 µm fraction was pure enough. Based on these results and keeping the same selection criteria already mentioned, the samples have been reduced to three. Their mineralogical and chemical characteristics are the following:

			Chemical composition of the <2 µm fraction (%)										
	Clay mineral	Content in total sample	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	MnO	CaO	MgO	H_2O	Na_2O	H_2O^+
M-15	Illite	73,5 %	52,73	19,56	5,15	1,29	0,40	<0,03	0,81	6,57	5,64	0,57	7,26
M-26	Montmorillonite	94,0 %	60,91	19,99	3,65	0,70	0,28	0,03	0,79	5,46	0,81	1,51	5,85
M-29	Beidellitic montmorillonite	96,0 %	60,38	22,28	2,03	0,73	0,17	0,07	0,56	5,36	0,57	0,86	6,98

The physico-mechanical properties, which have been studied, are the specific weight, Atterberg limits and Hg-measured density and shrinkage limits. The liquid and plastic (Atterberg) limits show that 83 % of the materials are more or less plastic with the highest values for smectite and the lowest for the illitic materials. The results from the Hg-measured density and shrinkage indicate that the volume decrease due to drying is moderate for the majority of the samples, with the exception of those with a very high content of smectite, where the volume decrease is from 50-85,8 %.

According to the dispersion analyses of the clays due to the water action, the sodic smectites are highly dispersive (>68 %), therefore, they have been rejected, whereas the montmorillonites are scarcely dispersive and the illites are stable.

The study of the physico-chemical properties includes the determination of the specific area, the cation exchange capacity (CEC) and the distribution coefficient. With the exception of some smectite-rich materials, the CEC values are moderate. The distribution coefficient of some of the materials has been determined to assess their radionuclide retention capacity, although the results should be considered only as initial guidelines.

Based on the microscope studies, X.R.D. and chemical analyses of the granitic rocks, the granite from Colmenar Viejo corresponds to a biotitic granite (adamellite) and the one from El Berrocal to a two mica alkaline feldspar granite. The most significant difference between the two types of granites is the higher content of quartz in El Berrocal.

The compaction capacity is acceptable in clays and mixtures. The dry density is greater than 1,98 g/cm^3 in the clays for an uniaxial pressure of 123 MPa, and greater than 2 g/cm^3 in the mixtures for a pressure of 60 MPa.

According to the swelling capacity measured by an oedometer, it has been determined that the swelling pressure of the illites is smaller than 3,46 MPa for dry densities greater than 1,90, whereas in the smectites, for similar densities, it is greater than 24 MPa. In the 50 % montmorillonite-granite mixtures, the swelling pressure is still greater than 7 MPa.

The montmorillonite's height increment during free swelling is greater than 100 %. Under the experimental conditions, the swelling has been a very fast process; the maximum height increment was produced between 10 to 80 minutes, and the highest speed, 670 µm/min, was reached at the beginning of the test.

According to the tests on the degree of alteration of the materials, a high, easily-leachable, saline content $-SO_4^{=}$, Cl^-, NO_3^-- has been detected in the granite from Colmenar Viejo. In general, the ion concentration in solution decreases and tend to reach a constant value of equilibrium during the leaching processes. The highest leachability is produced in the <63 µm fraction of crushed granite.

CORROSION TESTING OF SELECTED CONTAINER MATERIALS FOR DISPOSAL OF HLW GLASS

Contractor: KfK, Karlsruhe, Federal Republic of Germany
Contract No.: FI1W/0032
Duration of contract: May 1986 - December 1989
Project Leaders: E. Smailos, R. Köster

A. OBJECTIVES AND SCOPE

In order to 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 the 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 sujected 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 preselected 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 3×10^4 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 of the material specimens and welded Hastelloy C4 tube sections stored in Asse for corrosion attacks. The testing conditions are similar to those under item B.2.3.

C. PROGRESS OF WORK AND RESULTS OBTAINED

Summary

During the period of reporting additional in-depth laboratory-scale and in-situ corrosion studies have been performed on two unalloyed steels which in the preceding studies had proved to be promising HLW packaging materials. In the laboratory-scale experiments the influence has been examined of gamma dose rates (1 Gy/h and 10 Gy/h) which are relevant to the thick-walled HLW packaging discussed on the corrosion behaviour of fine-grained steel (material no. 1.0566) at 90 °C. The steel has been examined in the two-phase corrosion media rock salt/NaCl-rich salt brine and rock salt/$MgCl_2$-rich salt brine as may occur in certain accident scenarios in a repository. Corrosion studies under gamma irradiation in one-phase brine have already been reported /1/.

In the in-situ corrosion experiments carried out in the Asse salt mine the corrosion behaviour has been studied of cast steel GS16Mn5 under the influence of both selected characteristics of container manufacturing (welding, dimension) and simulated disposal conditions. Besides, the in-situ corrosion experiments have been continued under various disposal conditions with material specimens and electron-beam welded tubes made of Hastelloy C4 and Ti99.8-Pd.

PROGRESS AND RESULTS

B.2.1.1 Corrosion studies on unalloyed steel in moist rock salt (rock salt/rock salt brine and rock salt/Q-brine) without gamma irradiation

completed in 1986 (published in /2/)

B.2.1.2, 2.2, 2.4.1 Investigations into the influence of gamma radiation on the corrosion behaviour of unalloyed steels and Hastelloy C4

The investigations into the influence of the gamma dose rate (1 Gy/h to 100 Gy/h) on the corrosion of three selected steels and Hastelloy C4 in one-phase brine at 90 °C were completed last year. The results have been reported in /1/.

During the period of reporting the corrosion experiments carried out under gamma radiation at 90 °C have been supplemented by experiments on the fine-grained steel (reference steel) conducted in the two-phase corrosion media rock salt/NaCl-rich brine and rock salt/$MgCl_2$-rich brine. The steel (0.17 wt.% C; 0.44 wt.% Si; 1.49 wt.% Mn) has been examined at dose rates which are realistic for the thick-walled HLW packaging discussed, namely 1 Gy/h and 10 Gy/h. The maximum testing period has been twelve months.

The rock salt used was taken from the Na-2 region of the Asse salt mine. The brines added to the rock salt were composed as follows (in g/l):

- NaCl-rich brine:
  136.75 Na^+; 1.48 K^+; 0.34 Mg^{2+}; 1.4 Ca^{2+}; 201.9 Cl^-; 5.19 SO_4^{2-}.
- $MgCl_2$-rich brine (Q-brine):
  7.1 Na^+; 31.8 K^+; 91.9 Mg^{2+}; 297.3 Cl^-; 14.4 SO_4^{2-}.

The selected rock salt/brine mass ratio was 5:1 which gave an H_2O content of the rock salt of about 11 wt.%. The ratio of specimen surface to brine volume (S/V) was 100 m^{-1}.

All material specimens have been examined for general corrosion, pitting corrosion and crevice corrosion (plane specimens) and for stress-corrosion cracking (U-bent specimens). In addition, the influence has been studied of welding - tungsten inert gas (TIG) welding and electron-beam welding - on the corrosion behaviour of the material.

The results of corrosion obtained after the maximum testing period of twelve months for fine-grained steel stored in the two-phase media have been summarised in Tab. 1. Besides the results applicable to the conditions characterised by gamma irradiation, the corrosion rates determined earlier in the absence of irradiation have been entered /2/. The most important results can be summarised as follows:

- Gamma dose rates of 1 Gy/h and 10 Gy/h have not increased the corrosion rates of fine-grained steel in rock salt/NaCl-rich brine and in rock salt/$MgCl_2$-rich brine at 90 °C. This result is in good agreement with the results of earlier investigations performed in one-phase brine /1/.

- The maximum rates of penetration of non-uniform corrosion of steel in the two two-phase corrosion media have been 50 µm/a which implies acceptable corrosion allowances for the thick-walled HLW packaging discussed. At the end of twelve months testing the steel was resistant to pitting and crevice corrosion or stress-corrosion cracking, and welding (TIG welding and electron-beam welding) did not exert a noticeable influence on its corrosion. For these reasons, fine-grained steel continues to be regarded as a promising HLW packaging material and will be further investigated.

B.2.3, 2.4.1 In-situ corrosion experiments

In the framework of the in-situ corrosion investigations of selected HLW packaging materials in the Asse salt mine the influence has been studied of selected container characteristics (welding, dimension) on the corrosion behaviour of cast steel (GS16Mn5). The material has been tested in saturated NaCl brine. For this, an electron-beam welded cast steel tube was stored for 18 months in a 2 m deep heated borehole and the annular gap between the tube and the borehole was filled with NaCl brine. The vertical temperature profile in the borehole was in the range from 90 °C to 200 °C. The maximum temperature occurred in the center of the heated zone and the minimum temperature in the upper part of the tube.

The significant in-situ corrosion results can be summarised as follows:

- The surface profiles and the metallographic sections of specimens taken from three characteristic temperature zones (90 °C, 140 °C, 200 °C) of the cast-steel tube have shown that corrosion attacks have been non-uniform and differed in extent. The corrosion attack was heaviest (120 µm/a) for the specimens from the cooler upper part of the tube (T = 90 °C) where the evaporated water of the salt brine condensed. For the specimens taken from the 140 °C and 200 °C zones in the vapour space the maximum rates of penetration were much lower, namely 40 µm/a to 50 µm/a.

- Pitting and crevice corrosion in the sense of an active-passive corrosion element or stress-corrosion cracking have not occurred. Furthermore, electron-beam welding has not noticeably influenced the corrosion of steel.

In general, it can be stated that the in-situ corrosion rates of the cast steel imply acceptable corrosion allowances for a thick-walled container and are in good agreement with the values obtained in laboratory-scale experiments. Further in-situ and loboratory-scale corrosion studies are under way.

References

/1/ SMAILOS, E., SCHWARZKOPF, W., KÖSTER, R., KfK Report 4426 (1988).

/2/ Commission of the European Communities, EUR 11354 EN/2 (1988).

List of publications in 1988

SMAILOS, E., SCHWARZKOPF, W., KÖSTER, R., GRÜNTHALER, K.H., Proceedings of the Symposium on Waste Management at Tucson, Arizona, February 28-March 3, 1988, Vol. 2, p. 985 (1988).

SCHWARZKOPF, W., SMAILOS, E., KÖSTER, R., KfK Report 4324 (1988).

SMAILOS, E., SCHWARZKOPF, W., KÖSTER, R., KfK Report 4426 (1988).

Commission of the European Communities, EUR 11354 EN/2 (1988).

Table I Average general corrosion rates and maximum rates of penetration of non-uniform corrosion of fine-grained steel after one year immersion in rock salt/salt brines at 90 °C

Corrosion medium	Average general corrosion (µm/a)			Maximum rate of penetration (µm/a)		
	no γ	1 Gy/h	10 Gy/h	no γ	1 Gy/h	10 Gy/h
Rock salt plus NaCl-rich brine	13±2	10±5	10±4	40	50	50
Rock salt plus $MgCl_2$-rich brine (Q-brine)	24±5	29±4	29±11	60	50	50

CORROSION OF CONTAINER AND INFRASTRUCTURE MATERIALS

UNDER CLAY REPOSITORY CONDITIONS

Contractor : S.C.K./C.E.N., Mol, Belgium
Contract No : FI 1W-0033-B
Duration of contract : May 1986 - December 1989
Project Leader : W. Debruyn

A. OBJECTIVES AND SCOPE

Objective of the programme is to determine corrosion rates of selected candidate materials under realistic repository conditions over long exposure periods, to determine the in-situ clay 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 radiation 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, B2 and B3 and in the segments of laboratory experiments B4 and B6.

One in-situ corrosion test tube (B1) in direct contact with solid clay at 90°C has been overcored after an exposure period of 1019 days. The metal specimens and the surrounding clay are being analysed.
Two experimental techniques to measure corrosion rates directly in-situ (B2) have been evaluated : LPR (corrator) and ER (corrosometer) equipment was installed to monitor a corrosion allowance and a corrosion resistant material. The ER-technique was found to be reliable and has been selected for further application.
The in-situ chemical characterization (B3) of the clay aggressivity has been extended to the higher temperature corrosion configurations. A number of modified pH and Ag/AgCl-electrodes has been installed. These electrodes are generating on-line information.

C-steel, Hastelloy C4 and Ti/0.2 Pd specimens have been irradiated (B4) for exposure periods up to 1000 hours under a gamma radiation field

of 10^3 gray/hour. The test medium was solid clay at 90°C.
To be able to predict corrosion rates and mechanisms after long exposure periods (B6) (hundreds of years) the adaptation of an existing mathematical model (UKAEA Harwell) is under development. A cooperation on this subject with UKAEA Harwell will be initiated in 1989.

Progress and results

In the underground laboratory at SCK/CEN a corrosion test tube in direct contact with clay has been overcored based on a specific retrieval technique developed earlier. Metal specimens and clay samples from the corrosion tube are being analysed. A claywater concentration of (18-19 % wt) was obtained; the water velocity at the tube surface has been 1.2 mm/year.
The corrosion tubes in contact with humid clay atmosphere have been equipped with a purging installation; they are in a fully automatic mode of operation which guarantees a proper test procedure by preserving the tubes from flooding.

Two experimental techniques to monitor in-situ corrosion rates on line have been evaluated : one technique based on LPR-, the other on ER-measurements. In each case corrosion allowance and corrosion resistant specimens were introduced as probe material. It could be concluded that the ER method is a viable technique whereas the LPR method is not. The corrosion rates measured are below 0.5 micron/year, even for the cast iron probes; these extremely low corrosion rates confirm the also very low rates derived from coal mine shaft material examined after 90 year exposure to a marl environment.

Electrodes to characterize the clay aggressivity (pH, Eh) have been emplaced around the 90°C and 170°C corrosion tubes in direct contact with solid clay. All electrodes have been connected to the scanner/electrometer set up and branched to the data acquisition system. They start generating on-line information.

Apart from the in-situ experiments, overground laboratory experiments have been performed, which can be subdivided into conventional and gamma irradiation experiments.

Conventional corrosion experiments have been conducted on C-steel, Hastelloy C4 and Ti/0.2 Pd-samples in interstitial claywater at 170°C in an autoclave test rig. The corrosion rate of C-steel drops considerably with increasing temperature : whereas at 90°C the general corrosion rate ranges from 20.6 µm/y (anoxic) to 73.2 µm/y (oxic) under similar conditions, it drops to low values (1-2 µm/y) at 170°C. The change in corrosion mechanism is under investigation.

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 90°C. A radiation field of 10^3 gray/hour has been applied for exposure times up to 1000 hours.
Ti/0.2 Pd and Hastelloy C4 show extremely low general corrosion rates; no localized corrosion attack could be detected under none of the experimental conditions considered. The corrosion mechanism of C-steel in contact with solid clay and in contact with claywater (tested earlier) are, under influence of gamma irradiation, essentially the same. Both general and localized (pitting) corrosion rates are about a factor 2 higher in the claywater case than in the solid clay case (the general corrosion in solid clay amounts to around 100 µm/y). The sulphidation of the material might be the driving factor under anoxic conditions, in which case localized corrosion is somewhat more pronounced.

The mathematical corrosion model developed at UKAEA Harwell will be adapted to predict corrosion rates and mechanisms in clay environments at expanded time scales. These models can predict the corrosion behaviour over a few hundred years; both localized and uniform corrosion rates can be calculated; the models are however restricted to carbon steel corrosion. The overall model consists of three entities which play an interactive role in making an assessment of container corrosion : the aeration period model, the pit propagation model and the uniform corrosion model.

D. LIST OF PUBLICATIONS

1. Debruyn W., Dresselaers J., Tas H., NIRAS/ONDRAF, R & D programme on radioactive waste disposal, semi-annual report, first semester 1988.
2. Debruyn W., Dresselaers J., Tas H., NIRAS/ONDRAF, R & D programme on radioactive waste disposal, semi-annual report, second semester 1988.
3. Debruyn W., Tas H., In-situ testing of candidate overpack materials in deep argillaceous HLW disposal environments, Spectrum '88 - Pasco WA-proceedings, p. 217-221.
4. Debruyn W., Tas H., Corrosion resistance of candidate overpack materials in deep argillaceous disposal environments, MRS Scientific basis for nuclear waste management '88 - Berlin.

CORROSION OF CARBON STEEL OVERPACKS FOR THE GEOLOGICAL DISPOSAL OF RADIOACTIVE WASTE

Contractor:	UKAEA, Harwell Laboratory, Didcot, Oxon, UK
Contract No:	FI 1W.0034.UK(H)
Working Period:	January 1988 to March 1989
Project Leader:	Dr G P Marsh

A. OBJECTIVES AND SCOPE

The main objectives have been to complete the assessment of the long term corrosion of carbon steel overpacks in granite or clay-like formations and to finalise the mathematical model for localised corrosion. The validity of the previously developed general corrosion model and the improved localised corrosion model will be tested by the results from the experimental programme.

The overall programme will yield generic models for general and localised corrosion which may be applied to evaluate overpack life, or the metal thickness needed to achieve a specific life, in granite or argillaceous disposal sites.

B. WORK PROGRAMME

B.1 Completion of long term tests to validate the mathematical model of general corrosion.

B.2 Continuation and completion of long term tests to evaluate the localised corrosion model.

B.3 Completion of the mathematical model for localised corrosion.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Long term tests to measure general and localised corrosion in carbon steel have been concluded. Additional tests with the reference 0.1% carbon steel supplied by the Commission also have been completed. Improved electrokinetic data have been obtained experimentally for carbon steel in ferrous chloride under anaerobic conditions to assist in the development of an improved mathematical model for localised corrosion.

B.1, B.2 and B.3 are progressing normally.

Progress and Results

1. Long Term Tests - General Corrosion (B.1)

Eighteen long term immersion tests to investigate the general corrosion of three different carbon steels in both plain and welded form have been concluded after 5 years' exposure. Coupon specimens were embedded in granite or bentonite backfill flooded with synthetic granitic groundwater and held at temperatures of 25°, 50° and 90°C. Rest potentials of selected coupons were measured and recorded twice daily throughout the exposure period and their corrosion rates monitored periodically by the polarisation resistance method. After dismantling, the corrosion that had occurred was evaluated by visual examination and by the weight lost by individual coupons. Localised corrosion, which was observed particularly on specimens embedded in crushed granite at 50° and 90°C, was about 15% of the maximum depth predicted by the empirical pit growth rate equation (see 2 below). Identical tests initiated with plain coupons prepared from the Commission's reference carbon steel (EEC MS) also have been dismantled after 12 and 24 months exposure. The results of these tests, which are summarised in Table 1, are being applied to test the validity of the appropriate mathematical model.

2. Pit Growth Measurements - Localised Corrosion (B.2)

Pit growth rate measurements made on disc specimens prepared from carbon-20 (0.17% C) steel had attained test periods of 10,000 hours by the end of the 1980-84 programme. These tests have been extended to longer exposure periods to establish a more accurate empirical relationship between maximum pit depth and exposure time. One set has been examined after an exposure of 17,500 hours and another after 30,000 hours. A modified empirical pit growth rate equation has been derived from these and the earlier measurements and has the form $P_{max} = 3.0\ t^{0.44}$ (P in mm, t in years). Using extreme value statistics to project these data to a canister of surface area 4 m^2 produces the equation $P_{proj} = 7.02\ t^{0.42}$ (P and t, as above). Similar tests with the Commission's reference steel (EEC MS) using disc specimens with the same surface area (8 cm^2) as before and also larger area (x30) plate specimens have been concluded. Measurements were made on sets of disc specimens up to a maximum exposure of 10,000 hours and on plates to 12,000 hours. Disc data was similar to that obtained with carbon-20 steel but significantly smaller penetrations were recorded for the plate specimens. The reason for this is still under investigation.

3. Localised Corrosion Model (B.3)

An improved finite element method of modelling cavity propagation has been developed to overcome inadequacies of the previous models. This new model now includes active corrosion on the cavity walls as well as the blocking effect of solid precipitation products on ionic diffusion and migration. To assist in the development of this model experimental polarisation and conductivity measurements have been made in 2.5M and 4.5M ferrous chloride solutions, under anaerobic conditions, at 25°, 50° and 90°C. The improved electrokinetic data (eg anodic Tafel slopes, exchange current densities and transfer coefficients) obtained have been utilised in the model's predictions for corrosion rates which are now assuming more realistic values.

LIST OF PUBLICATIONS

Marsh, G P, Bland, I D and Taylor, K J, Br Corros J, 1988, Vol 23, No 3.

Table 1

Average General Corrosion Rates ($\overline{\Delta t}$) from Weight Lost Data

Designation*	Temperature (°C)	Exposure (yrs)	$\overline{\Delta t}$ ± s.d. (μm/yr)
F/G	Ambient	5	1.2 ± 0.6
C/G	"	"	1.5 ± 0.7
LC/G	"	"	1.6 ± 0.6
All/G	"	"	1.5 ± 0.6
F/B	"	"	1.7 ± 0.4
C/B	"	"	2.0 ± 0.5
LC/B	"	"	2.4 ± 0.4
All/B	"	"	2.0 ± 0.5
F/G	50	5	15.4 ± 2.5
C/G	"	"	14.0 ± 2.1
LC/G	"	"	15.2 ± 4.8
All/G	"	"	14.6 ± 3.8
F/B	"	"	3.3 ± 0.5
C/B	"	"	2.9 ± 0.3
LC/B	"	"	2.8 ± 0.6
All/B	"	"	3.0 ± 0.5
F/G	90	5	27.4 ± 4.8
C/G	"	"	31.6 ± 4.0
LC/G	"	"	24.9 ± 5.2
All/G	"	"	27.9 ± 5.4
EEC MS/G	"	1	22.2 ± 2.5
EEC MS/G	"	2	45.4 ± 3.7
F/B	"	5	13.8 ± 3.9
C/B	"	"	7.2 ± 1.6
LC/B	"	"	7.7 ± 2.7
All/B	"	"	9.5 ± 4.1
EEC MS/B	"	1	11.6 ± 1.0
EEC MS/B	"	2	9.7 ± 4.0

Forged 0.2% C (F)
Cast 0.1% C (C)
Low Carbon 0.05% C (LC)
Common Supply Mild Steel 0.1% C (EEC MS)
Granite (G)
Bentonite (B)

EFFECT OF ANAEROBIC REINFORCEMENT CORROSION ON THE CONCRETE BARRIER IN LOW AND INTERMEDIATE LEVEL WASTE REPOSITORIES (Part A)

Contractor:	Harwell Laboratory, Didcot, Oxon, UK
Contract No:	FI 1W.0187.UK(H)
Duration of Contract:	1st January 1988 - 31st December 1989
Project Leader	A Atkinson

A. OBJECTIVES AND SCOPE

The programme is aimed at studying the corrosion of carbon steel 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.

B. WORK PROGRAMME

B.1 Investigation of the influence of hydrogen over-pressures up to 100 atmospheres on the electrochemical kinetics of the anodic and cathodic reactions constituting the corrosion cell.

B.2 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.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

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. 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.

Progress and Results

1. **Influence of Hydrogen Over-Pressure**

This aspect of the programme is being conducted in an autoclave facility which permits both potentiostatic and pulse electrochemical measurements to be made at hydrogen pressures up to 100 atmospheres. Work to date with this facility has involved a single test lasting 76 days with two carbon steel specimens in saturated $Ca(OH)_2$ solution. This test has shown that, even with quite substantial hydrogen pressures over previously argon purged solution, the time needed for carbon steel to reach an active (anaerobic) potential is of the order of 60 days. However, this time can be significantly reduced if the specimen is polarised cathodically to reduce any surface oxide layer.

Coulostatic pulse measurements have been made to monitor the charge transfer resistance (R_{CT}) of the specimens during their transition from passive to active rest potentials. R_{CT} fell by roughly an order of magnitude when the specimens became active. Since R_{CT} is inversely proportional to the corrosion rate, this indicates a roughly ten fold increase in the rate of attack between passive and active conditions.

The investigation of the influence of hydrogen over-pressure on corrosion at active potentials is at an early stage, but some preliminary rests are listed in Table 1. Surprisingly these results show no apparent relationship between the rest potential and the hydrogen over-pressure, although theoretically a trend towards more negative potentials with increasing pressure would have been expected. However, the results do show the charge transfer resistance (R_{CT}) increasing with increasing hydrogen pressure. R_{CT} is related to the corrosion current i_{CORR} through the relationship

$$i_{CORR} = \frac{B}{R_{CT}}$$

where the proportionality constant B is given by

$$B = \frac{b_a b_c}{2.3(b_a+b_c)}$$

b_a and b_c are the Tafel Slopes of the anodic and cathodic reactions constituting the corrosion cell. These have been estimated from polarisation curve measurements on the same carbon steel specimens and the results are included in the table. Using these results values for B at various hydrogen pressures have been calculated and then these used to estimate the rates of corrosion (i_{CORR}). Table 1 shows that these results follow a trend for the corrosion rate to fall with increasing gas pressure, such that the rate of dissolution was four times less at 80 atmospheres compared to 1 atmosphere of hydrogen.

Table 1
SUMMARY OF ELECTROCHEMICAL MEASUREMENTS UNDER HYDROGEN

H_2 Pressure (atmos)	Rest Potential (mV v SCE)	R_{CT} (KΩ cm^2)	b_a (mV/dec)	b_c (mV/dec)	B (mV)	i_{CORR} μA cm^{-2}
SPECIMEN 1 (No cathodic reduction)						
80	-926	84.9	55	35	9.3	0.11
61	-924	74.9	55	50	11.4	0.15
44	-950	56.7	58	66	13.4	0.24
22.5	-962	52.5	72	49	12.7	0.24
9	-	36.8				
1	-	31.7	78	82	17.4	0.55
SPECIMEN 2 (Cathodically reduced)						
80	-1005	49.1	49	37	9.1	0.19
61	-1012	46.9	47	43	9.8	0.21
44	-1015	43.3	46	54	10.8	0.25
22.5	-1014	36.0	48	59	11.5	0.32
9	-	27.3				
1	-	17.2	61	79	15.0	0.87

2. Long Term Anaerobic Corrosion Tests

These tests are being conducted with cement/concrete samples each containing two carbon steel specimens. Three different cement/concrete formulations are being investigated each with and without a chloride addition of 2% by weight of mix water, making a total of 6 mixes. Each mix is being tested while immersed in water and when stored at > 95% RH, conditions which simulated a saturated and unsaturated repository respectively. Three samples of each mix are being tested under each condition forming a total test programme of 36 samples. To quickly achieve anaerobic conditions all the tests were set up in an argon purged glove box with ingredients which were deaerated before posting into the box. The specimens are being stored individually in sealed jars within the glove-box, thus giving double protection against oxygen ingress.

All the tests are underway, and weekly measurements of the specimen rest potentials are indicating that all specimens in the first four mixes have settled at active (anaerobic) corrosion conditions. However, some of the specimens in the other two mixes, which were produced last, have yet to attain active rest potentials. Table 2 summarises the most recent rest potential measurements for all the mixes. Some preliminary coulostatic pulse measurements of R_{CT} have been made on selected specimens, and have yielded values ranging from 139.3 to 394.3 KΩ cm^2 for chloride free mixes and 21.2 to 38.8 KΩ cm^2 for those containing chloride. Using a value of 10 mV for the proportionality constant B (equation 1) these R_{CT} results are equivalent to corrosion rates ranging from 0.025 μA cm^{-2} (0.3 μm/a) to 0.47 μA cm^{-2} (5.5 μm/a) and imply that the anaerobic corrosion rate may increase with the chloride contact of the environment.

Table 2

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	8240	-979	± 3
2	Immersed	8240	-981	± 5
3	Immersed	7640	-944	± 3
4	Immersed	7640	-954	± 3
5	Immersed	4400	-902	± 85
6	Immersed	4400	-877	± 39
1	> 95% RH	7872	-994	± 13
2	> 95% RH	2728	-997	± 22
3	> 95% RH	7350	-993	± 7
4	> 95% RH	7350	-999	± 21
5	> 95% RH	4400	-829	± 186
6	> 95% RH	4400	-930	± 87

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 to December 1989.
Project Leader: K. Brodersen.

A. Objectives 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 have been used to follow the structure of 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 are used to demonstrate ageing effects in the materials.

B. Work Program

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

C. Progress of work and obtained results

State of advancement

The work during the 4. and 5. half-year of the contract has continued on most of the topics. However, the comparative studies of leaching and diffusion through slabs (B.2.) and the influence of ageing on flow properties of bituminized materials (B.8.) are finished and the results and conclusions are given in the annual report for 1987. The SANS (Small Angle Neutron Scattering) studies of degrading concrete (B.5.) are delayed due to rebuilding of the facility at Risø, but work will be resumed in 1989.

Progress and Results

1. Diffusive transport in porous barriers (B.1.)

The release of ^{134}Cs and ^{85}Sr from samples of cemented sodium nitrate (simulated RMA8) through barriers of concrete, kaolin or chalk are being followed for 16 systems representing various conditions. The barrier are of better quality (lower water contents) than the ones employed in similar experiments in 1987. Only preliminary results are available, but the previously noted increase of Cs-relases through concrete barriers under reducing circumstances has been confirmed. Simulation of this type of integral experiments using the COLUMN2 code has been initiated.

2. Deposition and degradation reactions in concrete (B.3-4.)

An experimental method for demonstration of crack-healing in damaged concrete has been developed. The closing of narrow cracks by deposits of calcium carbonate has been demonstrated to take place, when a slow flow of HCO_3- containing tap water is passed through the crack. Parameters such as crack width and length, flow rate, carbonate concentrations and diffusion properties of the concrete will influence the tendency to crack closure. A simple model describing these relationships has been developed and calculation results are beeing compared with the experimental results. Crack-healing by silicates is also a possibility, but only tentative results are available.

The studies of material transport between thin plates of two different types of concrete stored in a small amount of water have been continued. They support to some degree the above-mentioned tendency to crack-healing also in systems without any carbonate present.

3. Cemented ion-exchange resins (B.6.)

Wet/dry cycling of the four intact samples from the experiments reported last year has been continued. Only the two containing silica fume as additive have been able to withstand this treatment. Similar experiments should be performed on cemented ion-exchange resin based on blast furnace slag cement as a more realistic representative for the real waste type RMA3.

4. Hygroscopic properties of conditioned waste (B.7.)

Further studies have been made of water uptake from high humidity air into cemented or bituminized waste containing soluble salts or other hygroscopic materials, eg. RMA1,3,7,8 and 10. The tendency to hygroscopic water uptake is determined by the relative humidity of the air, and by the content and solubility of the salt(s) in the waste material. Below 70 to 80 % RH the phenomenon is probably not important. At high humidity the water uptake and the associated accumulation of contaminated strong salt solution on the sample is delayed but not prevented by a surrounding porous concrete barriere.

Hygroscopic water uptake may be an important release mechanism for activity from waste materials containing soluble salts when such materials are disposed of in facilities constructed in the unsaturated zone.

5. Water diffusion in bitumen, swelling, etc. (B.8-9.)

A set of experiments with diffusion of tritiated water and ^{134}Cs through ~2 mm thick bitumen membranes prepared from Eurobitum (RMA8) have been performed. The permeability coefficient for TOH is found to about 10^{-9} cm^2/sec or about a factor 10 to 20 higher than previous values obtained for pure bitumen. The break-through of Cs-ions are in general much slower. A supplementary method is under development where the electrical resistance over the membrane as well as in the solution on both sides of the membrane is followed as function of time. It is expected to give valuable additional information to the more conventional diffusion experiments based on activity measurements.

Diffusion cell experiments of this type may be used to obtain data necessary for the understanding of water uptake in and leaching from bituminized waste.

However, they are not likely to explain why there is a much lower tendency to water uptake in inactive than in real active Eurobitum. Experiments have been conducted where the swelling behaviour in water of samples of inactive Eurobitum irradiated by external gamma-radiation up to one MGy was followed as function of time, but at least this type of irradiation did not result in any significant increase in the tendency to water uptake.

A long-term experiment with measurement of swelling pressure due to water uptake in inactive Eurobitum tends to stabilize at a value of about 1.8 bar, but this may not be relevant for the real material.

6. Microbial degradation (B.10.)

The experiments with microbial degradation of precipitation sludges in contact with but not embedded in bitumen or concrete have been resumed. A sludge containing nickel ferrocyanide as well as barium sufate and cobalt sulfide is employed. The preliminary results indicate that the microorganisms may not thrive in contact with these materials. The previously demonstrated tendency to increased ^{134}Cs release from the nickel ferrocyanide at high pH is noticed again. Results for ^{85}Sr and ^{60}Co will also be available.

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 December 1989
Period covered : January 1988 - December 1988
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

2.2 Studies of colloids in cement leachates.
2.3 Characteristics of colloids in repository environments.
2.4 Characterisation of near-field materials in EC repository simulation tests.
2.5 Cement/steel interactions in the near field.
2.6 Colloid sorption behaviour.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In our earlier work it has been established that colloids and fine particulates can form in leachates derived from pure OPC cement and blends containing BFS and PFA. A range of physicochemical techniques has been used to characterise such colloids. These include ultrafiltration, photon correlation spectroscopy, electrophoretic light scattering, SEM/EDAX and X-ray diffraction. Sensitive elemental data on the composition of colloidal particulates has also been obtained using inductively coupled plasma emission and mass spectrometry (ICP-ES and ICP-MS). Our investigations have now been extended using such techniques to obtain details of the mechanisms by which such colloids are produced. Here we have measured the kinetics of release of a range of elements from cements (Na, Al, Si, S, K, Ca, Sr and Ba) into the aqueous phase at different temperatures. Of these elements, Al and Si exhibit anomolous behaviour showing a gradual rise to a maximum over a period of hours to days followed by a decline to a lower solubility limit. Such behaviour is marked at higher temperatures (60°C and above) and is consistent with a colloid formation process involving nucleation and growth. Extensive measurements of the kinetics of elemental release have also been made at different volume/mass (V/M) ratios of leachate to cement to simulate the evolution of the near- to far-field water chemistry. The behaviour of Al and Si is again anomolous, suggesting supersaturation processes may result in the formation of colloids composed of hydrated silicate and aluminate phases.

The effect of cement leachates on materials typical of those likely to be present in the near field (minerals, backfill) has been investigated. Here emphasis is being given to establish physical and chemical interactions which may result in either the release or formation of colloids. Initial studies with glass - a model system, made under accelerated conditions (60°C), show that surface chemical reaction and colloid formation do indeed occur. Such effects may result in important retention mechanisms for radionuclides in solution and are being investigated further. Other investigations of cement/steel interactions under near-field conditions have been undertaken.

A systematic investigation of the mechanism of colloid sorption processes under conditions typical of the near field has been started. Correlations in the sorption of a range of nuclides are being explored using several well characterised and natural colloid systems. Initial investigations of leachates and filter residues obtained from EC Repository Simulation Tests show evidence of colloids which have been characterised in detail.

PROGRESS AND RESULTS

2.2 STUDIES OF COLLOIDS IN CEMENT LEACHATES

Previous work has established that colloidal particulates can form in cement leachates /2,3/. More detailed studies have now been carried out on the kinetics of release of cement elements during leaching to determine the mechanisms of colloid and particulate formation. A wide range of leachate volume to cement mass ratios (V/M = 0.025 to 2.5 $dm^3\ g^{-1}$) was employed to simulate the evolution of the near-field conditions (drop in pH and Ca^{2+} concentration) in the long term. Leaching was carried out at two temperatures - 25°C (OPC and OPC/BFS cement formulations) and 60°C (OPC only). Inductively coupled plasma emission spectrometry (ICP-ES) was used to measure the concentration of elements in the leachates.

The release behaviour (kinetics, dependence on V/M) of Al and Si differs markedly from that of the other cement elements (see Figures 1a and 1b for example). The evidence suggests that nucleation and growth of solid phases containing Al and Si give rise to colloids and particulates. Light scattering measurements indicate a mechanism in which supersaturation occurs leading to growth of particulates followed by aggregation. Such processes could result in the incorporation of radionuclides present as soluble ions. It is also evident that the high ionic strength (Ca^{2+}) of the leachate destabilises any colloid species formed causing them to coagulate and either precipitate or become attached to the walls of the leaching vessel and outer surface of the cement. These processes may be an important retention mechanism for released radionuclides if the deposited material is immobile in the long term.

2.3 CHARACTERISTICS OF COLLOIDS IN REPOSITORY ENVIRONMENTS

The host rock and backfill materials associated with a repository are a potential source of colloids as a result of physical disturbance in the near field or through chemical interaction with cement leachates (high pH and ionic strength). Such fine waterborne particulates could serve as carriers for radionuclides from the repository. Accordingly some natural materials (granite, sandstone, clay) likely to be typical of a repository environment are currently being investigated for colloid generation. Suspensions of the clay and of crushed granite have been fractionated by sequential ultrafiltration and the filters examined by SEM/EDAX. An abundance of fine angular or flaky particles, especially rich in Si and Al, has been observed so far in the 1µm region, as well as particle agglomerates. More massive specimens of granite and sandstone are also being exposed to concentrated OPC leachate at 60°C and will be examined by SEM/EDAX for surface modification and the build-up of deposits. Glass surfaces have been found to be attacked under these conditions giving rise to gelatinous deposits and enhanced levels of Si in the leachate (see Figure 2). Such processes may lead to colloid formation initially, but are more likely to provide important retention mechanisms for radionuclides in solution.

2.4 CHARACTERISATION OF NEAR-FIELD MATERIALS IN EC REPOSITORY SIMULATION TESTS

EC Repository Simulation Tests involving the granite option with waste glass present are being conducted at Harwell. Leachates are filtered (0.45 µm pore size) before being sent for analysis. Four of the filters from tests of 364d duration have been obtained and examined using SEM/EDAX. Deposits on the filters appear to consist of material derived from the smectite/sand mixture used as the backfill layer in the tests. The leachates from the tests have also been examined by photon correlation spectroscopy. The results indicate the existence of colloids after filtering with size in the range 1-5 µm, suggesting that subsequent aggregation of smaller units occurs. Consequently there is a need to examine the effect of further ultrafiltration through membranes of smaller pore size to assess the colloid size and retention.

2.5 CEMENT/STEEL INTERACTIONS IN THE NEAR FIELD

Steel is an important repository component used for containment and reinforcement. As such it may act as a source of near-field colloids or be involved in their generation and speciation. Initial, exploratory leaching tests have been conducted under accelerated conditions at 60°C on OPC cement discs loaded with iron filings (20 wt%) to provide a high superficial area. Preliminary results up to 56d indicate that the iron remains largely inert under the O_2-free conditions employed. Analysis of the total leached material, including any particulates and deposits formed, revealed only traces of released iron. Levels were too low ($<10^{-6}$ mol dm^{-3}) for reliable measurement under the conditions. Long-term leaching tests (>200d) are in progress at 25°C and 60°C on OPC pellets incorporating mild steel bar. Small specimens of mild and stainless steel are also being exposed to the aqueous phase during leaching of OPC at 25°C and 60°C (>300d). The surface of these specimens will be examined by SEM for deposits and alteration.

2.6 COLLOID SORPTION BEHAVIOUR

Initially a range of well characterised colloidal suspensions (micronised mica, montmorillonite, kaolinite, silica, haematite and Mol clay fractions) has been exposed to a dilute solution containing a series of spike elements (Ce, Co, Cs, Eu, Ni, Th and U) simulating radionuclides. These colloids may be typical of those found in repository environments. After a suitable time the spiked suspensions were centrifuged to remove all particles >10nm. The supernates are currently being analysed by ICP-MS and ICP-ES to assess the degree of uptake of the spike elements by the colloids. The effect of colloid concentration is also included in the investigation.

LIST OF PUBLICATIONS

/1/ RAMSAY, J.D.F., The role of colloids in the release of radionuclides from nuclear waste, AERE R-11823 (1985).

/2/ RAMSAY, J.D.F. and AVERY, R.G., Colloids related to low level and intermediate level waste - Progress report for the period 1st July to 31st December 1986, AERE R-12538 (1987).

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/4/ 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 1988, AERE R-13200 (1988).

/5/ RAMSAY, J.D.F., AVERY, R.G. and RUSSELL, P.J., Physical characteristics and sorption behaviour of colloids generated from cementitious systems, Radiochimica Acta <u>44/45</u>, 119 (1988).

/6/ RAMSAY, J.D.F., The role of colloids in the migration of radionuclides from nuclear waste, Proc. of Conf. "Migration 87", Munich, September 1987. To be published in Radiochimica Acta.

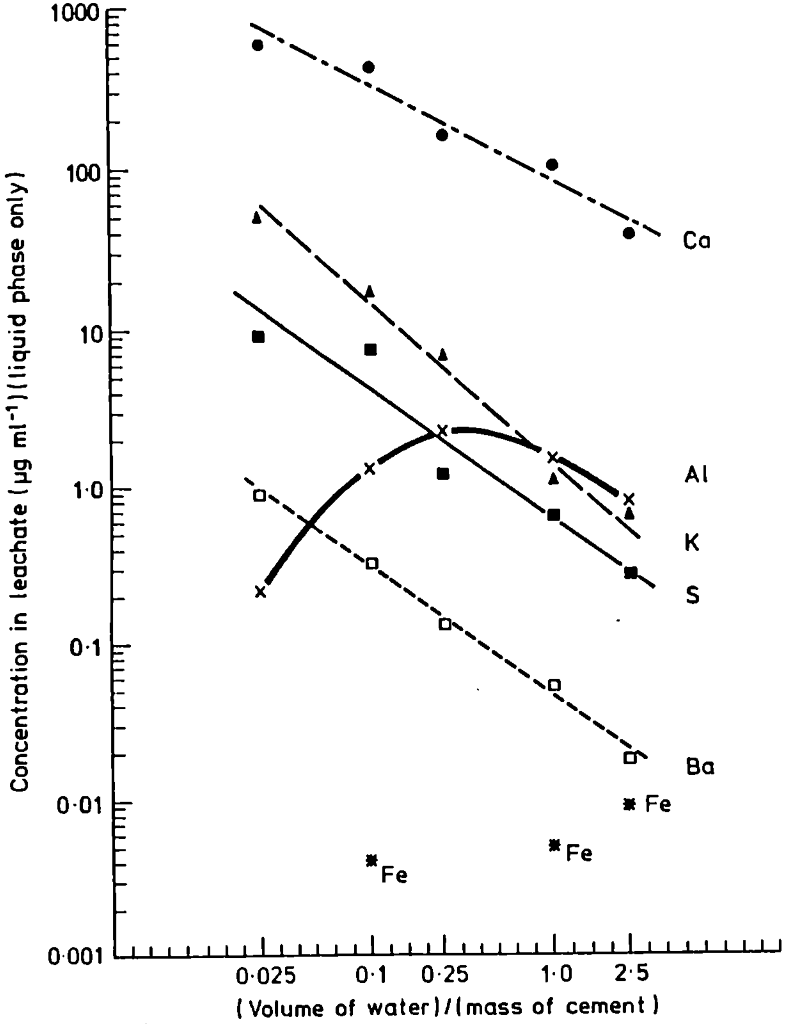

FIG. 1a

ALUMINIUM

RELEASE OF SELECTED ELEMENTS FROM CEMENT DISCS (OPC ONLY, W/C = 0·4) AT 60°C AFTER 28 DAYS

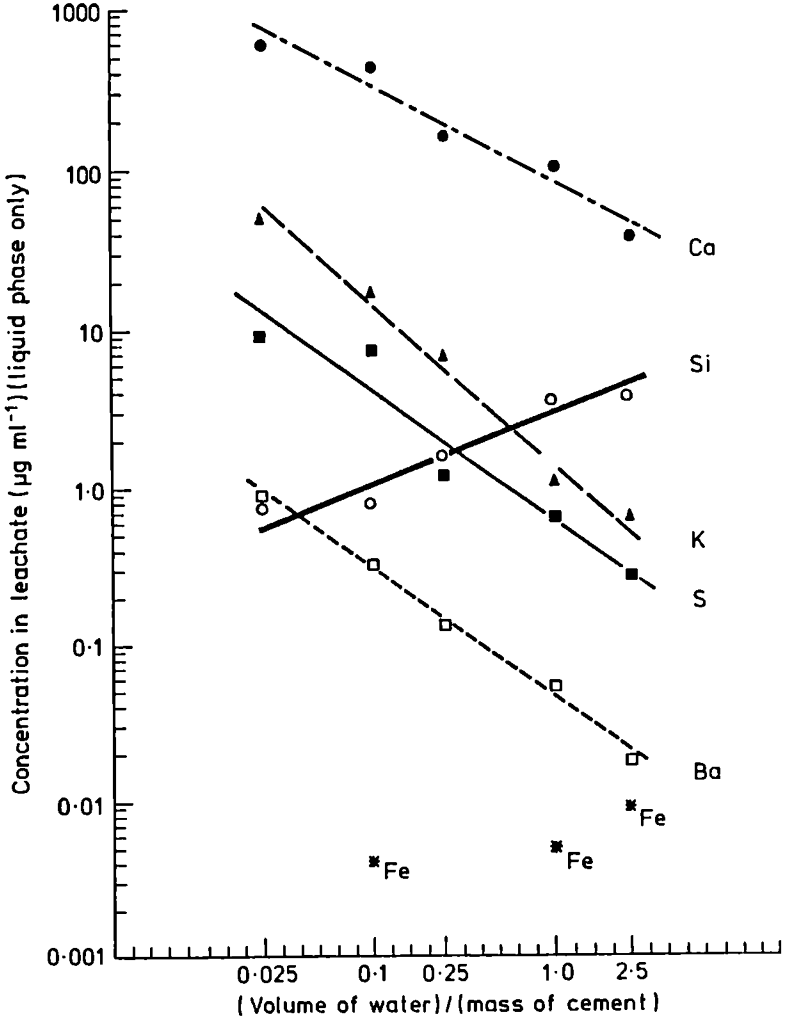

FIG. 1b

SILICON

RELEASE OF SELECTED ELEMENTS FROM CEMENT DISCS (OPC ONLY, W/C = 0·4) AT 60°C AFTER 28 DAYS

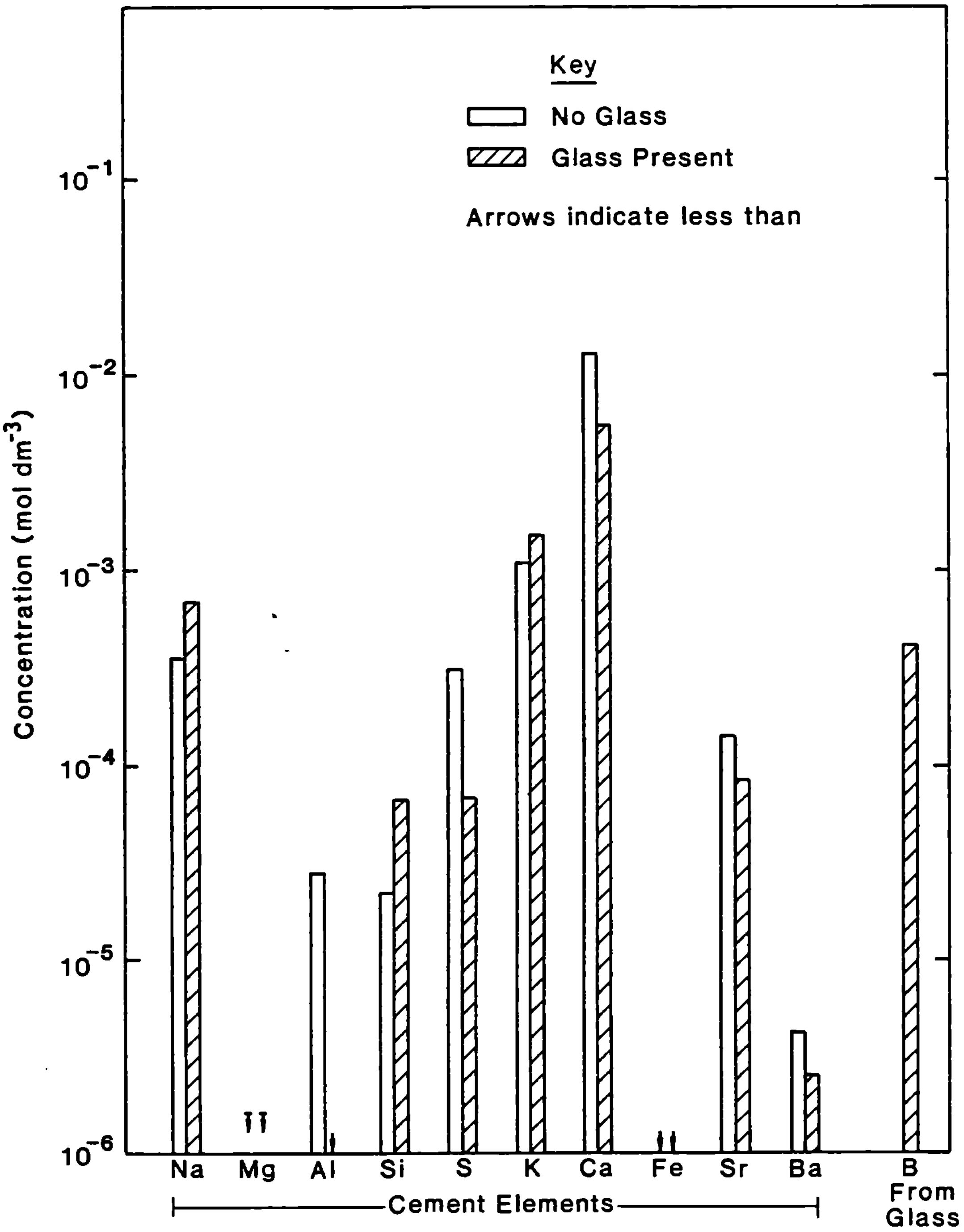

FIG. 2 ELEMENTAL COMPOSITION OF LEACHATES (LIQUID PHASE ONLY) FROM UNSPIKED OPC (W/C = 0.4) AFTER LEACHING AT 60°C FOR 113 DAYS IN FEP FLASKS, SHOWING THE EFFECT OF THE PRESENCE OF BOROSILICATE GLASS

Near-Field Modelling in Cement Environments

Contractor:	Harwell Laboratory, U.K.
Contract No:	FI.1W/0184/00
Working Period:	January 1988 - December 1988
Project Leader:	Dr. P.W. Tasker

A. Objectives and Scope

The primary aim of this work 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 radionuclides. This 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 Improvement of the numerical solving method used in the computer code CHEQMATE/1/. This code couples chemical equilibria (via. the PHREEQE code/2/) with ionic migration.

B.2 Application of CHEQMATE to coupled chemistry and transport problems relevant to the near-field of a repository, for example the space and time degradation of the cementitious backfill.

B.3 Participation in the code comparison exercise CHEMVAL.

C. Progress of Work and Obtained Results
State of Advancement

The numerical solving method in the CHEQMATE code has been replaced by a more stable 'implicit' method. This allows larger timesteps to be used. CHEQMATE has been applied to the problem of the space and time degradation of the cementitious backfill. The effect of aggressive ions from the groundwater surrounding a repository have also been considered. There has also been participation in CHEMVAL with both static PHREEQE and CHEQMATE for the coupled code comparison.

Progress and Results

1. Improvement of the Numerical Solving Method in CHEQMATE (B.1)

The original version of the computer code CHEQMATE/1/ combined one-dimensional transport of ionic species with chemical equilibria. The set of mass-transport equations is solved by firstly dividing a one-dimensional section of the repository into cells, and then calculating the flux of each species across each cell boundary from the finite difference representation of the transport equations. This method restricts the maximum timestep that can be used, so is being replaced by the more stable 'Gear's method'/3/ To implement this, a change in approach is needed. Only those species dominating the chemistry are migrated within the model section. Comparison with results from the original version of CHEQMATE show that agreement so far is good. Testing of this method continues.

2. Investigation of the Degradation of Cement in a Repository (B.2)

The current UK 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 general corrosion rate of the metal canisters is reduced and the solubilities low. Cement will degrade due to the leaching of the solid components and attack from aqueous species in groundwater. A preliminary model of the degradation of cement in a repository has been developed. The modelling involves the incorporation of a thermodynamic description of cement into a coupled chemistry-transport model using CHEQMATE/1/. The cement model used is that developed by Berner/4/ for use with the static geochemical speciation codes MINEQL/5/ and PHREEQE/2/. The description simulates the incongruent dissolution of cement by a mixture of congruently soluble components with variable solubility products.

The first stage of the modelling of the degradation of cement simulates the simple leaching of cement in pure water. This provides a useful verification exercise, as a direct comparison with the results from a THCCDM/6/ model can be made. The agreement between the two sets of results is found to be good. The effects of aggressive aqueous species on the degradation of cement are then investigated by contacting the cement separately with groundwater and seawater. Results from the model suggest that the pH in the cement porewater will fall more rapidly in both these cases than with pure water, and a large amount of mineral precipitation is observed, particularly when the cement is in contact with seawater. Sensitivity studies show that the fall in pH at the surface of the cement will be increased if mineral precipitation at the surface reduces the porosity. The calcium/silicon ratio in the solid cement matrix also decreases more rapidly if there is water flow through the repository.

3. Participation in CHEMVAL (B.3)

CHEMVAL is a code comparison exercise with the object of validating and verifying the chemical codes used in radioactive waste management. The first stage thermodynamic code comparison is now reporting on the test examples run with a standard database and each groups in-house data. Information collected from the exercises will be used in refining the CHEMVAL database. The first stage of the intercomparison of the coupled codes is currently progressing and we are participating in this part of the programme with CHEQMATE.

List of Publications

1. A. Haworth, S.M. Sharland, and C.J. Tweed.
   Proc. 12th Int. Symposium on The Scientific Basis for Nuclear Waste Management, MRS, Berlin 10-13 October 1988.

2. A. Haworth,.S.M. Sharland, P.W. Tasker, and C.J. Tweed.
   Nirex Safety Studies Report NSS.R111 (1988).

3. A. Haworth, S.M. Sharland, P.W. Tasker, and C.J. Tweed.
   Nirex Safety Studies Report NSS.R113 (1988).

4. A. Haworth, S.M. Sharland, P.W. Tasker, and C.J. Tweed.
   Nirex Safety Studies Report NSS.R115 (1988).

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MIGRATION AND RETENTION OF RADIONUCLIDES IN THE NEAR-FIELD, PART C, SORPTION MECHANISMS IN THE NEAR-FIELD

Contractor: Harwell Laboratory
Contract No. : FI.1W.0184/UK
Duration of contract : April 1988 - December 1989.
Period covered : April 1988 - December 1988.
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 process or 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

During the period of this report, the research work has been concentrated on the prepartion and characterisation of some calcium-silicate-hydrate (C-S-H) phases which are typical of a young cement. Some of these phases have also been prepared in the presence of lanthanum and neodymium which have been used as actinide simulants. A bulk slag cement has also been characterised. Sorption studies of actinides and lanthanides onto these C-S-H phases and a bulk cement slag blend are being carried out.

Calcium-silicate-hydrate phases have been prepared by two methods: the reaction of calcium nitrate, sodium silicate and sodium hydroxide and the reaction of calcium oxide and silicic acid. It has been shown that although both methodologies result in the formation of C-S-H phase, the latter method is to be preferred as it results in greater phase purity.

The characterisation of the slag cement blend has shown that the majority of the microstructure is a largely fibrillar C-S-H- gel product. Some substitution of lanthanum for calcium ions has been observed after exposure of thin slices of cement paste to lanthanum solutions. The XRD analysis indicates the presence of poorly crystalline material typical of a young slag cement blend.

As a precursor to the sorption studies, the solubility of lanthanum in cement equilibrated water has been measured and is shown to vary with pH; at a pH greater than 10.5 the solubility is 3 x 10^{-8}M.

PROGRESS AND RESULTS

(i) Sorption onto discrete cement mineral phases

Calcium silicate hydrate (C-S-H) phases with CaO : SiO, ratios of 1.25:1, 1.5:1 and 1.7:1, typical of a young cement, have been prepared using two methodologies. The first method involves the reaction of sodium metasilicate, sodium hydroxide and calcium nitrate. The second method involves the direct reaction between calcium oxide and silicic acid. The C-S-H phases were also prepared in the presence of lanthanides (acting as actinide simulants), lanthanum and neodymium. The C-S-H phases were characterised by thermal analyses, X-ray diffraction and electron microscopy. This characterisation indicated that the C-S-H generated by the second method gave greater phase purities and is recommended for use in further work.

A necessary precursor to the study of lanthanum sorption onto the C-S-H phases and a bulk cement slag blend, is the knowledge of the solubility of lanthanum under the high pH conditions of water equilibrated with these phases. The solubility of lanthanum for a range of pH conditions has been studied and the results are shown in Fig. 1. At a pH greater than 10.8 the solubility of lanthanum is about 3 x 10^{-8}M. Lanthanum sorption studies will therefore be carried out at lanthanum inventories in the aqueous phase of less than 10^{-8}M. Americium sorption studies have commenced at 10^{-10}M aqueous americium inventories for the bulk cement slag blend.

(ii) Crystallography of C-S-H phases

The C-H-S phases prepared in phase (i) and the C-S-H phases in a bulk cement slag blend, of a type which will probably be encountered in a repository, have been characterised using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and analytical electron microscopy (AEM). The AEM technique was used to determine the location of lanthanum and neodymium ions incorporated into C-S-H or on C-S-H surfaces.

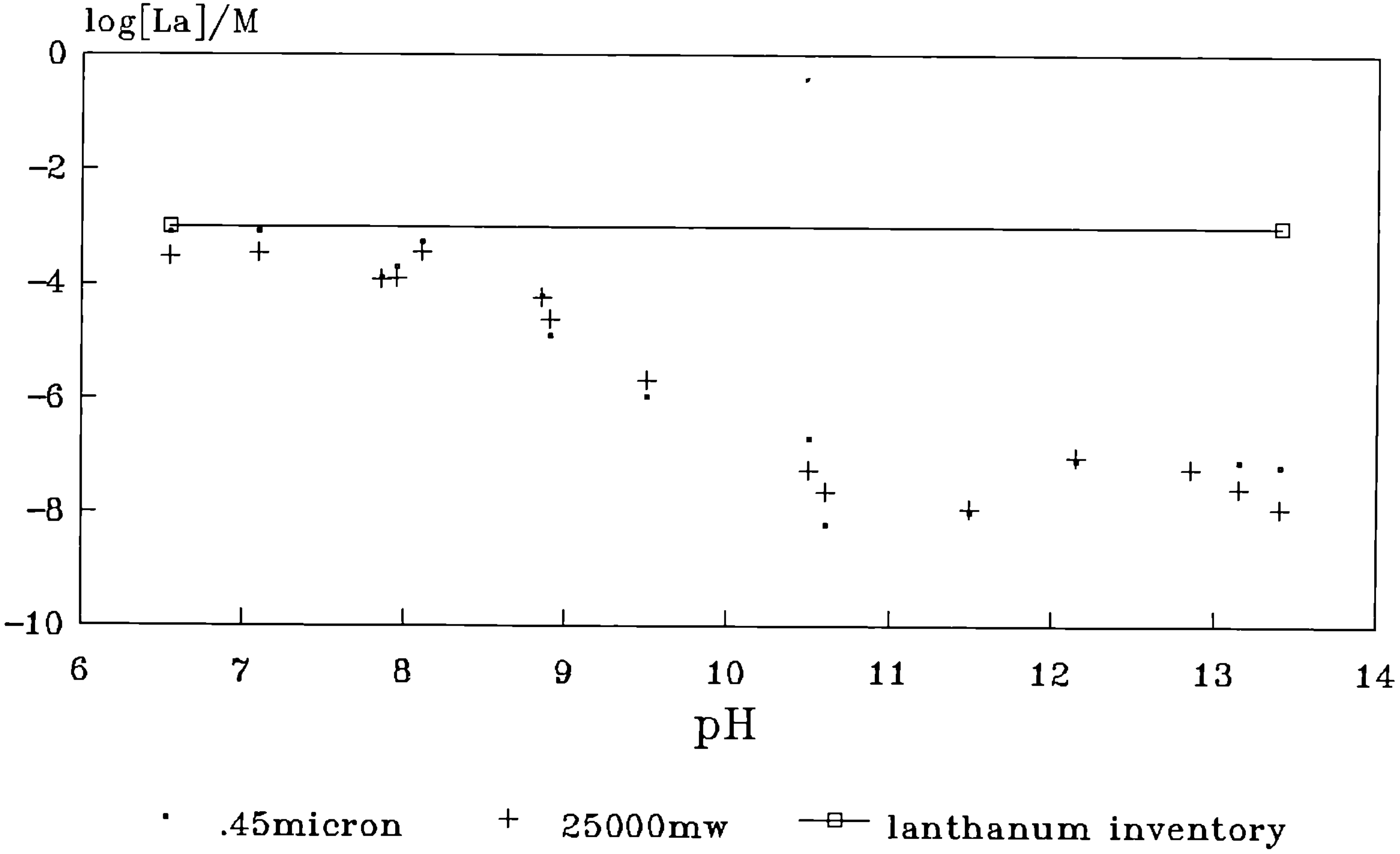
The characterisation of the slag cement blend has shown that the majority of the microstructure is a largely fibrillar C-S-H gel product. Some unreacted slag grainare observed which are surrounded by layers of C-S-H of varying Ca:Si ratio and magnesium and aluminium content. Some substitution of lanthanum for calcium ions has been observed after exposure of thin slices of cement paste to lanthanum solutions. The C-S-H samples which were prepared in the presence of neodymium show no sign of discrete neodymium phases. The XRD analysis indicates the presence of poorly crystalline material typical of a young cement slag blend.

(iii) Surface sorption sites

The sites of sorption of lanthanides on the surfaces of the solid phases will be studied using the Extended X-ray Absorption Fine Structure (EXAFS) technique.

Fig. 1

Lanthanum solubility versus pH



RADIOLYTIC OXIDATION

Contractor : Harwell Laboratory
Contract No. : FI.1W.0029
Duration of contract : September 1986 - March 1989
Period covered : January 1988 - December 1988.
Project Leader : Mr. F.T. Ewart

A. OBJECTIVES AND SCOPE

Preliminary studies in the UK and USA have suggested that alpha and gamma radiation fields can increase the oxidation state of some elements important to radioactive waste management. This programme will establish the significance of these effects as a mechanism for causing enhanced aqueous concentrations in the near field of a repository. Because of the flux of radiation necessary to cause these oxidation state changes the effects are only likely to be found in cemented ILW or vitrified HLW; the programme therefore addresses only these waste forms.

The experimental results of this programme will be used in the construction of a model compatible with the geochemical codes that are used for modelling repository behaviour.

B. WORK PROGRAMME

B.1 Effect of gamma irradiation on neptunium and uranium solubility limits.
B.2 Electrochemical study of the dissolution of oxides of Tc, Np, Pu and Am.
B.3 Effect of enhanced alpha radiation on the solubility of elements selected by studies under B.2.
B.4 Effect of radiolysis on sorption of Tc, Np and Pu.
B.5 Study of overall effects of radiation, waste matrix and backfill.
B.6 Effect of colloids.
B.7 Modelling studies.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Measurements of the solubility of neptunium under oxic conditions have found concentrations of approximately 10^{-8}M at pH13, lower than those previously published in the literature. Alpha irradiation has been shown to cause rapid oxidation of technetium (IV) to a more soluble oxidation state in water equilibrated with a Blast Furnace Slag/Ordinary Portland Cement grout. In contrast gamma irradiation under argon has been found to result in the reduction of pertechnetate in this water with a consequent decrease in solution concentration. Gamma irradiation in the presence of a grout based on Pulverised Fuel Ash does not lead to reduction. The planned electrochemical studies of the effects of alpha irradiation on dissolution have not succeeded due to the difficulty of fabricating a satisfactory working electrode. Sampling of the overall effects experiments is due to commence at the beginning of 1989. Computer based modelling studies of radiolytic oxidation have continued to develop an understanding of the processes involved. During this year the model has been applied to the radiation chemistry of plutonium in the presence of carbonate and to the neptunium system.

The current state of work progress is as follows:

B.1 Completed
B.2 Unsuccessful, work ceased.
B.3 Progressing normally.
B.4 Work in progress.
B.5 Progressing normally.
B.6 Recently started.
B.7 Progressing normally.

PROGRESS AND RESULTS

1. Gamma Irradiation and Solubility (B.1)

Previous work /1/, /2/ has shown that gamma irradiation of Np(IV) hydroxides in contact with cement equilibrated water at pH12 or greater results in aqueous concentrations of less than 3 x 10^{-8}M. This data when compared to published values for the solubility of Np(IV) /3/,/4/ and Np(V) /5/ were interpreted to show that radiolytic oxidation of Np(IV) did not occur at high pH in contrast to the behaviour at lower pH. As a check upon this information the solubility of neptunium has been measured under oxic conditions at high pH with solid/liquid separation effected by filtration through Amicon Centricon-30 filters (30,000 molecular weight cut-off). These studies have found a minimum solubility of 10^{-8}M at pH13, lower than that previously published/5/, and comparable with the solubility of Np(IV). Further work would therefore be required to determine unambiguously the behaviour of Np(IV) under gamma irradiation at high pH.

2. Effect of enhanced alpha radiation on solubility (B.3)

Studies have been made of the dissolution of technetium(IV) hydrous oxide in the presence of alpha irradiation from plutonium-238 in contact with water equilibrated with a 3:1 BFS/OPC cement under a nitrogen atmosphere. The concentration of Tc in solution was determined after filtration through Centricon-30 filters over a period of approximately 80 days. The results obtained are given in Table I for two sets of experiments (A and B) and clearly show enhanced dissolution of technetium for the experiments containing plutonium with the higher alpha dose giving the most rapid dissolution. The addition of iron filings after day 20 (Set A) and day 51 (Set B) was found to have little effect on the alpha irradiated experiments over a hort timescale. These experiments demonstrate the potential for radiolytic oxidation of technetium during alpha irradiation. Oxidation of Tc(IV) to a more soluble oxidation state is rapid and clearly enhanced over control experiments.

3. Sorption (B.4)

Initial studies of the gamma irradiation of solutions of technetium (VII) in contact with 3:1 BFS/OPC have been reported /2/. These found that irradiation under argon resulted in a loss of the element from solution whilst irradiation under air did not. These studies have been extended to include a range of accumulated dose from 10 kGy to 72 kGy. As can be seen from Table II irradiation to 72 kGy results in the loss of nearly all the technetium from solution. In these experiments a dark solid appears to be present upon the surface of the cement. Irradiation of pertechnetate solutions in BFS/OPC equilibrated water in the absence of solid cement also results in a decrease in the concentration of technetium. The irradiation of pertechnetate solutions in the presence of 10:1 PFA/OPC has also been studied and no reduction in technetium concentration was found despite irradiation to 119 kGy. These results suggest that gamma radiolysis in the presence of BFS/OPC may not result in the formation of mobile technetium, Tc(VII), but that radiolytic oxidation of technetium in low oxidation states is possible in PFA/OPC. Confirmation of these possibilities is being sought by studying the desorption of Tc(IV) from the two cements during irradiation.

4. Modelling Studies (B.7)

The modelling studies have developed the description of plutonium ions in alkaline solution /2/ to include the effect of carbonate ions in solution. The inclusion of carbonate species has allowed more realistic modelling of expected repository conditions.

The same methodology of preliminary thermodynamic simulation has been applied to neptunium ions in solution. Having obtained good agreement between the thermodynamic and kinetic models, the inclusion of radiolytic reactions has been performed for both alkaline neptunium solutions and neptunium carbonate solutions. The model has been applied to realistic repository conditions. The model has also been applied to the experimental conditions used in earlier work in this project /2/, and has given good agreement with the observed solution concentration of neptunium in bentonite equilibrated water as shown in Table III.

5. Other Areas of Work (B.2, B.5 and B.6)

In the electrochemical studies it has not been possible to fabricate a satisfactory working electrode and work on this part of the programme has ceased. The overall effects experiments which simulate the near-fields of representative intermediate and high level waste repositories, will be analysed at the beginning of 1989. The effect of gamma irradiation upon the size distribution of humic acid species is being studied.

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Table I

Dissolution of Technetium(IV) Hydroxide in the presence of Plutonium-238 in BFS/OPC equilibrated water

Time/Days	Concentration of ^{99}Tc/M			Notes
	No Pu-238	7.4E+5 Bq/ml Pu-238	7.4E+6 Bq/ml Pu-238	
1	3.3E-8	4.0E-8	5.9E-6	Set A
3	1.8E-8	9.0E-8	8.2E-6	
6	1.8E-8	5.2E-7	2.1E-5	
10	2.1E-8	-	8.6E-5	
20	1.4E-8	-	3.2E-4	
21	2.1E-8	-	3.4E-4	+Fe
24	1.3E-8	-	3.5E-4	+Fe
51	1.4E-6	4.2E-5	3.1E-4	Set B
66	6.0E-8	5.4E-5	3.1E-4	+Fe
84	1.6E-8	6.9E-5	3.3E-4	+Fe

Table II

Irradiation of Technetium(VII) at 3.25 kGy/hr under argon in the presence of BFS/OPC

Size Range (1)	Contact Time/Days	Dose/kGy	[Tc]/M initial	[Tc]/M Final
F	7	10	8.3E-05	5.7E-06 2.5E-05
C	7	10		7.0E-05 6.9E-05
F	6	21	8.1E-05	4.8E-05 4.7E-05
C	6	21		6.7E-06 4.4E-05
F	7	37	8.3E-05	1.4E-08 1.2E-05
C	7	37		9.8E-08 3.7E-09
F	6	72	8.1E-05	1.1E-08 8.2E-09
C	6	72		2.8E-09 2.8E-09
#	14	119	4.2E-05	3.0E-06 6.5E-09

Notes

(1) F = fines, size range <0.125 mm.
C = coarse material, size range 2-5 mm.

= No solid present.

Table III

Comparison of Experimental and Calculated Results for the radiolytic oxidation of $Np(OH)_4$ in bentonite equilibrated water

Dose/ kGy	Total Np concentration/M	
	Experiment	Calculation
0	3.2E-8	3.0E-8
6.2	2.5E-6 3.5E-6	2.8E-6
12.0	3.9E-6 7.4E-6	5.4E-6
19.0	1.3E-5 9.7E-6	8.2E-6
25.0	1.2E-5 1.2E-5	1.1E-5
36.0	1.8E-5 1.5E-5	1.5E-5

Title : Etude des propriétés physico-chimiques des éléments transuraniens nécessaires à la compréhension des processus de retardement de la migration en champ proche dans la géosphère.

Contractor : CEA-IRDI/DRDD/SESD/SCPCS - Fontenay-aux-Roses - FRANCE
Contrat n° : FI1W-0035 F (CD)
Working Period : June 1986 - January 1989 **Project Leader** : A. BILLON

A. OBJECTIVES

The modelling of the transfer of the transuranian elements through the different barriers to the geosphere implies the knowledge of :

- the exact nature of the species which are able to migrate under the influence of the groundwater ; ions, molecules, colloïds,
- the equlibrium relationship between these species and the surrounding dominant other species either in a mineral or an organic form.

From this point of view it is admitted that carbonate (e.g. the different species CO_2, HCO_3^-, $CO_3^=$) due to its relatively high abundance in the geosphere play a major role in this sense that it forms complexes whith almost all the transuranian elements.

Therefore the present word is devoted toward the identification of the different carbonated complexes of the transuranian elements. The determination of their stability constant, their comportement in the geological medium in the vicinity of the source term and in the man-made barriers and finally the elaboration of a model which will describe the migration of these radioelements.

B. WORK PROGRAMME

B1 - Basic chemistry :

Measurement of solubility and stability constant of the transuranian elements with the ligand carbonate. Identification of the different species. E_h - pH diagramms.

B2 - Migration :

Experiment of transfer through argileous material. Preliminary assays of diffusion cells whith Cs and Sr. Application to the migration of americium(III).

B3 - Modelling :

A model wich take in account the chemical properties of the elements issued from the source term with be elaborated and tested.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of avancement

In **basic chemistry** (B1), work has been going on with an investigation of the hydrolysis of Np(V) and a thorough examination of the chemical properties of americium, in connection with the geochemical properties of this element (migration, speciation). The previous work (see ASR 1987) in carbonate media has been completed, leading to a more detailed set of diagrams such as those reported in Fig. 1 and 2. The obtained results in the systems Am(III)/OH^- ; Am(III)/OH^-/CO_3^- are discussed and compared with results available from the literature. A similar work has been made in the determination of the formal redox potentials of the americium redox couples.

Transfert experiments in clay (B2) have seen the completion of the measurement with strontium in various conditions. The parameters which have been investigated are the thickness of the clay probe, the amount of the strontium in the upper compartment of the diffusion cell. Attempt to explain the transfer by a diffusion process seems to be satisfactory after the depletion in the upper compartment and a partial leaching of the clay as well, have been considered.

Modelling as described in B3 deals with the setting up of the code CONDIMENT which include convection and diffusion phenomena to model the migration of radioelement in the vicinity of a repository (near-field). The code is now written up in the case of the migration of a soluble ion alone or in the presence of a precipitate (ions). The parameters which could be adjusted are the distribution coefficient between the two phases (K_d), the diffusion coefficient (D) an the Darcy velocity (U). At this step the work is to be considered as achieved.

PROGRESS AND RESULTS

Americium chemistry. Contradictory interpretations of the Am(III) - H_2O-CO_3^{2-} system are proposed in the literature. In order to know what are the existing complexes in solution, the solubility of solid americium carbonate $Am_2(CO_3)_3$ has been studied at a high ionic strength ($I = 3M$, $NaClO_4$). Two sets of experiments have been performed : the first one with known total carbonate concentration ($10^{-4} \leq (CO_3)_t \leq 1M$ and $7.5 \leq pH \leq 10.4$) ; the second one under controlled CO_2 partial pressure ($PCO_2 = 0.1$ or 0.3 or 1.0 atm) and $5.1 \leq pH \leq 7.8$. Only carbonate complexes ($Am(CO_3)_i^{3-2i}$; $i = 1;2;3$) were found. The values of the equilibrium constants at $I = 3M$, at 20 ± 1°C have been established ; ionic strength corrections are proposed on the basis of these results. No evidence of $Am(CO_3)_3^{5-}$ formation was found by spectrophotometry in the 0.1 to 3M carbonate concentration range. All the published results on Am(III) in carbonate media can be interpreted with this set of equilibrium constants.

The formal redox potentials at $pH = 9.4$ ($[NaHCO_3] + [Na_2CO_3] = 2M$) as well as the standard formation constants : $\ell g[\beta_3(V)/\beta_3(VI)] = 14 \pm 2$ and $\ell g[\beta_3(III)/\beta_5(IV)] = 24 \pm 2$, at zero ionic strength have been used to draw redox potential stability diagram in carbonate media, and to discuss americium speciation in groundwater.

Hydrolysis of neptunium, has been investigated by spectrophotometry, in two types of experiments, with and whithout adjusting the ionic strength of the solutions. The pH of an acid solution of Np(V) is progressively adjusted by addition of sodium hydroxyde. After each increment of OH^- and when the pH is stabilized, the spectrum of the solution is registered. Measurement in some cases are disturbed by Np(V) precipitation. Interpretation of results lead to the existence of soluble NpO_2OH with the following stability constant

$lg^*\beta = = -8.6 \pm 0.2$ at $I = 0.5M$ $NaClO_4$: $lg^*\beta_1 = -9.8 \pm 1.0$ at $I = 0.1M$ $NaClO_4$, where $\beta^*_1 = [NpO_2OH]\ [H^+] \Big/ \left[NpO_2^+\right]$.

(B2) **the transfert of strontium** has been measured in a-4 clay. Experiments of diffusion were completed by measurement in clay itself as well as desorption measurements. Three clay thicknesses have been studied with two Sr concentrations in the upper compartment of different diffusion cell. a-4 clay is efficient to trap this element as well as cesium. Modeling is some what more difficult as fore seen because the concentration are very low in the lower compartment (due to a strong sorption by clay) and the effective diffusion coefficient could be a little larger than the mean value of 10^{-4} $cm^2.j^{-1}$ we propose.

Modelling (B3) of a complete version of the CONDIMENT code, which include all the developments described in the precedent issue has been written up.

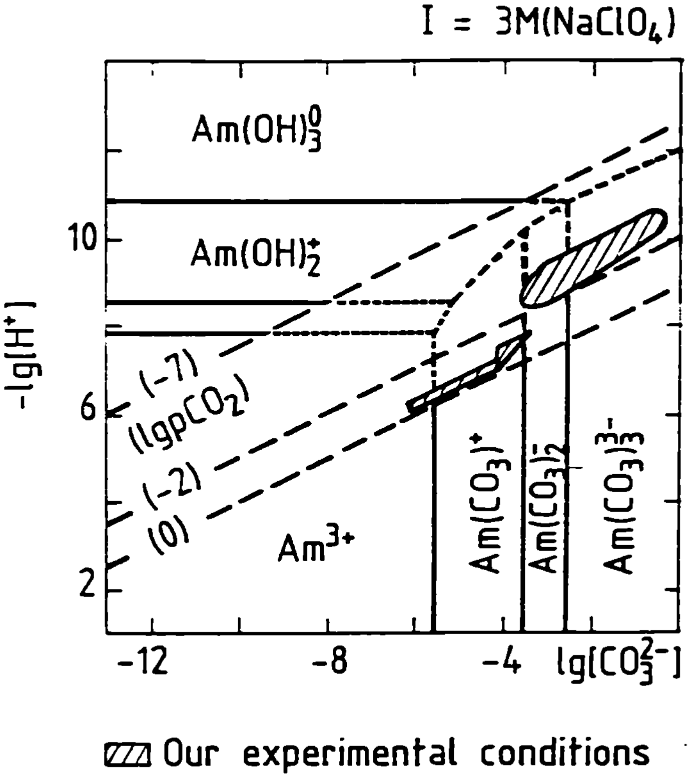


Figure 1. Predominance area of americium species in the system AM/OH$^-$/CO$_3^{2-}$, in function of pH and pCO$_3^{2-}$

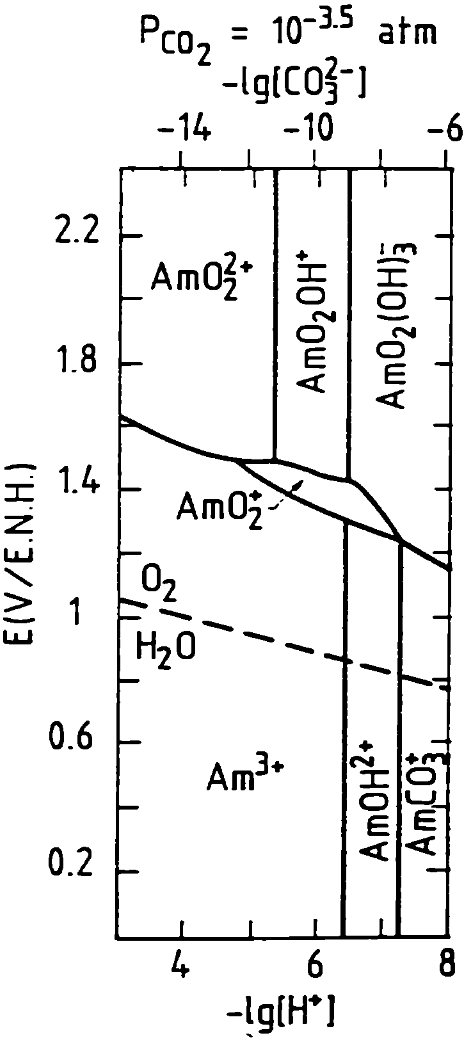


Figure 2. E$_h$ = pH diagram of Am(III) at P$_{CO_2}$ = 10$^{-3.5}$ atm

SOLUBILITY LIMITS OF RADIONUCLIDES IN INTERSTITIAL WATERS

Contractor : CEA-IRDI/DRDD/SESD/SCPCS
Fontenay-aux-Roses France
Contract No. : FI1W-0190(F)
Duration of contract: January 1988 - December 1989
Period covered : January 1988 - December 1988
Project Leader : Mr Vitoye

NO REPORT HAS BEEN RECEIVED FROM THIS CONTRACTOR

3.4. Development of Tests for Quality Control and Quality Inspection Purposes

EVALUATION OF NON-DESTRUCTIVE METHODS FOR QUALITY-CHECKING OF VITRIFIED HLW

Contractor:	UKAEA - Harwell Laboratory
Contract No:	FI1W/0036
Duration of contract:	August 1986 - March 1989
Period covered:	January 1988 - December 1988
Project Leader:	B H Patrick and B L Taylor

A. OBJECTIVES AND SCOPE

The aim of the programme is to evaluate the use of on-line non-destructive methods, based on x-ray absorptiometry and γ-spectroscopy coupled with advanced data processing techniques, for the quality checking and/or characterisation of vitrified HLW Particular emphasis will be placed on developing and demonstrating techniques that will be applicable to fully active glass samples. A cylindrical container of active vitrified waste produced by the Fingal process is available for this work.

Resulting from the proposed programme, we intend to demonstrate firstly the use of γ-emission measurements for determining the content and distribution of γ-emitting isotopes within a highly active sample container and secondly the use of X-ray absorptiometry for measuring the loading of active glass. On completion we aim to have sufficient information to enable the design of a plant instrument to be undertaken.

Harwell is collaborating with BAM in the exchange of data processing expertise and hardware developments, particularly with respect to detection systems.

B. WORK PROGRAMME

Task 1	Construction of the facility to enable γ-emission and x-ray absorption measurements to be carried out on highly radioactive samples, particularly the Fingal glass container.
Task 2	Adaption and improvement of computer algorithms required for the application of γ-emission tomography to the sample.
Task 3	Construction of an inactive simulant sample containing cavities to permit the introduction of sealed γ-sources.
Task 4	Use the inactive simulant sample to test the mechanical handling aspects of the equipment.
Task 5	With the inactive sample loaded with sealed sources; test the measurement and data processing parts of the γ-emission system.
Task 6	Carry out x-ray absorptiometry on the inactive sample.
Task 7/8	Repeat the emission and absorption measurements, respectively, on the active glass.
Task 9	Apply the equipment development for Fingal glass sample to small (1 litre) samples of cemented intermediate level waste available at Harwell.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

A major part of the work this year has been involved in preparing a detailed safety case for both the mechanical and radiological aspects of the experiment in order to obtain an "Authority to Operate". The required approval for unattended operation of the rig was obtained from both the Harwell Site Active Facilities Committee and the UK Health and Safety Executive.

The mechanical apparatus has been completed and installed. The initial tests made with the inactive glass specimen of closely similar dimensions to the active sample, showed that a number of minor modifications were necessary; these have been carried out.

Transmission and emission tomography have been performed on both the inactive and active glass specimens. As might be expected the intense γ-radiation from the active specimen results in some loss of resolution with respect to the measurement of linear attenuation coefficient and the appearance of some artefacts in the images.

X-ray absorptiometric measurements have been carried out on both active and inactive samples but due to the strong attenuation caused by the presence of high levels of uranium in the glass, little quantitative information has so far been obtained.

Progress and results

Task 1 - Construction of facility

The equipment is now installed and fully tested with both inactive and active full scale samples. (Task now complete).

Task 2 - Computer algorithms

The reconstruction algorithms which were developed in collaboration with Dr A Kettschau (BAM), use a conventional filtered back-projection. Attenuation corrections for emission studies are achieved using Chang's method.

Task 3 - Inactive glass simulant

A hole was drilled in the full scale inactive glass specimen to allow the introduction of sealed radiation sources (eg Cs-137) for the emission tomography trials. (Task now complete.)

Task 4 - Commissioning of the equipment

The mechanical commissioning of the equipment using the inactive specimen has been carried out. A number of minor modifications were necessary mainly as a result of unforeseen differences in the dimensions of the active and inactive specimens and the presence of an additional sleeve needed to prevent the spread of contamination from holes that had been drilled in the containment as part of an earlier experiment. (Task now complete.)

Task 5 - Tomography on inactive glass specimen

Transmission and emission studies (using an inserted Cs-137 source, see Task 3) have been carried out. Tomographs taken in the region of the sample hole showed all the expected features and the transmission images showed sufficient resolution to be able to distinguish the gap between the inner container and the thin outer sleeve. In other regions the transmission tomographs showed evidence of defects in the glass. (Task now complete.)

Task 6 - X-ray absorptiometry on the inactive specimen

Using a 160 keV X-Ray tube transmission measurements were made across the diameter of the inactive sample. The main purpose of this exercise was to check the means of aligning the source, collimators and detector. (Task now complete.)

Task 7/8 - Measurements on the active glass specimen

Tomography has been performed on the active specimen using a NaI detector and a Co-60 Source for the transmission measurements. A hole that had been drilled in the glass as part of an earlier sampling operation was clearly imaged both by transmission and emission tomography. In contrast with the inactive specimen, no evidence of voidage was discernible in the active glass. This may be due to the much poorer signal to noise ratio obtained due to the intense γ-radiation emanating from the glass. Certain image artefacts have been tentatively ascribed to effects such as pulse pile up from Cs-137 radiation (662 keV) which in the case of transmission measurements results in spurious counts in the counting window set for the Co-60 radiation (1170 and 1330 keV). Further work will be carried out to try to resolve some of the questions raised by the initial measurements. For example it is intended to carry out transmission measurements with a lower energy source (Ir-192) and a high resolution HpGe detector.

The X-ray transmission measurements on both active and inactive specimens is hampered by the strong absorption resulting from the high uranium level present. The active glass contained waste from the reprocessing of low burn-up Magnox fuel using the earlier Butex process. Waste originating from current Purex reprocessing plants will have much lower uranium levels. So far measurements have only been made using the detector collimator designed for tomography. These transmission spectra clearly show the K-edge absorption edge of uranium but the transmitted intensities at energies immediately above the edge are too low to permit an accurate determination of the uranium concentration.

Quality Assurance of Radioactive Waste Packages by Computerized Tomography

Contractor: BAM, Berlin, Germany
Contract No: FI 1W/0037 / FI 1W/0193
Working Period: January 1988 - December 1988
Project Leader: P. Reimers

A. Objectives and scope

According to task 3 "Testing and Evaluation of Conditioned Waste and Technical Barriers" quality assurance is a main scope of research concerned with the handling of radioactive waste. It is provided to characterize medium and high active waste by standard test methods which are to be developed and experienced in this contract. Quality evaluation of radioactive waste packages is preferentially done by nondestructive testing methods.

Our proposal is mainly concerned with the elaboration of specific testing methods for ready conditioned waste packages as well as the matrix materials themselves (e.g. bitumen, concrete, ceramics and glass). CT with X-rays is one of the best methods for the comprehensive nondestructive characterization of the physical and technical properties of the above described test objects. The method is especially suitable for the nondestructive evaluation of the absolute density value, of the density distribution, of the gamma activity distribution, of the localization of voids, cracks and inclusions, of the visualization 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 properties to be investigated.

B. Work Programme

- B.1 Choice and acquisition of a radiographic linear accelerator, installation and acceptance test
- B.2 Development, construction and testing of a HECT detector
- B.3 Investigation of the crack formation of non-radioactive HAW glass simulate
- B.4 Nondestructive evaluation of the internal surface of a glass cylinder
- B.5 Investigation of cemented cladding waste
- B.6 Investigation of swelling, shrinking and segregation in LAW and MAW containers
- B.7 Nondestructive evaluation of the compressive strength of cemented waste
- B.8 Evaluation of the activity distribution in MAW-containers by combination of ECT and TCT-measurements
- B.9 Combination of simulated HAW-ECT-measurements with TCT-measurements

C. Progress of work and obtained results

Summary

The first contract with the scope "Quality assurance of radioactive waste packages by computerized tomography" ended on June 30, 1988. During the contract time the BAM-Tomograph was equipped with a 9 channel HECT detector thus enabling the CT investigation of heavy attenuation objects with an old radiographic linear accelerator. The working programme comprised the examination of five different types of radioactive waste packages:

A 50 l barrel filled with bituminized waste housed in a 200 l barrel, a 80 l steel conatiner filled with HAW glass simulate from KfZ Karlsruhe, a 160 l steel container filled with HAW glass simulate from CEN Valroh, a 200 l drum with cemented waste simulate with artifical voids and a simulated waste drum with additional concrete shielding (outer diameter 960 mm).

As a consequence of the results of these investigations it seemed to be necessary to be able to tomograph at least objects with a total wall thickness of more than 1000 mm of concrete or 300 mm of iron. Therefore it was decided to upgrade the new radiographic linear accelerator which was ordered by BAM in January 1988. The upgrade supported by the European Communities in the new contract will improve the pulse dose by a factor of 30 compared to the originally planned machine. Due to the pulsed nature of linac radiation the most important parameter for CT sensitivity is the pulse dose, not the average dose rate. After checking all offers it turned out that the X-4000 of the British Raytech Company delivers the highest pulse dose available from a magnetron machine. Higher doses are only obtainable with klystron machines which have a considerably higher price (far out of the projects budget). The new working programme deals mainly with high attenuating waste packages and CT-measurements with better spatial resolution than possible with a cobalt-60 source used during the first contract. Until now the following types of waste packages have arrived in our laboratory:

A cemented drum from CEN Cadarache with an outer diameter of 960 mm and a volume of 870 l, a 200 l barrel with simulated cladding tube waste from a reprocessing unit, a 160 l steel container from CEN Valroh with HAW glass simulate for the investigation of crack propagation, several 400 l drums filled with real waste from a decommissioned reactor which were blown up by internal gas presure, a 80 l container with HAW glass simulate to test the tightness of weldings by a drop test, and the model of a new type of HAW container where glass and the steel housing are moulded together in a HIP process.

These packages will be tomographed as soon as the new accelerator is in operation.

D. Progress and results

1. Choice and acquisition of a new radiographic linear accelerator

As a consequence of the results of former investigations of the current programme it seemed to be necessary to be able to tomograph at least objects with a total wall thickness of 100 cm of concrete or 25 cm of iron. Therefore it was decided to upgrade a new radiographic linear accelerator (X-4000) which was ordered by BAM in January 1988. The upgrade will improve the pulse dose by a factor of 30 compared to the originally planned machine (Minac, cf. tab. 1). Linear accelerators are the most powerful radiation sources for high energy computed tomography (HECT). Due to the pulsed nature of linac radiation the pulse dose is the most important parameter for CT-sensitivity, not the avarage dose rate. After checking all offers it turned out that the X-4000 (new company name is "Raytech") delivers the highest pulse dose available from a magnetron machine. Higher doses are only obtainable with klystron machines which have a considerably higher price (far out of the project's budget).

2. Development, construction and testing of a single detector

As mentioned in the last report we have improved the detector efficiency and the dynamic range of the amplifier. The $CdWO_4$- single crystal is 60 mm long and has a cross section of 4×6 mm^2 to increase the absorption of high energy radiation. The light emitted from this scintillator is detected by the following photodiode with an active area of 6×6 mm^2. The output current is integrated by a special fast, very low noise amplifier. We are using a 14 bit 20 kHz ADC to convert the amplifier output into digital data which are then transmitted via the CAMAC bus into the intermediate data memory. Due to the limited (14 bit) accuracy of the ADC the new detector has two sample and hold stages in parallel, one measuring a tenfold amplified signal thus covering a range of 17 bit overall. Between the linac pulses the integrating capacitor is set to zero by an optocoupler system using feedback control thus avoiding the switching noise and correcting for dark current bias.

The integrating and sampling circuits are gated by the synchronizing pulse of the linac. Therefore the detector is open only for the very short period of the linac radiation pulse. Thus the continuous background radiation of the waste package is reduced by the factor of the sampling ratio of the linac which is 1:2000 for the present machine. Additionally one has to keep in mind that by the careful shielding of the detector system only the waste activity located in the pencil beam volume in the object slice contributes to the noise of the measured signal.

Before setting up the new linac the two stage detector was tested with the old Super X (500 rads/m/min). The maximum attenuation measured with a statistical error of $\leq \pm 10$ % is $\mu \cdot d = 9.5$ corresponding to a dynamic range of $\exp(9.5) = 13{,}000$. From these results it is derived that the maximum wall thickness which can be investigated with our HECT-scanner is 40 cm steel or 20 cm lead corresponding to 150 cm of ordinary concrete as calculated from published data.

5. Investigation of cemented cladding waste

One type of medium active waste of a reprocessing plant are the fuel canning sections. After a several years cooling period they are filled in 400 l drums and fixed with cement milk.

To simulate such a MAW package a 200 l drum was filled with 40 kg of steel tubes and then fixed with cement. The steel tubes (steel: ST 55) had a diameter of 10 mm and a length of 50 mm. The wall thickness is 0.75 mm. From the average density a maximum attenuation of 20000 is calculated, assuming an energy of 1.25 MeV (Co-60). Due to this extreme attenuation factor the measurements on this drum can only performed with the new electron linear accelerator.

6. Investigation of shrinkage and swelling

Due to the various materials embedded in waste containers e.g. metals, organics, fluids together with the cement matrix unexpected physical and chemical reactions can take place.

As an example for an undesired and non understood matrix reaction a 200 l drum was investigated, which was blown up by high gas pressure. For reason of security the 200 l drum was put into an 400 l overpackage.

The CT images revealed a perforation of the steel containment and many aluminium parts embedded in the cement matrix.

The most reasonable reason for the overpressure is hydrogen generation caused by the close contact of aluminium and cement during the filling process.

8. Evaluation of the activity distribution in MAW-containers by combination of ECT and TCT-measurements

In addition to the attenuation correction programs for ECT which were written as part of the working programme of the proceding contract a first real emission tomogram was measured during the working period.

The emitter was a point source (185 GBq Ir-192) inserted into one of the artificial voids in the heavy concrete test drum (described in the second report of the first contract). Fig. 8.1 shows the transmission tomogram (TCT) of this package in the upper halve and the corresponding ECT in the lower halve. It is obvious that the total activity is concentrated in the Ir-192 point source. In the zoomed pictures (A02, A03) it is clearly visible that the circular activity distribution of the cylindrical Ir-192 radiator is imaged as an oval spot. This image distortion is caused by the high attenuation of the Ir-192 radiation in the direction of the longer axis of the ellipse. This artifact is inherent to the Chang-method of attenuation correction for ECT. Further effort will be necessary to quantify the error of the activity values measured by this method.

STUDY OF A NON DESTRUCTIVE TESTING METHOD FOR PACKED RADIOACTIVE WASTE CONTAINERS

Contractor : CEA, CEN Cadarache, France
Contract n° FI 1W-0038
Duration of contract : from 1 May, 1986 to 30 April, 1988
Period covered : from 1 January, 1988 to 30 April, 1988
Project leader : J.F. MONTIGON

A. Objectives and scope

A computerized tomograph is developed in order to test the physical homogeneity of radwaste packages, that will be 200 l drums filled either with polymer or bitumized radwaste, and also inactive glass packages.

Special studies are required to design such a machine; first, a feasibility study gave the preliminary features of this drum-scanner; then its design and realization have been undertaken.

The objective of this programme is to start operation on this drum scanner by the end of 1988.

B. Work programme

B.1. Dedicated feasibility study for the drum-scanner, aiming at defining a low-cost, easy-to-build tomograph.
B.2. Design and realization of mechanical and electrical hardware.
B.3. Design and realization of measurement electronics.
B.4. Design and realization of the computer system.
B.5. Design and realization of the shielding.
B.6. Assembly of the components and tests on the machine.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In 1988, the detailed design of the hardware has been nearly completed and its realization has begun. Some development remains to be done on electronics. The study of the software has begun.

Progress and results

B.1. The feasibility study had been completed in 1987
B.2. The mechanical and electrical hardware comprises :

- a motorized device to hold and move the drum; the drawings of this part have nearly been completed; the components of machine-tool which are the mainframe of the system have been supplied and checked, and their machining has begun.
- an irradiation and detection module; its general study is completed, and the gamma-source container has been supplied (without its Co-60 source).

B.3. The measurement electronics is composed of 10 identical detection channels whose detectors, photomultipliers, preamplificators and racks have been supplied. The detection geometry has been defined (the slots in the collimators will be 4.2 mm wide x 2.1 mm high). Some trouble occurred because of saturation on the end detectors, but this problem is being dealt with by experimental work.

B.4. The computer system was not yet delivered by the end of the contract. The study of the software has begun on a PC-type microcomputer. The work under way consists in writing the simulation software which allows to create the measurement files.

B.5. Shielding : the accurate calculations of the shielding's thickness are under way. They depend on the attenuation of scattered gamma-rays, since the leaden collimators are designed so as to shield completely direct rays.

B.6. The assembly of components has not yet begun.

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 1988
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 Conditioning 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-exchange 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 with the execution of full scale and some further labo. scale tests.

Full scale tests

The tests on the full package included:

- stackability test
- drop test from 1.2 m
- penetration test
- drop test along the horizontal axis.

Each package was a 400 l drum and contained pozzolanic cemented ion-exchange resins (R2, R3), Portland cemented filter sludges (F2, F3) and Portland cemented BWR evaporator concentrates (C2, C3).

The samples had been prepared by means of the MOWA plant and left to cure and harden for not less than 28 days.

The method followed for the full scale tests was the one proposed by the IAEA, with the aim at verifying the maintenance of the physical integrity of the containers under the conditions reported in the regulation.

Labo. scale tests

Mechanical and leach tests were completed. Studies concerning the influence of some parameters on leaching mechanisms (temperature, leachant renewal, initial amount of the chemical tracer, size of the sample tested, composition of the leachant) were initiated.

Progress and results

3.1 Labo. scale tests

The tests conducted on small scale samples included the completion of mechanical and leach tests, as well as the evaluation of the surface water absorption, according to BS 1881 (1970).

3.1.1 Mechanical tests

The mechanical tests concerned the evaluation of compressive, tensile and flexural strength, compressive strength on samples broken under flexural load, surface hardness, drop test from 9 m onto a target, ultrasonic pulse velocity , elastic modulus and Poisson's ratio.

The trend of such properties as a function of time during the first 28 days was quite normal.

3.1.2 Leach tests

The leaching results after 6 months are reported in Table I.
The tests were made according to ISO standard with deionized water at +40 C.

The pH of the leachant, measured after each renewal, was about 11.5 in any case for the samples tested.

The percentage of Cs released for bead resins and filter sludges (21.9 and 22.4% respectively) is acceptable, while the result for evaporator concentrates (74.3%) is not satisfactory.

3.1.3 Surface water absorption

The surface water absorption is defined as "the rate of flow of water into concrete per unit area after a stated interval from the start of the test and at a constant applied head and temperature".

The plot of the water absorption as a function of time decreases fairly rapidly until a steady value is reached. This represents the flow-through rate when water has entirely penetrated the specimen to the undersurface. In spite of the high leachability the lowest permeability (ab. 4.5 * 10E-8 m/s) was recorded for cemented evaporator concentrates. 2.5 and 1.0 * 10E-7 m/s are the values obtained for bead resins and filter sludges respectively.

3.2 Full scale tests

3.2.1 Stackability test

The packages R2, F2 and C2 were subjected to a load of 3550 kg (corresponding to 5 times the weight of the package), uniformly distributed on the top cover.

Due to the metal structure of the container, phenomena of plastic shear were excluded; consequently the test was limited to 2 hours instead of 24 hours as required by the IAEA regulation.

No deformation occurred during the test.

3.2.2 Drop test from 1.2 m

The test, made on the same containers used for the stackability test, was conducted in order to concentrate the impact of the waste package in the area corresponding to the edge of the top cover, near the clippable lid.

The drop was produced by means of a compressed air system. The inclination along the vertical axis was about 28°.

The damage due to the impact was limited to a restricted area of the drum. The deformation suffered by the cover was not enough to separate it from the container, and, what is more, no release of material was noticed.

3.2.3 Penetration test

According to the IAEA requirements the penetration test was made with a bar of 6 kg, diameter of 3.2 cm and with a round edge, dropped from 2.1 m onto the surface of the drum.

A very little damage was caused by the impact of the bar.

3.2.4 Drop test along the horizontal axis

The packages R3, F3 and C3 (identical to R2, F2 and C2) were dropped along their horizontal axis from 1.2 m.

The results of the test were like the ones due to the drop along the vertical axis, with some damage to the cover and without any release of material.

<u>List of publications</u>

G. De Angelis, "Use of an Italian pozzolanic cement for the solidification of bead ion exchange resins", presented at the International Symposium on Management of Low- and Intermediate-Level Radioactive Wastes, jointly organized by IAEA and CEC, Stockolm, Sweden, 16-20 May 1988.

TABLE I

Leaching of Cs and Sr from cemented samples (180 days of leaching)

(average of two values)

cement/waste	PZ/IER		PC/FS		PC/S	
chemical tracer	Cs	Sr	Cs	Sr	Cs	Sr
leaching rate (Kg/m2.s)	$1.0\ 10^{-7}$	$2.2\ 10^{-8}$	$7.5\ 10^{-8}$	$8.0\ 10^{-9}$	$3.0\ 10^{-7}$	$1.9\ 10^{-8}$
leaching factor (m/s)	$2.9\ 10^{-11}$	$1.2\ 10^{-11}$	$4.0\ 10^{-11}$	$4.3\ 10^{-12}$	$1.4\ 10^{-10}$	$9.3\ 10^{-12}$
cumulative leached fraction % (m)	0.18	0.02	0.18	0.02	0.65	0.05
% release	21.9	2.9	22.4	2.6	74.3	5.1

RADIOACTIVE WASTE PACKAGE ASSAY FACILITY

Contractor:	Taylor Woodrow Construction Ltd, Southall, UK
Contract No:	FI.IW.0102 UK (H)
Duration of Contract:	January 1987 to July 1990
Period Covered:	January 1988 to December 1988
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.2.4 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.2.7 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

The programme was enhanced through extensions in three areas: optimisation of interrogation assembly configuration, use of a unified approach to separate parameters of the data processing model, greater range of waste forms and immobilising media.

Stage 1 of the programme, except for the data processing work, was completed by June. This established the feasibility of integrated waste assay, the independent review body agreeing that experimental confirmation of the theoretical predictions should be obtained. The intermediate progress report /1/ described the main findings. A paper was presented to the IAEA/CEC symposium on management of low and intermediate level radioactive wastes, held in Stockholm during May /2/. The meeting agreed the need for independent verification of the contents of waste packages.

Stage 2 work was started. Responsibility for supply of the linac neutron target was transferred from Ray Technologies to Harwell. A feasibility study report on data processing was issued in December by Plessey.

The main features of a composite assembly for either active neutron or active gamma interrogation were established and were used in the design of the experimental unit being constructed at Harwell.

Suitable electron beam energies required for gamma interrogation are 7 MeV and 5 MeV, both being required in order to eliminate the effect of photoneutrons generated by deuterium, and to obtain a measure of the latter.

Sensitivities under active neutron and active gamma interrogation are estimated to be around 0.14g fissile actinide and 30g total actinide respectively.

Progress and Results

Active Neutron interrogation (B.1.2)

A conceptual design for a composite assay arrangement using either active neutron or active gamma-ray interrogation was developed from the requirements of both techniques. Both forms of interrogation use an asymmetric system where interrogating source and neutron detectors are on opposite sides of the drum, thus helping to minimise spatial variations in response.

A tantalum-beryllium target driven by a ~15MeV electron beam provides interrogating neutrons. Dimensions are tantalum ~3mm thick, beryllium ~ 300mm in direction of electron beam/bremsstrahlung beam axis and a maximum 100mm radial to the drum.

A 300mm borated concrete shield surrounding the drum prevents neutron leakage from target to counters. ^{3}He neutron counters are located at 90°, 180° and 270° for fast neutrons generated during active neutron interrogation. Each is surrounded by 10mm polythene moderator, wrapped in 1mm cadmium sheet inside a 100mm thick lead shield. Thermal neutron counters are located at 135° and 225° for use during active gamma interrogation.

Responses were calculated assuming 1g of fissile actinide located in one of 54 regions throughout the drum. For the 180° detector, rotation averaged response was 3×10^{-10} counts per source neutron per gramme actinide. Spatial variation was 2 at midplane and 6.7 overall. (Figure 1).

Expected sensitivity is 0.14g assuming 1×10^{9} neutrons per linac pulse, 100pps run length 1000s.

Active gamma-ray interrogation (B.1.2)

Bremsstrahlung at 7 MeV and 5 MeV were selected. All actinides plus deuterium are measured at 7 MeV, deuterium only at 5 MeV.

Responses were calculated for the conceptual design using the 135° detector. The rotation averaged response was 0.0045 counts per microcoulomb of electron beam per gramme actinide, with a mid-plane variation of 1.3 (Fig 2). The considerable vertical variation can be greatly reduced by scanning the electron beam vertically before the bremsstrahlung radiator, using vertically sectioned counters or moving the drum vertically.

Expected sensitivity is about 30g for $\sim$1m A beam current and run length 1000s.

Spatial distribution of actinides (B.1.2)

The responses measured the neutron counters vary according to the position of actinide within the drum. Using vertically sectioned counters and noting the angular orientation of the drum, it should be possible to obtain a measure of actinide distribution which may also be correlated with gamma-ray radiography data.

Passive neutron counting (B.1.2)

High attentuation within the cement matrix restricts passive neutron measurement to the outer regions of the drum. Concentrations of actinides near the surface could be located and correlated within other measurements.

Effects of high gamma radiation levels on neutron counters (B.1.2)

The potentially high background gamma radiation level (possibly over 1000 Rad. hour^{-1}) may cause difficulty in discriminating between neutrons and background and may also shorten the counter lifetime. It is considered that shielding will be needed to limit the gamma background to 25 Rad. hour^{-1}. Use of activated charcoal coated cathodes is expected to ensure adequate counter life.

Data Processing (B.1.3)

A feasibility study was carried out into data processing for an integrated assay facility. Concepts of the assay system were examined and it was shown that to achieve independence, the axiomatic concept is required in which measurement data are treated as different observations of the same set of waste drum features, but under different conditions. The requirements for a mathematical model have been identified, together with the likely computer hardware.

Provision of experimental assay system (B.2.1)

An experimental assembly capable of use in either active neutron or active gamma-ray modes is being set up in the low energy cell of the Harwell linac HELIOS (Fig 3). The arrangement is generally similar to that of the conceptual composite design, and is constructed in modular form for ease of rearrangement and access. An air pad base supports the assembly structure and provides for easy repositioning. Cell modifications included raising of the roof and installation of an overhead travelling crane.

Electrical data links are being made to an existing data acquisition station, and between the local computers and the Harwell main frame computer.

A reconfigurable water cooled bremsstrahlung radiator and aluminium residual electron beam stopper has been made. From one to six 0.6mm tantalum plates can be used. Two water cooled neutron generating targets have been made each consisting of a block of beryllium inside a 4.5 per cent magnesium aluminium casing 2mm thick with a ~3mm clearance. Dimensions are 200mm x 200mm x 100mm and 200mm x 200mm x 50mm respectively, enabling at least three target combinations to be assembled.

Measurements have been made of neutron output from beryllium blocks 100mm x 100mm x 50mm using ^{115m}In activation. Similar sized graphite blocks were used to permit subtraction of the photoexcitation component of the ^{115m}In activity. Experiments have been on two blocks, using in turn two, one and zero beryllium blocks. The measured/calculated neutron ratio was 1.07 and 1.56 for one and two beryllium blocks respectively. Hence target neutron calculations should be reliable to ~50 per cent.

Detector package decay time constants (B.2.1)

Detector decay time constants of much less than 150 μs are necessary in order to be able to measure the fission neutron signals. The effect of lead shielding may increase the constant, and this was tested using $^{10}BF_3$ and ^{3}He counters and a time tagged ^{252}Cf source. Counters were surrounded by 10mm of polythene, and 1mm of cadmium sheet and/or 100mm lead were used in different combinations. Decay time constants were about 23 μs for ^{3}He and about 35 μs for ^{10}BF, lead having no adverse effect on the constant except when cadmium was omitted. Neutron detection efficiency was increased by the presence of lead.

Gamma flash tests on neutron detectors (B.2.1)

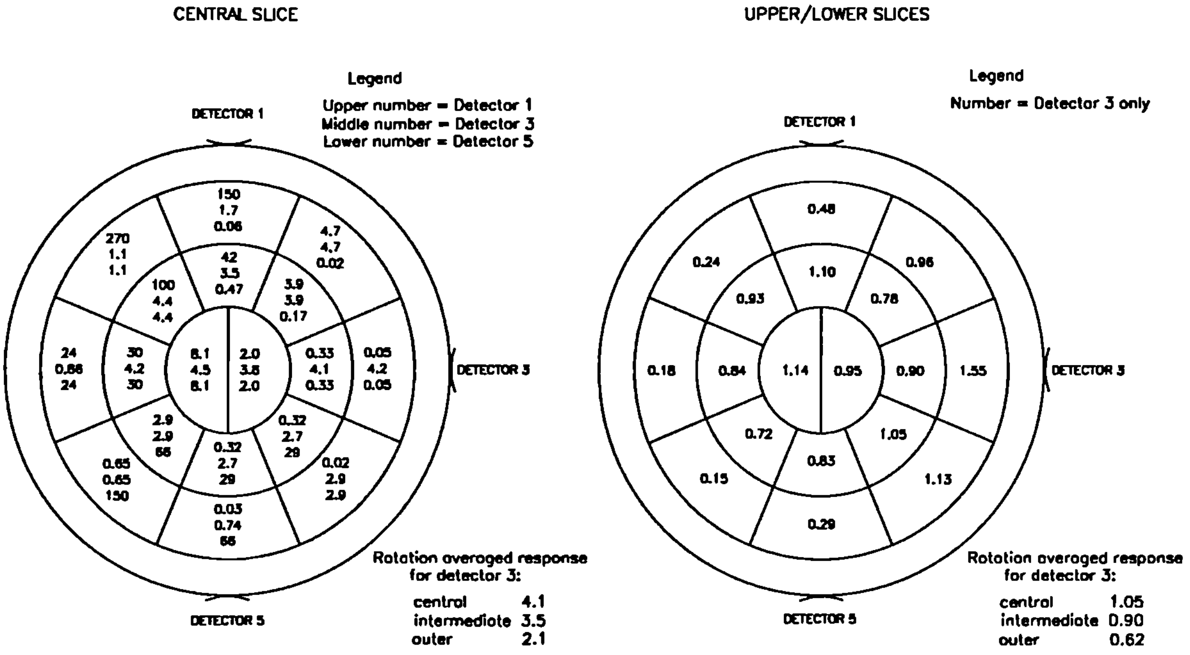
Of the two obvious candidates, ^{3}He neutron counters have advantages ie., lower voltage, greater reliability, and lower decay time constant, but there is little available information on their performance in a high gamma background. A comparative test was carried out using the HELIOS low energy cell, a 0058 preamplifier and 2151 pulse shaping main amplifier. For the same size of neutron signals, the ^{3}He counter gamma flash signal was only ~ 15 per cent longer, and a ^{3}He counter should be satisfactory for assay purposes.

A test with and without a diode across the feedback loop capacitor of a preamplifier showed that a diode was unnecessary, if a suitable AC coupling was provided between preamplifier and main amplifier.

References

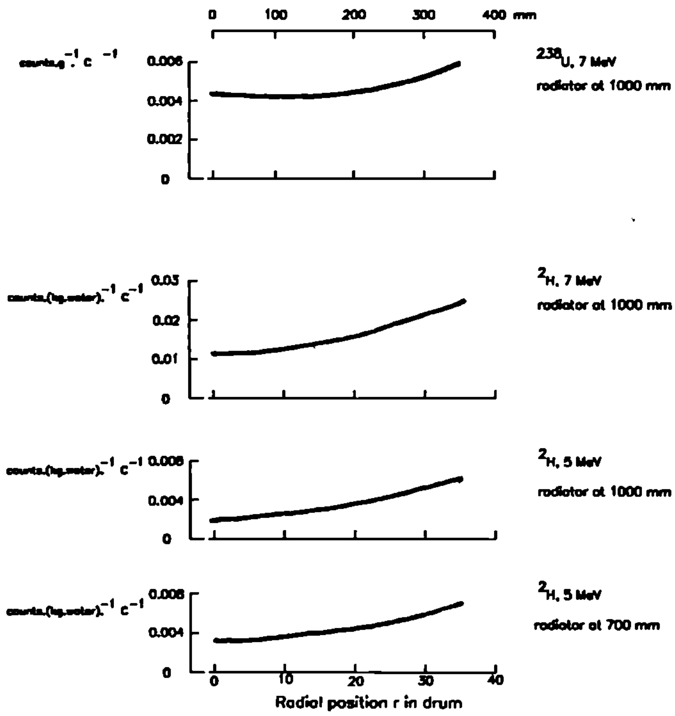
/1/ FINDLAY, D.J.S., SENÉ, M.R., SWINHOE, M.T., MOLESWORTH, T.V., WISE, M.O., FORREST, K.R., Radioactive Waste Package Assay Facility. Taylor Woodrow Intermediate Progress Report 8250/R/DD/0008 (July 1988)

/2/ DAVIES, I.Ll., MOLESWORTH, T.V., FINDLAY, D.J.S., GREEN, T.H., The Assay of Radioactive Waste Packages in a Quality Programme Paper IAEA SM303/7. International Symposium on Management of Low and Intermediate - Level Radioactive Wastes, Stockholm, 16-20 May 1988 (Proceedings awaiting publication).



Response of active neutron interrogation system in units of counts per g(of ^{238}U) per 10^{10} interrogation neutrons for 3 equal divisions. Interrogation beam enters drum from left.

FIGURE 1

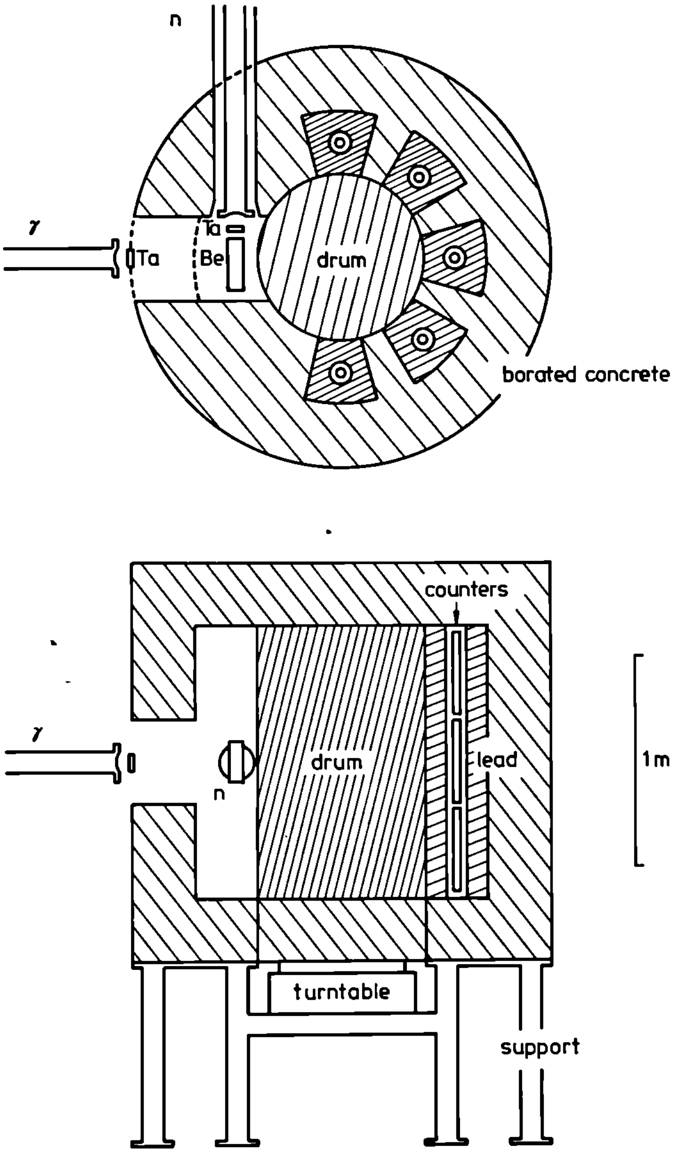


Response of active gamma-ray interrogation system in units of counts per g(of ^{238}U)(or per kg of water for ^{2}H) per microcoulomb of electron beam on the bremsstrahlung radiator in the plane of the bremsstrahlung beam axis

Detector at 135°

Radial response function R(r)

FIGURE 2



Schematic diagram of experimental interrogation unit. Although electron beam lines and targets for both neutron and active gamma–ray experiments are shown, only a single beam line and target would be used at any one time. The support framework is mounted on an air–pad base, not shown here. The concrete is formed from interlocking blocks.

FIGURE 3

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 1988 - December 1988
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

The first device was designed in 1988 for incorporation inside a standard glass canister, and can thus be implemented in any vitrification facility under highly radioactive conditions. Glass is sampled by filling a graphite crucible mounted on an articulated arm which swings into position beneath the molten glass stream in the middle of the casting operation. Once filled, the crucible moves aside to a stowage position away from the casting stream. The sample is then removed from the canister using a telemanipulation device specially designed for this purpose.

Progress and Results

B.1 Device No 1

On the basis of previously available data, a preliminary design study of a mechanism suitable for device No 1 led to the following options:

- The glass sample is taken automatically inside the canister during casting without any outside action.
- A sample carrier arm is placed in the canister before the latter enters the cell. The arm has no effect on the external canister geometry.
- The sample carrier arm automatically moves sequentially through three positions: an initial standby position, a sampling position beneath the molten glass stream, and a final stowage position after the sample crucible is filled.
- The crucible is moved into position beneath the glass stream by a torsion spring actuated by the melting of a fusible disk.
- The crucible is moved to its stowage position after filling, when its own weight again trips the return spring release mechanism.
- The sample crucible is not automatically returned to the center of the canister after casting is completed and the glass has cooled. Suitable mechanical provisions are included on the sample recovery device.
- The crucible itself is designed to yield a glass block for leaching and a smaller diameter specimen for examination (Figure 1).

Additional theoretical and experimental work was required to determine a suitable fusible material (*Castolin 1802* soldering alloy with a melting point of 608-615°C) and its position in the canister to ensure that the sample is taken in the midst of the 200 kg melt (i.e. between the 50th and 150th kilogram of glass poured into the canister).

Inconel 600 or *Inconel 601* will be used for the spring that ensures the necessary rotational motion, in order to maintain satisfactory mechanical properties despite the severe thermal conditions.

After manufacturing and preliminary testing, the device was submitted to full scale tests in standard canisters filled under the actual conditions of an industrial prototype vitrification facility. The mechanism operated normally, and the graphite sampling crucible was satisfactorily filled at the proper moment during the casting process.

A telemanipulation device (Figure 2) was designed, built, tested and qualified for recovery of the specimens after filling the sample crucible.

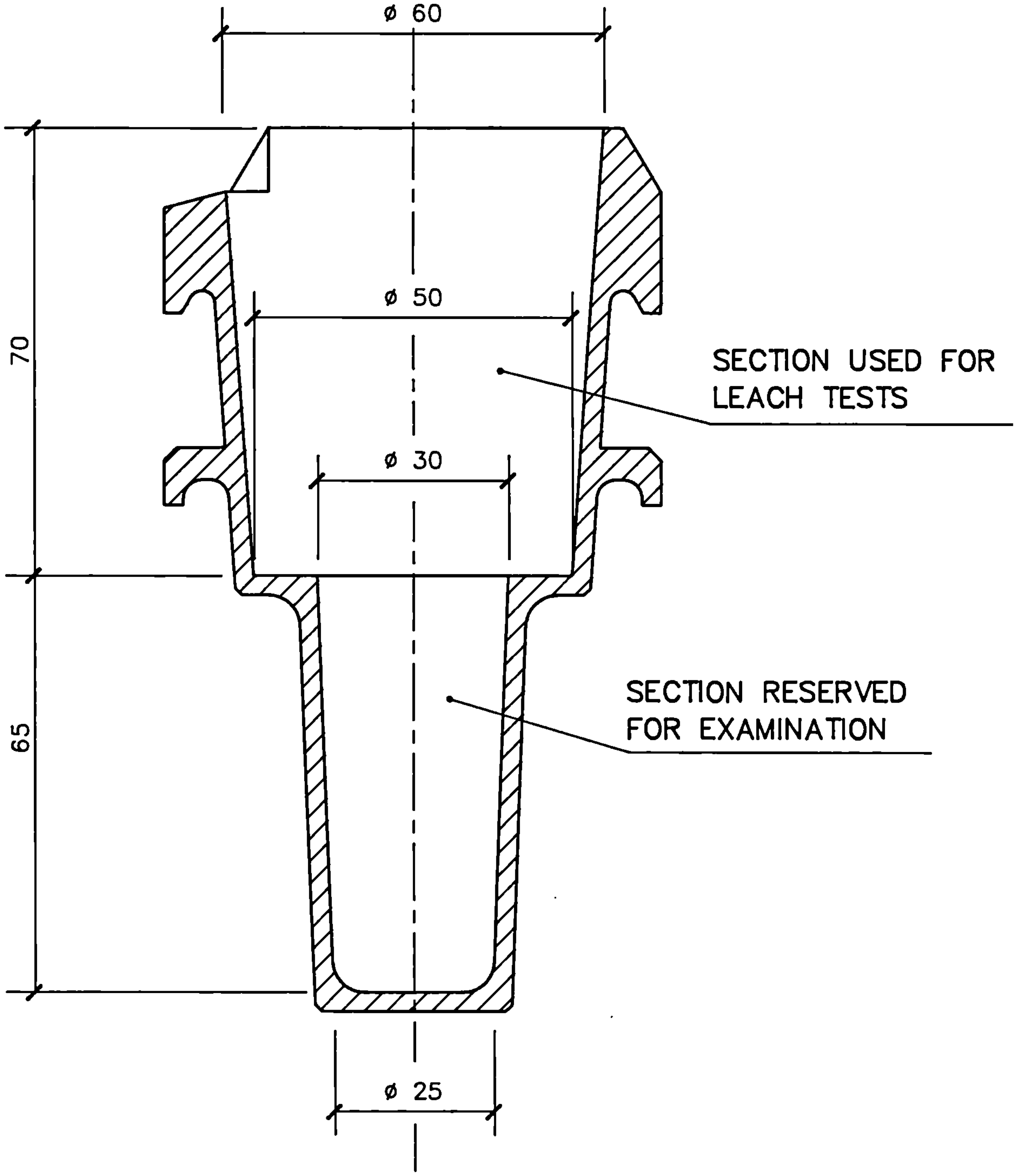


Figure 1 – GRAPHITE SAMPLING CRUCIBLE

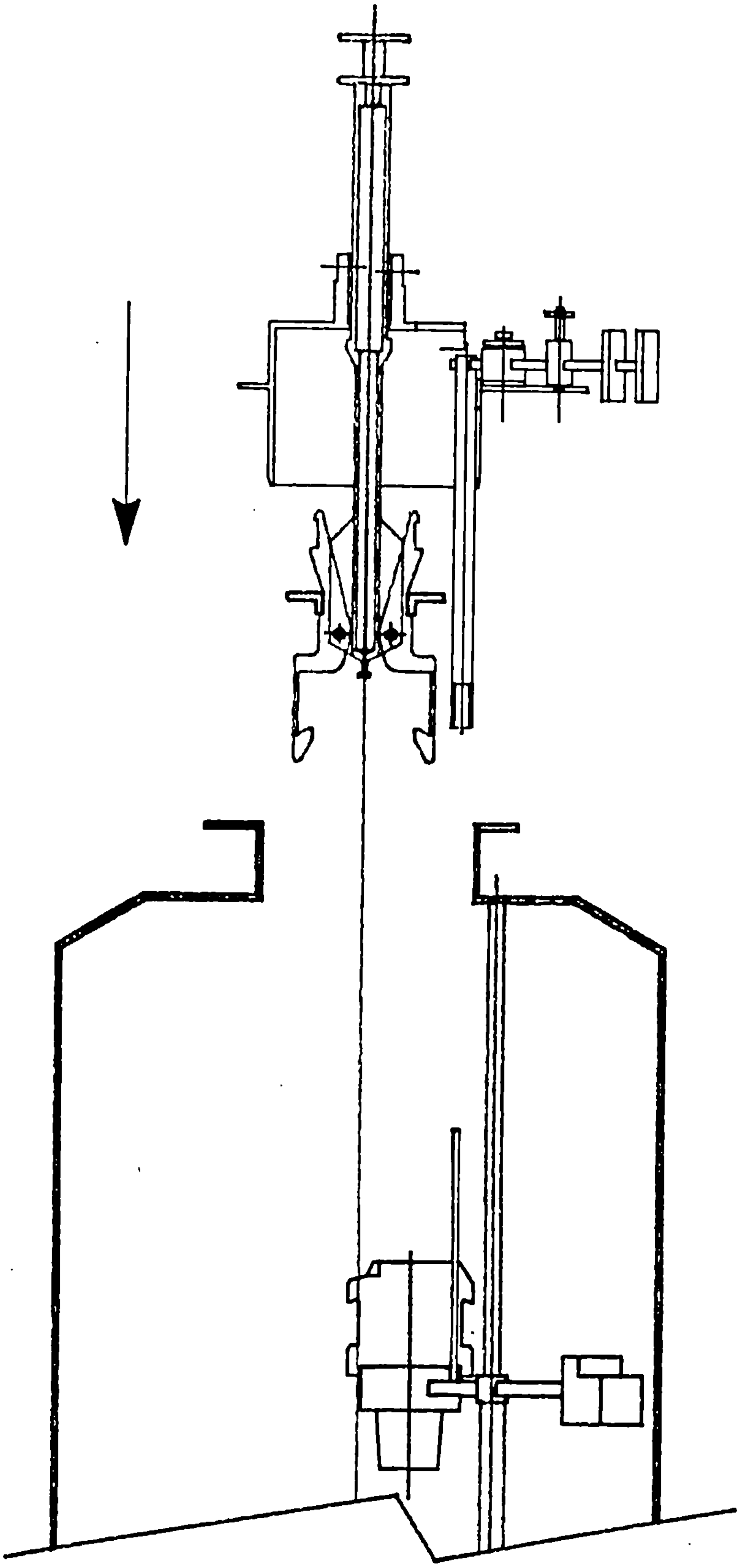


FIGURE 2.- SCHEMATIC DIAGRAM OF TELEMANIPULATOR DEVICE FOR RECOVERY OF REMOVABLE CRUCIBLE CONTAINING GLASS SAMPLE

QUALITY CONTROL METHODS FOR LOW AND MEDIUM ACTIVE WASTE

Contractor : CEA-Cadarache-France
Contract No. : FI1W-0220 (F)
Duration of Contract : January 1989 - December 1989
Project Leader : Mr. MONTIGON

DUE TO DELAYS IN SIGNING THIS CONTRACT THERE IS NO PROGRESS TO MENTION IN THIS REPORT.

Destructive and Non-Destructive Tests for Radioactive Waste Packages

Contractor: KFA Jülich GmbH, Federal Republic of Germany
Contract No.: FI1W-0222-D (AM)
Duration of Contract: October 1988 - February 1990
Period covered: October 1988 - December 1988
Project leader: Dr. Reinhard Odoj

A. Objectives and Scopes

On the basis of preliminary waste acceptance requirements quality control of radioactive waste has to be performed prior to interim storage or final disposal. The quality control can either be achieved by random tests on conditioned radioactive waste packages or by process qualification of the conditioning processes.

One of the most important criteria is the activity of the radioactive waste product or package. To get some first informations about the nuclide inventory of the radioactive waste package γ-spectrometric investigations can be performed as non-destructive test. Besides the γ-emitting nuclides the α- and β-emitting nuclides can be estimated by calculation if the waste is generated in nuclear power plants and the nuclide relations are known.

If the non-destructive determination of nuclides is not sufficient or the non-radioactive content of the waste packages has to be identified sampling from the waste packages has to be performed. This can best be done by core drilling. To avoid for cooling the drill head the need of water, air cooled core drilling is investigated.

As mixed wastes is not allowed for final disposal the determination of possible organic toxic materials like PCB, dioxin and furane-compounds in cemented wastes is conducted by GC-MS-investigations.

For getting more knowledges in the field of process qualification concerning super compaction instrumentation of the super compaction process is investigated and tested. Therefore the plot of the pressure versus the time or the distance is measured during supercompaction in industrial scale of about 100 drums with different content.

B. Work Programme

2.1 Non-Destructive tests
2.1.1 γ-Spectrometric determination of nuclides
2.1.2 Investigation of process data during supercompaction of radioactive wastes
2.2 Destructive tests
2.2.1 Core drilling for sampling of solidified radioactive wastes
2.2.2 Determination of toxic materials in radioactive wastes.

C. Progress of Work and obtained Results

State of advancement

2.1.1 γ-spectrometric determination of nuclides

The direct result of the γ-spectrometric measurement of a waste package is the count-rate in the peak region of the γ-spectrum. The aim of our investigation is to find the quantitative relationship with the (specific) activity of the waste matrix/package. This relationship must fit in for different activities, densities and shielding material.

2.1.2 Supercompaction

A subcontract with GNS (Gesellschaft für Nuklearservice, Essen) an owner of a supercompaction plant for radioactive wastes was concluded. Instrumentation of the plant was specified and installed. The compositions of the content of the drums provided for the test were specified.

2.2.1 Core drilling

The core drilling equipment was specified and ordered from Gölz-company. The core drilling rig was completed and instrumented. The core bits were specified and supplied. Besides the common used polycrystalline diamond as cutting and drilling material investigations of potential ceramic material have been started.

2.2.2 Measurement instrumentation

A GC/MS measurement system was installed and first tentative separations and qualitative detections of PCB isomers were performed. Additional equipment has been identified for ordering in 1989.

Progress and results

2.1.1 γ-spectrometric determination of nuclides

Calibration measurements were done for homogeneous drums with point sources and homogenous sources as well. In case of an inhomogeneous filling the internal structure shall be detected by (passive) scanning of the drum with a collimated gamma detector. A movable table was designed and prepared for preliminary scanning tests. A special scanner is constructed and fabricated which permits scanning in the vertical direction and manual movement in the horizontal direction. It is aimed to determine by this system the dimension of the activity filled volume and the non-active shielding material.

2.1.2 Supercompaction

In the supercompaction experiments 100 industrial scale drums (180 l) filled with scrap iron, scrap aluminium and copper, rubble, insulation materials, ash, paper and plastics, pure, mixed and mixed with low melting materials (Tm < 70°C) and burnable low melting materials (Tm < 300°C) will be compacted. The compositions of the content of the drums were specified. The contract with GNS (Gesellschaft für Nuklearservice, Essen) includes the instrumentation of the plant and the compaction of the drums. The instrumentation installed in the report period, includes a motion and a pressure pickup system which allow recording of the pressure versus the press plunger motion and the investigation of the spring-back effect.

2.2.1 Core drilling

As the programm includes qualification testing of the air cooled core bits, drums with different kinds of (simulated) solidified waste (partly containing plastics or scraps metal) and drums with inner canisters (lead, steel) or concrete shielding were prepared.
The core drilling rig was completed, the air clearing/cooling system for the core bit and the exhaust system for the boring dust were installed. The instrumentation, completed in the report period, includes a measurement and recording system for feeding power and velocity and for the current consumption of the drill drive. The core bits were specified and supplied. Investigations of potential ceramic materials capable of being used as drilling tools to replace polycrystalline diamonds have been started. Powder composites of silicon carbide, silicon nitride and boron carbide were prepared.

2.2.2 Set-up of measurement conditons

A GC/MS measurement system was installed on a SIEMENS SiCHROMAT 2 gas chromatograph and a FINNIGAN MAT INCOS 50 mass spectrometer. Operational tests performed to optimize the measurement conditions were set up for the separation and detection of some charateristic PCB isomers. First qualitative measurements were made. An optional chemical ionization equipment was selected for the INCOS 50 mass spectrometer and will be ordered in January 1989.

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 - August 1989
Period covered:	September 1988 - December 1988
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-Caderache, France; and SCK/CEN-Mol, Belgium).
3. To prepare test pieces and representative samples from the extracted cores in Task 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 September 1988 - December 1988, ie four months only). The main achievements are:

- Demonstration of remotely-operated vertical mode coring technique for destructive sampling of 3:1 Blast Furnace Slag: Ordinary Portland Cement (Task 1).
- Technical visit to Kfa, Germany and preliminary evaluation of air-cooled coring techniques (Task 2).
- Development of technique for hollow-drill sampling of BFS:OPC samples (Task 3).
- Development of techniques for dissolution of BFS:OPC samples using mineral acids and fusion techniques (Task 5).
- Confirmation of potential of X-ray fluoroscopy for NDT examination of drummed LLW (Task 6).

1. IDENTIFICATION AND DEVELOPMENT OF TECHNIQUES FOR EXTRACTION OF MATERIAL FROM WASTE PACKAGES BY CORING TECHNIQUES

About 70 experiments have so far been conducted 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 a remotely-operated water-cooled core-bit which can operate in a horizontal as well as a vertical mode. During coring operations a vacuum-mounted "sleeve" on top of the waste drum ensures that the cooling water is contained and the resultant water and sludge drawn off for analysis.

The experiments conducted to date have demonstrated the feasibility of coring and core-extraction in the vertical mode by remotely-controlled methods, and also that it is possible to contain the core-bit cooling water and thus minimise spread of aqueous contamination.

Appropriate equipment has been assembled to begin coring trials in a horizontal mode.

2. COMPARISON OF UK CORING PROGRAMME AND CONCLUSIONS FROM THOSE FROM SIMILAR CEC PROGRAMMES (Kfa, WEST GERMANY; CEA/CEN-CADERACHE, 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.

A preliminary evaluation of the German (Jülich) air-cooled coring experience has been made, but more results from the UK studies are necessary before a proper comparison can be made.

3. PREPARATION OF TEST PIECES AND REPRESENTATIVE SAMPLES FROM EXTRACTED CORES FOR CHEMICAL AND PHYSICAL ANALYSES

Tests have been conducted (using hollow drill-bits and a vacuum collection system) to extract powdered sub-samples from 100 mm diameter cementitious cores.

Preliminary results indicate that it is possible to extract such samples in a dust-free manner, and improvements are currently being made to the prototype drilling machine.

4. ASSESSMENT OF IMPORTANCE OF CHANGES TO SAMPLES ENGENDERED BY WATER-COOLED CORING OPERATIONS

Drums containing cements and trace levels of inactive species (Na, K, Cs, Sr, Fe and Co) have been made up and cores extracted using the coring rig described in Section 1.

Analyses (by atomic absorption, X-ray fluorescence and emission spectroscopy) of the cooling water and sludges, as well as samples of the extracted cores, are underway.

Leaching experiments on small BFS:OPC samples containing active and inactive simulant fission products are currently being set up.

5. DEVELOPMENT OF RAPID, NON-LABOUR INTENSIVE METHODS FOR DISSOLUTION OF POWDERED SAMPLES OF CEMENTED INTERMEDIATE LEVEL WASTE

Over 200 experiments have been conducted on the dissolution of BFS:OPC test samples containing either no additives or known concentrations of impurities.

Variations in acid type, acid strength, heating time and cement particle size have been investigated. Tables 1 and 2 show a representative selection of results from some of the early experiments. The rapid dissolution rates achieved by microwave heating were the main feature of these experiments.

Several fusion/dissolution techniques have also been investigated. Powdered cement samples were fused (at ca 1000°C) in a range of alkalis and dissolutions of the resultant mixtures undertaken. The most promising methods (ie those with percentage dissolutions greater than 98%) are being investigated further.

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, Tc-99, Ni-63, Fe-55) have been made up and left to cure for at least three months. Sub-samples 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

Video X-ray fluoroscopic analysis of uncompacted, in-drum compacted and high-force compacted 200 litre drums containing simulant LLW have been carried out in conjunction with Rolls Royce plc, Bristol and available as video recordings. The results confirm the applicability of the technique and provide information to allow a specification for a suitable instrument for QC of LLW to be drawn up.

Table 1: Representative results of preliminary dissolution experiments on 3:1 BFS:OPC cement blend

Acid Type	Concentration	Quantity (ml)	Type	Weight (g)	Quality of dissolution
HNO_3					
EC1	16M	10	powder	0.5	) Incomplete
EC2	8M	10	powder	0.5	) dissolution
EC3	4M	10	powder	0.5	) Silicic acid
					) gel forms
H_2SO_4					
EC4	18M	20	powder	1.0	) Precipitate of
EC5	9M	20	powder	0.5	) sulphates plus
EC6	3M	20	powder	0.25	) silicic acid gel
HBF_4					
EC7	conc	10	powder	0.5	Incomplete dissolution
*HNO_3/HBF_4					
EC8	conc	10	powder	0.5	) Incomplete
EC9	50%	10	powder	0.5	) dissolution
EC10	25%	10	powder	0.5	)
‡Aqua Regia					
EC11	conc	20	powder	1.0	)
EC12	conc	20	powder	0.5	) Silicic acid
EC13	50%	20	powder	1.0	) gel forms
EC14	50%	20	powder	0.5	)

[In each of the experiments EC7 - EC10 the reaction mixture was warmed from room temperature to boiling point over a period of 15 minutes: dissolution remained incomplete.]

* 70% HNO_3 and 49% HBF_4 in ratio 1:1

‡ Aqua Regia - HCl: HNO_3 in ratio 3:1

Table 2: Microwave dissolution experiments on 3:1 BFS: OPC cement blends

Acid - HCl
Powder size - < 0.01 mm
Hammered size - 2.0 mm - 5.00 mm
Microwave - 650 watts at 100% power

Sample			Acid		Microwave		Dissolution Quality
Number	Type	Weight (g)	Vol (ml)	M	Time (s)	Power (%)	
MEC1	powder	1.0	20	12	30	100	) Incomplete
MEC2	powder	1.0	20	12	30	100	) dissolution
MEC3	powder	0.5	20	6	60	100	) Silicic acid
MEC4	powder	0.5	20	6	60	100	) gel forms
MEC5	powder	1.0	10	12	60	100	) Complete
MEC6-8	powder	1.0	20	6	60	100	) dissolution;
							) gels after 48 hrs
MEC9-13	powder	0.5	20	6	60	100	Complete dissolution stable to gelling for minimum 72 hrs
MEC14	hammered	1.0	10	6	120	100	) Incomplete
MEC15	hammered	0.5	10	6	180	100	) dissolution
MEC16	hammered	0.2	5	6	60	100	)
MEC17	hammered	0.2	10	6	120	100	) Complete
MEC18	hammered	0.2	20	6	90	100	) dissolution
							) Stable to gelling
							) for minimum 72 hrs

TITLE: Development of a non destructive experimental method and a calculation procedure for the identification and quantification of gamma emitter radionuclides in packages containing low and medium level radioactive wastes.

Contractor: CIEMAT. Madrid, Spain.

Contract N°: FI1W-0226-E(EL).

Duration of contract: November 1988 - March 1990.

Period covered: November - December 1988.

Project leader: J.A. Suárez G. del Rey

A. OBJETIVES AND SCOPE

The purpose of this research is the development of an experimental method and calculation procedure for identification and quantification of gamma radionuclides in drums containing radioactive wastes of low and medium level.

The main of research will be the following:

1. Studies and tests to identify and quantify gamma radionuclides in drums containing:
   a) homogeneous matrices of cement with liquid radioactive wastes.
   b) heterogeneous solid radioactive wastes.
   c) ion exchangers in cement matrices.
2. Development of a methodology and computer codes for the determination of the geometrical distribution of gamma radionuclides in drums containing real radioactive wastes.

B. WORK PROGRAMME

B.1. Preliminary tests

B.2. Packages (drums) to be tested

B.3. Experimental tests

B.4. Development of calculation code

C. PROGRESS OF WORK AND OBTAINED RESULTS

The aim of this project is to develop a non destructive method and a calculation procedure for identification, geometrical distribution and quantification of gamma emitters radionuclides in packages (drums) containing low and medium radioactive wastes.

Previons assays showed very good results qualitative identification of radionuclides in drums containing liquid radioactive wastes incorporated in cement (homogeneous), solid radioactive wastes (heterogeneous) and radioactive sources.

Energies from 50 to 1400 KeV have been studied and only the identification of Am-241 gave bad results.

It is very important selection and preparation of a secondary standard to be used for efficiency determination of the system as previons stage to the quantification of radionuclides.

The standard radionuclide selected has been Eu-152.

The efficiency calibration determined in function of abundance of different energies of Eu-152 is different to the obtained with standard cocktail (QCY-44) used for gamma efficiency calibration.

To adjust Eu-152 efficiency calibration, a standard QCY-44 is necessary to modifie abundance values given on bibliographie and It's posible to use Eu-152 as secondary standard.

DEVELOPMENT OF ON-LINE AUTOMATIC SYSTEM FOR THE MEASUREMENT OF ALPHA EMEITTERS IN SOLUTION

Contractor : ENEA, C.R.E. Casaccia, Italy
Contract No. : FI1W-0228-I (A)
Duration of contract : September 1988 - December 1989
Project leaders : M. Aparo, S. Scaglione

A. OBJECTIVES AND SCOPE

The overall aim of the research programme will be to develop and characterizate an "on-line" alpha monitoring system for measuring actinide concentration in liquid streams.This kind of measurements is of great interest for the determination of nuclide inventories, such as Pu and Am, especially in the case of laboratory working actinides or process streams from radioactive waste treatement plants.
In this contest, the use of alpha monitoring technique has the advantage of high sensitivity, low detection limit (less than 10^{-5} Ci/l) and the possibility to discriminate alpha emitting isotopes of different elements.

These are the goals of the project:

- Study and development of a thin film to protect the window of the detector in order to place it in contact with corrosive liquids without altering its properties and without significant spectrum degradation.
- Improvment of sensitivity, precision and reliability of the measuring system.
- Reduction of the contamination effects on the detector window (memory effects).
- Development of a mathematical model able to evaluate the single contribution of different alpha emitting isotopes.
- Demonstration of the possibility to carry out a simultaneous measurement of alpha and beta emitters.

B. WORK PROGRAMME

2.1 Assessment of the chemical/phisical parameters characterizing the film, namely impermeability, resistance to corrosive liquids and to alpha radiation.
2.2 Realization of film deposition on different detectors
2.3 Investigation on the alpha energy degradation effects due to the film.
2.4 Realization of a measuring head for alpha monitoring and its off-line characterization.
2.5 Development of an on-line circuit including the automatic system for measurement control and data elaboration.
2.6 Dynamic characterization of the measurement system for performances evaluation.
2.7 Development of a mathematical model able to determine the partial concentration of each alpha emitter (spectrum deconvolution).
2.8 Feasibility study and experimental tests of a system for the simultaneous and independent measurements of both alpha and beta activity in solution.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Measurement of alpha emitters in solution has required the study and development of a method for detector coating. Such a coating can allow the measurements to be carried out by placing the detector in contact with the assayed liquid.
Thin film deposition of hydrogenate amorfous carbon and Silicon dioxide were carried out on glass substrates coated with Aluminum films. Such targets, simulating the detector window were then placed in contact with nitric acid solution to reveal impermeability and resistence of the deposited thin films.
Due to some troubles encountered, namely breakdown of deposition system and failure of the targets, this activity is still in progress. As a consequence, the other tasks, which are mainly dependent on activity 2.1, have been delayed.
In preparation for detector coating, in order to investigate on the alpha energy degradation effects due to the film, a serie of measurements were carried out with alpha sealed source on the detectors to be used for deposition.
In the meantime, a preliminary mathematical model for determining the single contribution alpha emitting isotopes was developed. Such a model was positively tested with some spectra simulating a mixed source.

Progress and results

2.1 A dual ion beam sputtering system has been used to deposit hydrogenated amorfphous carbon (a-C:H) and silicon dioxide thin films.
Such system is composed by two Kaufman Ion Sources.
The beam of the first ion gun, feeded with Ar gas, impinges on the pyrolitic graphite target for a-C:H films or pure quartz target for SiO_2 thin films. The beam of the secon ion gun, feeded by a mixing of Ar and H_2 gases for a-C:H films and only Ar for SiO_2 films,impinges directly on the growing films.
To obtain a good adhesion of the film on the substrate the deposition parameters (ion beam energy, ion beam current and deposition rate) have been optimized.
Typical values of the deposition parameters are reported in Table I.
Hydrogenated amorphous carbon and silicon dioxide films have been deposited on glass substratus coated with an aluminum film. Such aluminum films have been produced by thermal evaporation.
The thickness of aluminum films has been varied in the range between 500 to 2000 A°.
Such multi-layer system (glass substrate, aluminum film and a-C:H or SiO_2) were then placed in contact with a nitric acid solution (7M).

Detachment from the substrate of the a-C:H and SiO_2 thin films can be caused by intrinsic stress.
To evaluate the critical thickness (thickness where detachment phenomena do not appear) of the aluminum, a-C:H and SiO_2 films further studies are in progress.

2.3 A preliminary tests in order to investigate the alpha spectrum degradation effects have been carried out.
A mylar foil (6 micron thickness) was coated with a-C:H and SiO_2 films with variable thickness.
Using alpha sealed source (^{241}Am and ^{241}Am/^{244}Cm/^{239}Pu-mixed), both reference myler foil and coated foils were measured.
Alpha spectra obtained with coated myler foil show an acceptable alpha energy degradation with respact to the reference myler foil.

2.8 The first step in developing a mathematical model for alpha peak deconvolution was the study of a procedure for single alpha pek fitting. Each alpha spectrum can be subdivided in two regions, below and above of the peak maximum. The peak analysis has been carried out by using an exponential polynomial fit of the second and the third order respectively, according to the following formula:

$$Y = \exp(\Sigma\, a_{i-1} (X-x^*)^{i-1})$$

where a X axis translation has been performed in order to impone passing through the peak maximum.
Figure 1 shows a measured alpha spectrum and the curve obtained by weighted least squares fitting.
Multiplet deconvolution is then performed by an iterative procedure which subtracts the nearest peak contribution from the peak under evaluation. Figure 2 shows the results of deconvolution on a double alpha peak.
It must be pointed out that this study was just a preliminary approach for solving the problem and that the spectra to be analysed were obtained by summing two different alpha spectrum. Further activity will be devoted to optimize the procedure and to test it on spectra coming from solution of different alpha emitters.

Table I : Optimized values of the deposition parameters

material	Eb(eV)	Ib(mA)	R(A°/sec)	Pback(mbar)	Pwork(mbar)
a-C:H	800	5	0.3	4×10^{-7}	2×10^{-4}
SiO_2	800	4	0.5	4×10^{-7}	3×10^{-4}

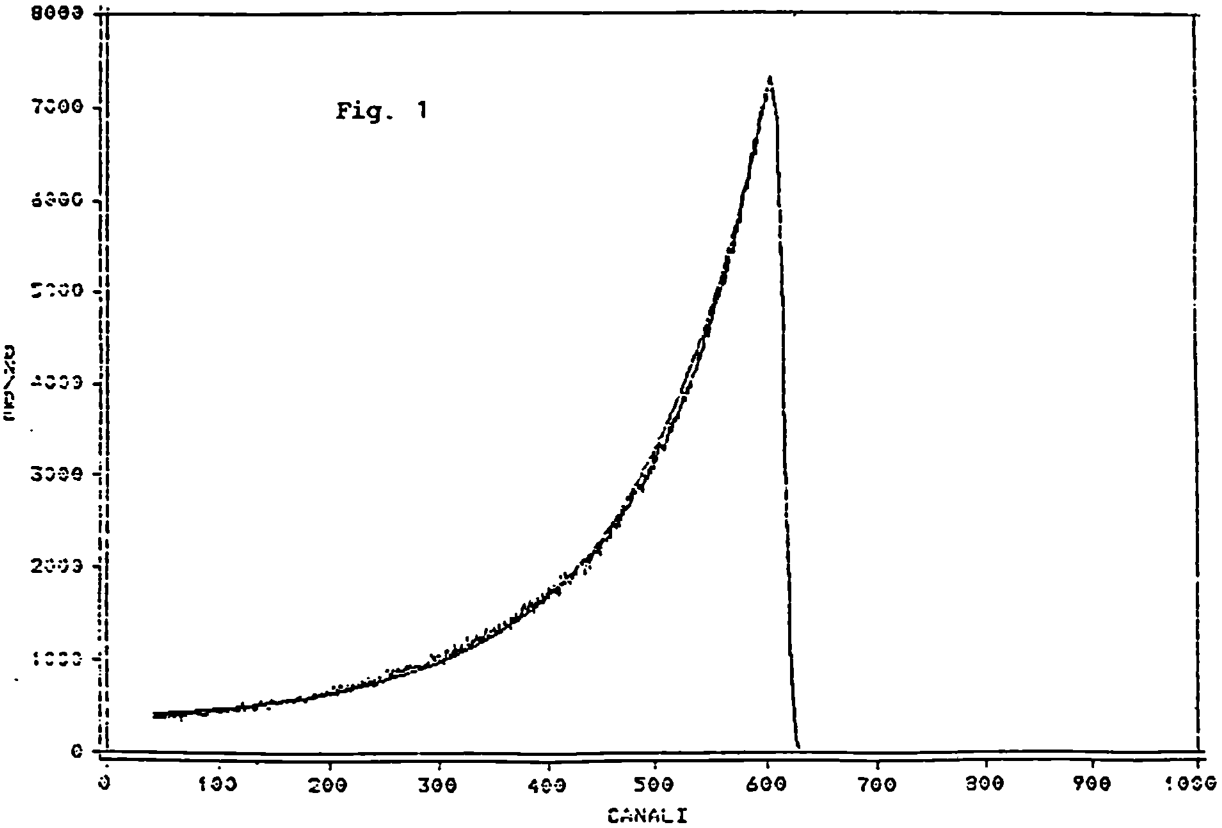


Fig. 1

8000
7000
6000
5000
4000
3000
2000
1000
0
0
100
200
300
400
500
600
700
800
900
1000
CANALI

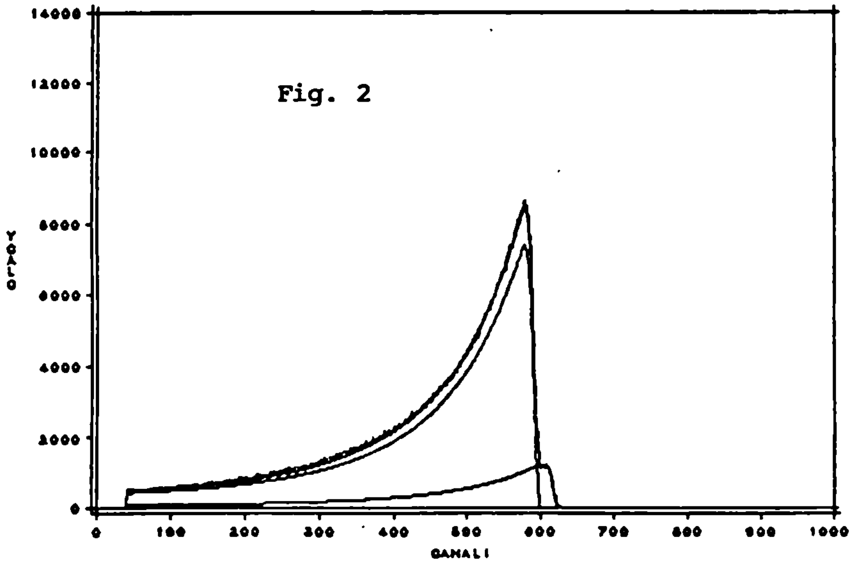


Fig. 2

14000
12000
10000
8000
6000
4000
2000
0
YCALC
0
100
200
300
400
500
600
700
800
900
1000
CANALI

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:	November 1988 - December 1988
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

2.1, 2.2, 2.3 (Sample Preparation and Corrosion Rate Measurements). Test samples have been cast of magnox in cement with different levels of voidage and cement blanks. Acoustic emission monitoring is underway. No results are available to date.

2.4. Electronic equipment has been designed and is being constructed that will allow the monitoring of a number of samples/canisters simultaneously.

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 : September 1988 - December 1988
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 for the main waste streams.

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 OBTAINED RESULTS.

A selection of representative analysis samples has been made. Practical difficulties connected to the collection of the samples in the power plants and to their transport to the analysis laboratories are being resolved. A great part of the samples has been collected and the first analyses of non-conditioned waste are in progress.

2.1. Investigation of non-conditioned waste.

2.1.1. Collection of a selection of representative non-conditioned waste samples.

Samples of primary water from the seven PWR units operated in Belgium were collected (4 units in Doel, 3 in Tihange). Samples from several batches of evaporator concentrates were also taken, both in Doel and in Tihange. The collection of representative samples of ion exchange resins in Tihange has revealed some difficulties, and it has been judged opportune to acquire a special sampling device. The implementation of this equipment will cause a delay of a few months in the collection and the analyses of the resins samples. It must be pointed out that, both in Doel and in Tihange, the samples of evaporator concentrates and resins are taken from large storage vessels which are common to the different units ; it is therefore not possible to take samples wich are specific to one unit.

Five filter cartridges have been selected in Doel. These filters are supposed to be representative for the most active filters produced at Doel.

2.1.2. The preparation and the radiochemical analysis of the first samples of primary water and evaporator concentrates are in progress. No definitive results have been made available so far.

2.2. Investigation of conditioned waste.

2.2.1. Preparation of ten representative full-scale cemented waste packages.

These ten packages are subdivided as follows : evaporator concentrates (4), resins (4), filters (2).

Two packages of evaporator concentrates have been prepared from two batches analysed in the first part of the programme.

The other packages are expected to be prepared in the coming months.

2.2.2. and 2.2.3. Non-destructive and destructive examination of the waste packages.

Contacts with a view to implementing the necessary equipment are in progress.

QUALITY ASSURANCE - PROCEDURES - STANDARDIZATION

Contractor : CEA CEN CADARACHE - FRANCE
Contract N° : FI1W/0095 Task 5/5
Duration of contract : From August 86 to December 89
Period covered : January 88 - December 88
Project leader : A. SAAS
Executant of task 5 : M. A. SAAS - CEN CADARACHE

A) OBJECTIVE AND SCOPE

The three first items earlier exposed are the whole characterization programme lead by the CEA laboratories.

To valid the result obtained, we must do data comparaison in according to general schedule. The 1988 objective programme has been to present typical cases.

With this programme, we close studies connected with assurance quality of homogeneous waste's measures.

B) WORK PROGRAMME

B.1. Validation of non destructible measures
B.1.1. Full scale package measure
B.1.2. Core measure
B.1.3. Normalized sample measure
B.2. Validation of destructive and non destructive measure of embedded wastes
B.2.1. Non destructive measures on full scale package
B.2.2. Non destructive measures on core
B.2.3. Non destructive measures on sample
B.3. Validation of destructive and non destructive measure of raw wastes
B.3.1. Non destructive measure on a portion
B.3.2. Non destructive measure on a portion's sample
B.3.3. Non destructive measure on an embedded sample
B.3.4. Destructive measure on sample

C) PROGRESS OF WORK AND OBTAINED RESULTS

The three validations foreseen B1, B2, B3 have been treated during the first half year.

We have use the case of evaporator concentrate embedded in hydraulic binder for B1. The results have shown a data's correct correlation. Wherely, it has been possible to agree a package's homogeneity by gamma scanning. The accuracy is about ten percent.

The B2 programme has been also treated from data issued of evaporator concentrate embedded in cement.

A satisfactory correlation is shown between destructive and non destructive data. Destructive measures from a 10 g sample give representative values.

From this procedure, it is possible to valid 241Am and 90Sr results in spite of the data can be obtained only by destructive analysis.

We have used the case of ionic exchangers from reactor's waste for the programme B3.

The results obtained by a non destructive test show the necessity to use a 10 g sample. Only, the comparison of destructive and non destructive data allows to valid the results of beta emitters long lived.

European Communities — Commission

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Shared cost action
Annual progress report 1988 – Volume 1

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This report describes the work to be carried out under research contracts already concluded before the end of 1988, as well as the work performed and the results obtained so far.

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