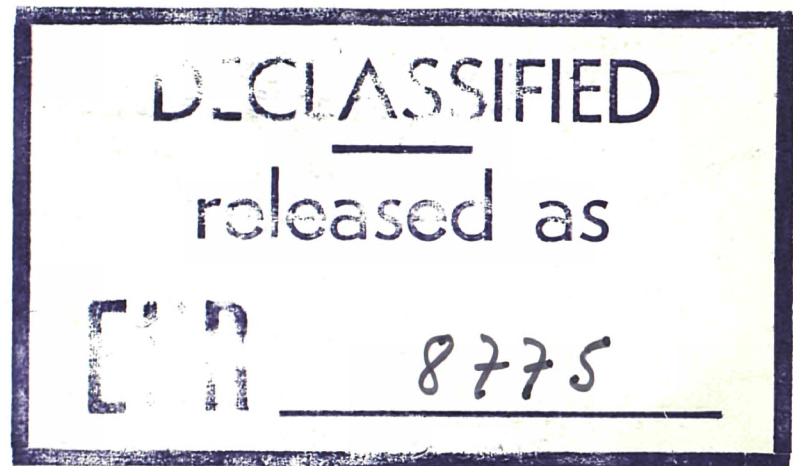




COMMISSION OF THE EUROPEAN COMMUNITIES  
JOINT RESEARCH CENTRE  
Ispra Establishment  
Italy

**PROGRAMME  
PROGRESS  
REPORT**

July - December 1981



**COMMUNICATION**

Category **1.3**

Nr **3925**

# Safety of nuclear materials

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## **July-December 1981**

Programme Progress Report - JRC Ispra  
July-December 1981

### **SAFETY OF NUCLEAR MATERIALS**

#### **Abstract**

This document is the progress report of the JRC programme Safety of Nuclear Materials for the period July-December 1981.

On the basis of the Council decision on the JRC plan 1980-1983, the activity on radioactive waste management which is carried out in the framework of the programme Safety of Nuclear Materials, has been organized into 4 projects:

- Risk Evaluation
- Protective Barriers
- Actinide Separation
- Actinide Monitoring

The main results obtained during the reporting period are the following:

#### **Project 1. Risk Evaluation**

The risk analysis methodology for geological disposal of radioactive waste, developed by the JRC, is being applied to the Boom clay formation in Belgium.

Consequences of various release scenarios are under evaluation; the analysis of the uncertainty in the results is carried out by means of a Monte Carlo method.

In the framework of the assessment studies on alpha-waste management an integral waste management strategy, based on the utilization of the OXAL process, has been developed.

#### **Project 2. Protective Barriers**

In the field of radiation damage in borosilicate glasses, work has been continued to provide information on the basic mechanisms of damage.

Leaching and corrosion tests have been carried out on borosilicate glasses and materials for waste containers.

In the field of interaction of radionuclides with the environment, results have been obtained on the chemical forms of radionuclides leached from borosilicate glasses and on their behaviour in the migration in geological media.

#### **Project 3. Actinide Separation**

Experimental work has been carried out on the separation of plutonium from medium level waste (MLW) streams of reprocessing plants. In particular the OXAL process has been successfully tested on a simulated MLW concentrate.

#### **Project 4. Actinide Monitoring**

Progresses have been made in the setting-up of a reference monitor for passive neutron assay.

The JRC methodology for non-destructive assay of plutonium is being applied to waste monitoring systems installed at DNPDE, Dounreay.







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# **Safety of nuclear materials**

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# INTRODUCTION

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The safe and economic management of the radioactive waste, produced in the exploitation of nuclear energy at an industrial level, requires a considerable effort of R and D.

The Joint Research Centre started work in the field of radioactive waste management in 1973. Two multiannual plans 1973-1976 and 1977-1979 have been completed.

In the framework of the 1980-1983 plan of the JRC the activity on radioactive waste management is carried out in the programme Safety of Nuclear Materials.

This programme is part of the activity of the JRC in the field of Nuclear Safety and the Fuel Cycle which includes also the programmes Reactor Safety, Plutonium Fuels and Actinide Research, and Fissile Materials Control and Management.

The staff allocated to the programme Safety of Nuclear Materials consists of 52 research-men corresponding to about 5% of the total JRC research staff.

The programme is carried out at the Ispra Establishment with a participation of the Karlsruhe Establishment.

The Commission of the European Communities started in 1975 an indirect action programme on Radioactive Waste Management. In this programme, which is conducted by means of contracts with national laboratories, various aspects of waste conditioning technologies are studied and a large coordinated action for the study of waste disposal in various types of geological formations is established.

The first plan 1975-1979 of the indirect action programme has been completed. The second plan 1980-1984 is in progress.

Strict relations are maintained between the two programmes.

In addition to the research programmes, the Council approved in February 1980 the Community Plan of Action in the field of Radioactive Waste (1980-1992). This plan entrusts the Commission with a wider role in the implementation of the waste management practices.

In the management of the research programmes and of the Community Plan of Action a very important contribution is given by the Advisory Committee for Programme Management (ACPM).

The programme Safety of Nuclear Materials of the JRC has been organized into 4 projects:

## **Risk Evaluation**

The project includes:

- Risk analysis of geological disposal of radioactive waste including sea bed disposal.
- Assessment studies on alpha-waste management.

## **Protective Barriers**

The project includes:

- Studies on the long-term stability of conditioned waste.
- Studies on the interaction of radionuclides with the environment.

## **Actinide Separation**

The project is mainly directed to develop chemical methods for the reduction of the plutonium content in various waste streams.

## **Actinide Monitoring**

The project is directed to the development of methodology and instrumentation for the measurement of the plutonium content in various waste streams, by means of non-destructive assay techniques.



# EXECUTIVE SUMMARY

M. BRESESTI - Programme Manager-Projects Directorate - JRC Ispra

## Introduction

Following the Council decision, the programme Safety of Nuclear Materials has been organized into 4 projects:

- Project 1. Risk Evaluation
- Project 2. Protective Barriers
- Project 3. Actinide Separation
- Project 4. Actinide Monitoring

The J.R.C. programme is essentially dealing with long-term safety aspects of radioactive waste management, the two main objectives being:

- the assessment of the long-term safety of geological disposal
- the optimization of the alpha-waste management taking into account mainly cost and long-term safety.

The multidisciplinary group of about 50 people working at the JRC - Ispra constitutes the most important single group of the Community working in the area of long-term safety of radioactive waste management.

The relations between the various projects are indicated in Fig. 1.

Project 1 groups the theoretical activities of the programme which are related to the various experimental activities.

The activity of development and testing of models for safety assessment of geological disposal (Project 1) is strictly connected with the experimental activities (Project 2) concerning the barriers constituted by long-term stability of conditioned waste and retention of radionuclides in the environment.

The activity of assessment on alpha-waste management (Project 1) is strictly connected with the laboratory work on the plutonium separation from various waste streams (Project 3); at present the connections are less strict with the activity on actinide monitoring (Project 4).

The development of the programme will be presented on the basis of the subdivision by projects, indicating the various interrelations.

## Project 1. Risk Evaluation

### *Risk analysis of geological disposal of radioactive waste*

The activity on safety assessment of geological disposal is at present mainly directed to the application of the methodology developed at the J.R.C., on the potential disposal site constituted by the Boom clay formation in Belgium.

The activity is carried out in the framework of a collaboration with CEN/SCK, Mol.

The JRC approach includes a probability assessment of the possible failure of the geological containment and an analysis of the consequences for different release scenarios.

The work in progress on the Boom clay formation constitutes the first exercise in the Community of complete assessment (release probabilities and release consequences) for a specific site.

The probability assessment using Fault Tree Analysis, was completed during 1980. A summary of the work was published as Topical Report in the previous Programme Progress Report. The complete work has been recently published in the Journal Radioactive Waste Management (see Section J.R.C. Publications).

The assessment has indicated the probabilities of various scenarios of failure of geological containment.

For the most important scenarios, a consequence analysis has been undertaken to assess doses to man, in particular dose rates to the maximum exposed individual; multiplication of doses by the corresponding event probabilities permits to quantify the risk.

In agreement with the planning (see APPENDIX 1 - Table I) the consequence analysis for the scenario involving a permeable fracture across the repository, has been completed; a Monte Carlo method has been utilized to generate the probability distribution of the consequences, given the distribution of the input parameters: this method has been applied to take into account the input parameter uncertainties for the consequence analysis related to the permeable fracture; a draft version of the work has been prepared. The entire methodology is described in a paper which has been submitted for publication.

During the reporting period consequence analysis has also been started on a glacial erosion scenario.

For the first semester of 1982 it is planned (see APPENDIX 2 - Table I) in particular to prepare a draft version of the glacial erosion scenario analysis and a final version of the consequence analysis for the permeable fracture scenario including uncertainty evaluation.

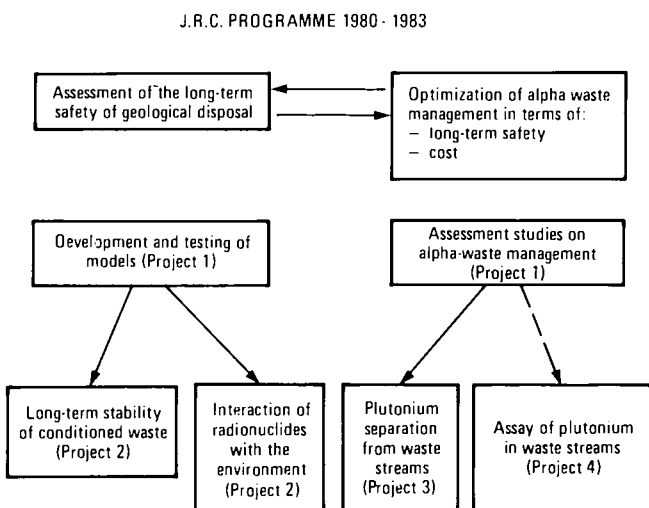


Fig. 1. J.R.C. Programme 1980-1983: Safety of Nuclear Materials

In the area of seabed disposal it is worth mentioning that the Commission is now an official member of the NEA Seabed Working Group. This involves the participation of staff members of JRC and of the indirect action programmes in various task groups. The JRC staff contributes particularly to the activity of the System Analysis task group and to the coordination between Systems Analysis and Engineering Studies task groups.

In agreement with the planning a base-case model for risk analysis has been developed on the basis of which the importance of the retention phenomena in the sediments, in controlling radionuclide migration, has been confirmed.

In view of a possible enlargement of the activity on seabed disposal, in the framework of the next multiannual JRC plan, programme proposals are under evaluation in various research areas; in particular the role and the characteristics of high pressure facilities are being evaluated through a study contract.

In September 1981 the coordinated study on the Geological Disposal Risk (GDR) to be carried out in the framework of the Community Plan of Action has received a favourable advice of the Advisory Committee for Programme Management.

Objective of this study is to obtain in about 6 years a harmonized evaluation of the main waste disposal options presently under study in the Community (salt, granite, clay, sub-seabed).

The activity of the JRC will particularly deal with the clay and sub-seabed disposal options.

Coordination of the study will be assured jointly by JRC and indirect action programmes.

In view of the importance of this initiative an increase of staff is planned in the group working on risk analysis of geological disposal.

### *Assessment studies on alpha-waste management*

The activity in this area started in the second semester of 1980 following the reduction of the activity on chemical separation and nuclear transmutation of actinides. Aim of the study is the optimization of the waste management procedures on the basis of various parameters and in particular of cost and long-term safety.

As first step of the study a Baseline Waste Management Strategy (BWMS) has to be defined. The introduction of alternative options in this reference strategy will be evaluated in terms of cost/benefit.

During the reporting period the BWMS has been completed with the definition of a Reference Waste Treatment Facility.

In agreement with the planning, taking into consideration the results obtained at laboratory level, an integral waste management strategy, based on the utilization of the OXAL process, has been developed. This strategy considers both HLW and different categories of MLW.

Various incentives for this strategy have been qualitatively evaluated. It is the intention of the JRC to present this proposal at Community level in view of a possible integrated effort in this area.

During the first semester of 1982 it is planned to evaluate in more details feasibility at plan level and incentives in terms of cost/benefit, of the application of the OXAL process to the liquid MLW streams from reprocessing plants, taking the BWMS as reference.

The planning of Project 1. Risk Evaluation, for the first semester 1982, is reported in APPENDIX 2 - Table I.

## **Project 2. Protective Barriers**

### *Long-term stability of conditioned waste*

The JRC activity in this area includes radiation damage studies on borosilicate glasses, leaching and corrosion experiments and an exploratory investigation on a special matrix for conditioning of actinides + rare earths.

In the field of radiation damage the study at the HV electron microscope of the growth of bubbles under electron irradiation in borosilicate glasses made possible to evaluate the swelling parameters and to associate it to the displacement process of single defects. In any case it has been confirmed that this effect starts at dose rates much higher than those expected during storage of HLW.

Other information on the basic aspects of radiation damage is being obtained by means of irradiation experiments on silica.

Following results obtained in a French laboratory which indicated a strong increase of leaching rates in damaged borosilicate glasses, a critical review of radiation effects on borosilicate glasses has been carried out at the JRC.

This review is presented as a Topical Report in Section 2: Protective Barriers.

The conclusions of this review are quite reassuring; in fact it is stated "The existing values for the examined properties seem to indicate that the effects of radiation will not greatly influence the stability of the glass at the doses and dose rates expected. An extension of the experiments to higher doses could increase the confidence in the results obtained".

Concerning relations between radiation damage and leaching rate, experiments carried out at the JRC during the past years indicated negligible effects on the leaching rate due to radiation damage. This point has to be checked again by performing leaching tests on borosilicate glasses irradiated in the HFR reactor, Petten (fission fragment simulation) at a dose equivalent to a vitrified waste irradiation of 1 million years.

The start of the leaching tests has been delayed to 1982 due to difficulties in handling the irradiated capsules (see APPENDIX 1 - Table II and APPENDIX 2 - Table II).

The JRC planning in the area of radiation damage envisages to conclude the activity on bulk properties for the end of 1982.

In the area of the leaching tests on borosilicate glasses the major effort is being spent to study the leaching in normal repository conditions i.e. with the glass in contact with limited amount of water and the backfilling materials.

The results of laboratory experiments conducted for 60 weeks on glasses in contact with a paste of montmorillonite and sand indicate that the leaching rates in these conditions are similar to those measured in a large amount of flowing water.

A possible explanation of these results is that the various elements leached from the glass are trapped by the montmorillonite which acts as an ion exchanger.

In these conditions the composition of the water in contact with the glass is not modified by the element release so that the leaching rate is similar to that obtained in flowing water. Only when the ion exchange capacity of the montmorillonite is saturated, the water composition is modified by the element release with a consequent effect on the leaching rate.

Thus the leaching rate is controlled by the absorption capacity of the clay and by diffusion. From the results obtained it appears that it is not possible to separate the leaching of the glass from the study of the backfilling or more in general

of absorbent systems like clay, in which the transport is controlled by diffusion.

For this reason we are setting-up experiments in which the glass leaching and the diffusion in clay are studied simultaneously.

For the same reason we are envisaging a deeper integration between the experiments of leaching and the studies of radionuclide migration.

The JRC intends also to contribute to a better knowledge of the basic mechanisms of leaching which is required to make possible correct evaluations of the long-term stability of borosilicate glasses for various repository conditions.

In this connection an experimental facility is being set-up at the JRC Ispra for the measurement of the relevant surface quantities which determine the mechanisms of leaching.

The activity on surface analysis will be carried out employing the staff made available by a reduction of activity in the field of radiation damage.

In the area of corrosion of waste containers exploratory investigations are in progress concerning corrosion of punctured containers and diffusion controlled corrosion in mild steels.

Finally concerning a special matrix for the conditioning of actinides + rare earths an exploratory investigation has been carried out on the use of monazite type ceramics.

It has been realized that the main problem to be resolved is of technological nature. In fact the real problem is not the preparation of a material with a low leaching rate but the preparation of blocks of considerable size having a low specific surface. Thus it would be necessary to perform technological tests which are outside the present possibilities of the J.R.C. programme.

As a consequence it was decided to stop the actual tests and to follow the developments in progress in various laboratories on synthetic materials.

Comparisons between planned activities and achievements for the second semester of 1981 and the planning for the first semester of 1982 are reported in APPENDIX 1 - Table II and APPENDIX 2 - Table II respectively.

### *Interaction of radionuclides with the environment*

The JRC activity in this area is mainly directed to investigate the migration behaviour of the radionuclides following the leaching of vitrified waste in a repository.

Thus the leachate of the borosilicate glasses, containing the radionuclides to be studied, is used in the laboratory experiments.

The tests carried out in the past years have indicated that the presence in the leachate of colloidal forms, which can be subjected to filtration by the soil layers, has an important role in governing the radionuclide migration in the short term; the tests have also indicated that the formation of carbonate complexes of actinides, which are not retained by geological media, can favour their migration and consequently increase their potential risk.

Thus the JRC experiments are mainly directed to study formation and behaviour of colloidal forms and carbonate complexes.

Initially the work concerned actinides; now an investigation is in progress also on the behaviour of technetium.

The other important line of activity concerns the relations between chemical forms and bioavailability, this aspect being investigated in the framework of collaborations with laboratories working in the indirect action programme Radiation Protection.

The activity on colloidal forms includes:

- laboratory experiments on the retention and subsequent release of radionuclides in columns of various media
- characterization of the colloids
- development of a model for deep bed filtration.

The whole activity is directed to provide an overall description of the colloid behaviour in geological media.

During the reporting period the laboratory experiments mainly concerned the elution of Am from a glauconitic sand column. The experiments were carried out in such a way to simulate the conditions existing in the porous media overlying the Boom clay formation.

Various aspects of the colloid retention and successive dissolution are presented in Section 2: Protective Barriers in the Topical Report "Underground migration of long-lived radionuclides from a borosilicate glass matrix".

Concerning characterization of colloids a photon correlation particle analyzer has been set-up and measurements have been started on leachates of borosilicate glasses.

The deep filtration model which takes into account the various retention mechanisms is under development by the Ecole des Mines de Paris (Armines) in the framework of a study contract.

In the area of carbonate complexes the work concerning compositions and stability constants of Am complexes has been completed. On the basis of the results obtained it is possible to evaluate the relative importance of the various soluble species of Am in groundwater.

It was planned to start in the second semester of 1981 a similar work on Np complexes: due to some competition in the staff utilization with the activity on technetium behaviour, the work on neptunium will be started only in the first semester of 1982.

Concerning the technetium behaviour the results obtained in the first semester 1981 have indicated a tendency to migrate more important than for other long-lived radionuclides.

However due to a poor reproducibility of the results it was realized that, in order to obtain significative data, it is necessary to operate out of contact with atmospheric oxygen. Thus during the reporting period a special experimental arrangement has been set-up.

Finally the studies on the biogeochemical behaviour of plutonium and americium and the relations between chemical speciation and bioavailability have been continued.

The significant achievements compared to planning for the second semester of 1981 and the planned activities for the next period are reported in APPENDIX 1 - Table II and APPENDIX 2 - Table II, respectively.

The reported planning refers to the utilization of the staff presently allocated to the project.

It is worth mentioning that the possibility to increase the effort in the area of protective barriers and in particular of radionuclide migration is being considered. A reinforcement of this activity can be obtained by means of a parallel reduction of effort in the area of the plutonium separation from waste streams.

We are pushed in this direction by various considerations:

- Interest to apply our methodology to situations relevant to other geological formations in addition to clay, following requests of collaboration by national organizations.
- Interest to increase the contribution to the project Geological Disposal Risk (GDR) to be developed in the framework of the Community Plan of Action.
- Advise in this direction by members of the Advisory Committee for Programme Management (ACPM).

As already reported above, an increase of staff should make possible in particular to set-up experiments in which various aspects of corrosion, leaching and migration are studied as a whole simulating at laboratory level conditions of geological repositories.

### Project 3. Actinide Separation

The JRC has carried out in the past years an important activity on the study of the actinide separation from high level waste (HLW) in view of their transmutation in nuclear reactors or of a special conditioning and disposal. The flow-sheets developed by the JRC for the actinide separation from HLW are being tested on a larger scale, by continuous countercurrent experiments, at Fontenay-aux-Roses in the framework of a collaboration contract between JRC and CEA.

The typing of the final version of the summary report of the JRC programme on chemical separation of actinides, has been started. It is planned to have the report printed during the first semester of 1982.

Starting in the second half of 1980 the laboratory activity has been progressively transferred from the study on actinide separation from HLW to the study on the plutonium separation from medium level waste (MLW) in view of separated conditioning or recycling.

During 1981 the application of the OXAL process, previously developed for HLW, to MLW concentrates from reprocessing plants, has been extensively investigated.

The work has been carried out on simulated solutions; their compositions had been defined in the framework of the Assessment Studies on Alpha-Waste Management. The laboratory experiments have indicated that the oxalate precipitation, adding Ce carrier, makes possible to recover more than 99% of plutonium; the contamination of the precipitate by other materials is limited. The process is compatible with current precipitation methods which can successively be applied to separate other radionuclides.

During the reporting period the experimental work on the plutonium recovery from exhausted TBP, by means of oxalic acid washing, has also been completed. Plutonium can be recovered with a very high yield; if the oxalic washing is applied the successive washing of TBP with  $\text{Na}_2\text{CO}_3$  solution, required for the removal of dibutylphosphate (HDBP), would produce an alpha-free solution. It has to be reminded that the  $\text{Na}_2\text{CO}_3$  solution is one of the important waste streams of the reprocessing plants.

Experimental work has also been carried out concerning treatment of dissolution residues with formic acid in view of a possible plutonium recovery. It may be expected that formic acid in presence of noble metals dissolves plutonium by its reduction to the more soluble trivalent state. The laboratory tests have given negative results.

The various tests on the utilization of the OXAL process are the basis for the integral waste management strategy which has been developed in the framework of the Assessment Studies on Alpha-Waste Management.

During the next months it is planned to complete the work concerning application of OXAL to MLW concentrates of reprocessing plants.

As already reported a reduction of effort in this area is being considered in order to make possible a reinforcement of the activity dealing with protective barriers.

It is planned to take a decision on this matter during the next months also in connection with the orientations which will be given by the General Director in view of the preparation of the programme proposals for the new JRC plan to be started in 1984.

At the same time a decision will also be taken concerning possible utilization of the ADECO cells.

The significant achievements compared to planning for the second semester of 1981 and the planned activities for the first semester of 1982 are reported in APPENDIX 1 - Table III and APPENDIX 2 - Table III respectively.

### Project 4. Actinide Monitoring

The JRC activity on actinide monitoring is carried out following two main lines:

- development of methodology and instrumentation for the non-destructive assay of plutonium content in waste streams.
- application of the JRC methodology and instrumentation in nuclear plants of the Community.

Concerning the first line of activity the JRC is spending a particular effort in the area of passive neutron assay.

During the reporting period a  $4\pi$  geometry detection head has been completed and assembled. Progresses have been made in the development of the software required for the connected computerized system. The detection head and the computerized system constitute the passive neutron reference monitor which makes use of an upgraded time correlation analysis.

It is planned to perform an assessment of the various methods applied for passive neutron assay, using the computerized system and a Monte Carlo simulation. This assessment should provide indications of possibilities and limits of the various methods.

Concerning application of the JRC methodology in nuclear plants, the major effort is directed to the evaluation of various NDA systems applied at DNPDE Dounreay for the monitoring of plutonium contaminated solid waste streams.

During the reporting period the first draft of Part 1 of the final report on Interpretational Models and Calibration Methods, has been prepared.

The JRC methodology will find application also in the framework of the Interlaboratory Comparison organized by the indirect action programme.

The significant achievements compared to planning for the second semester of 1981 and the planned activities for the first semester of 1982 are reported in APPENDIX 1 - Table IV and APPENDIX 2 - Table IV respectively.

**APPENDIX 1 - SIGNIFICANT ACHIEVEMENTS COMPARED TO PLANNING**

*Table 1. Project 1: Risk evaluation*

Activities		7	8	9	10	11	12	1982
		second semester 1981 (month)						
Risk analysis of geological disposal	1				X			
	2	A	a			Y	b	B
Assessment studies on sea bed disposal	3				C	c		
Assessment studies on alpha-waste management	4				D	d		
Assessment studies on nuclear transmutation of actinides	5						e	E

○ PLANNING

△ ACHIEVEMENTS

- 1 Promotion and coordination of risk analysis activities in the Community in collaboration with DG XII
- 2 Application of the JRC methodology on the Boom clay formation
  - a) Final version of the consequence analysis ready
  - b) Draft version of the uncertainty analysis ready
- 3 Assessment studies on seabed disposal
  - c) Draft of risk analysis model ready
- 4 Assessment studies on alpha-waste management
  - d) First evaluation of the alternative management scheme based on oxalate precipitation
- 5 Assessment studies on nuclear transmutation of actinides
  - e) Summary report ready

- X) Start of the coordinated study on the Geological Disposal Risk (GDR) in the framework of the Community Plan of Action
- A) Revised version of consequence analysis ready
- B) Draft version of the consequence analysis including uncertainty analysis ready
- Y) Draft version of a paper illustrating the JRC probabilistic approach for the long-term risk, prepared
- C) Base-case model developed
- D) Integral waste management strategy based on OXAL, developed
- E) Draft of the summary report ready

# APPENDIX 1 - SIGNIFICANT ACHIEVEMENTS COMPARED TO PLANNING

Table II. Project 2: Protective Barriers

Activities	second semester 1981 (month)						1982
	7	8	9	10	11	12	
Long-term stability of conditioned waste	1	(a) △A			(b)		(c)
	2						(d)
	3		(e) △E	(g) △G	(h) △H		(f)
	4		(i) △I				
	5					(j) △J	
Interaction of radionuclides with environment	6				(k) △K		
	7	(l) △L					
	8	(m) △M				(n)	
	9						(o)
	10						

○ PLANNING

△ ACHIEVEMENTS

- 1 Radiation damage in vitrified waste
  - a) Transport to Ispra of the BONI III capsules
  - b) Start of long term leaching tests on BONI III samples
  - c) End of the leaching tests
- 2 Methodology for glass surface analysis
  - d) Installation of the ESCA instrument
- 3 Leaching tests on vitrified waste
  - e) Start of leaching tests on Tc spiked glasses
  - f) End of leaching tests on Tc spiked glasses
  - g) End of the leaching tests in montmorillonite paste
  - h) Start of the tests of leaching and diffusion in montmorillonite paste
- 4 Corrosion tests
  - i) End of corrosion tests on punctured containers
- 5 Study of special matrices
  - j) Conclusions on the use of monazite type ceramics for the conditioning of actinides + rare earths
- 6 Technetium behaviour
  - k) Results on the influence of chemical environment on mobility
- 7 Long-term behaviour of leached radionuclides
  - l) Am elution profile through pure sand column
- 8 Colloid behaviour
  - m) Start of the experimental programme on colloid identification in leachate
  - n) First deep bed filtration model available
- 9 Actinide complexes in natural water
  - o) Completion of the study on carbonate complexes of Np (V)
- 10 Chemical forms and bioavailability of radionuclides in collaboration with laboratories of the indirect action Radiation Protection
  - A) Transport carried out
  - E) Technetium glass prepared; leaching tests cancelled
  - G) Tests in montmorillonite completed
  - H) Tests of the apparatus for combined study of leaching and diffusion started
  - I) First series of tests completed
  - J) Conclusions drawn on the problems connected with the development of a suitable matrix
  - K) box under inert atmosphere and oxygen monitor set-up
  - L) data obtained on Am elution (100 bed volume washing)
  - M) Experimental programme started



**APPENDIX 1 - SIGNIFICANT ACHIEVEMENTS COMPARED TO PLANNING**

*Table III. Project 3: Actinide separation*

Activities		7	8	9	10	11	12	1982
		second semester 1981 (month)						
Plutonium separation from MLW	1				(a)	△A		
	2				△B	(b)		
Actinide separation from HLW	3			(c)	△C			
	4			(d)	△D			

○ PLANNING

△ ACHIEVEMENTS

- |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                                                                                                                                                                     |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"> <li>1 Plutonium separation from liquid MLW                             <ul style="list-style-type: none"> <li>a) Completion of a series of experiments on oxalate precipitation followed by Pu-recovery</li> </ul> </li> <li>2 Plutonium recovery from dissolution residues                             <ul style="list-style-type: none"> <li>b) Completion of a first series of experiments</li> </ul> </li> <li>3 Actinide separation from HLW                             <ul style="list-style-type: none"> <li>c) Final summary report ready</li> </ul> </li> <li>4 Equipping of the ADECO hot cells                             <ul style="list-style-type: none"> <li>d) Decision on the operation</li> </ul> </li> </ul> | <ul style="list-style-type: none"> <li>A) Series of tests completed on MLW concentrate and exhausted TBP</li> <li>B) Experiments completed</li> <li>C) Typing of the final version started</li> <li>D) Evaluation of the operation continued: decision postponed to 1982</li> </ul> |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**APPENDIX 1 - SIGNIFICANT ACHIEVEMENTS COMPARED TO PLANNING**

*Table IV. Project 4: Actinide Monitoring*

Activities		7	8	9	10	11	12	1982
		second semester 1981 (month)						
Revision of the guide	1				△A			(a)
Passive neutron assay	2			△B	△C	(b)	(c)	
	3							
Experiments at DNPDE	4					(d)	(e)	△E
Intercomparison experiment	5							(f)
								(g)

○ PLANNING

△ ACHIEVEMENTS

- |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"> <li>1. Revision of the Guide                             <ul style="list-style-type: none"> <li>a) Publication of the revised version</li> </ul> </li> <li>2. Passive Neutron Assay                             <ul style="list-style-type: none"> <li>b) Setting-up of software for TCA</li> <li>c) Setting-up of hardware (detection head + electronics)</li> </ul> </li> <li>3. Variable Dead Time Counter</li> <li>4. Experiments at DNPDE                             <ul style="list-style-type: none"> <li>d) Final interpretation of NDA measurements</li> <li>e) Publication of final report Part 1</li> <li>f) Publication of final report Parts 2 - 3</li> </ul> </li> <li>5. Intercomparison Exercise                             <ul style="list-style-type: none"> <li>g) Samples to be measured at Ispra</li> </ul> </li> </ul> | <ul style="list-style-type: none"> <li>A) Draft of the revised chapter 1 completed</li> <li>B) Monte Carlo simulation software completed</li> <li>C) Association pulse to time converter to Plessey completed; Mechanical setting-up of detection heads completed</li> <li>E) Draft of part 1 completed</li> </ul> |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

## APPENDIX 2 - PLANNED ACTIVITIES AND IMPORTANT MILESTONES

Table I. Project 1: Risk Evaluation

Activities		1	2	3	4	5	6	2nd semester 1982
		first semester 1982 (month)						
Risk analysis of geological disposal	1							
	2	(a)		(b)			(c)	(d)
Assessment studies on seabed disposal	3				(e)		(f)	
Assessment studies on alpha-waste management	4					(g)		
Assessment studies on nuclear transmutation of actinides	5			(h)				

1. Implementation of the coordinated study on the Geological Disposal Risk (GDR) in the framework of the Community Plan of Action
2. Application of the JRC methodology on the Boom clay formation
  - a) Final version of a paper illustrating the JRC probabilistic approach
  - b) Draft version of glacial erosion scenario analysis
  - c) Final version of consequence analysis including uncertainty analysis
  - d) First revision of the clay model
3. Assessment studies on seabed disposal
  - e) Preparation of programme proposals for the next JRC plan
  - f) Risk evaluations in the framework of the NEA Systems Analysis Task Group
4. Assessment studies on alpha-waste management
  - g) Cost/benefit evaluation for the application of OXAL to liquid MLW of reprocessing plants
5. Assessment studies on nuclear transmutation of actinides
  - h) Publication of the summary report

## APPENDIX 2 - PLANNED ACTIVITIES AND IMPORTANT MILESTONES

Table II. Project 2: Protective Barriers

Activities		1	2	3	4	5	6	2nd semester
		first semester 1982 (month)						
Long-term stability of conditioned waste	1		a					b c
	2				d			
	3					e		
	4	f						g h
Interaction of radionuclides with environment	5						i	
	6				j			
	7			k			e	
	8	m						

1. Radiation damage in vitrified waste
  - a) Start of leaching tests on BONI III samples
  - b) End of the leaching tests
  - c) Completion of the studies on the bulk radiation damage
2. Methodology for glass surface analysis
  - d) Installation of the experimental facility including ESCA, AES and SAM
3. Leaching tests on vitrified waste
  - e) Completion of a first series of tests on leaching and diffusion in a clay paste using inactive glasses; decision for a possible use of spiked glasses
4. Corrosion tests
  - f) Start of diffusion controlled corrosion experiments on mild steels
  - g) Completion of a second series of tests on punctured containers
  - h) Completion of a first series of tests on mild steels
5. Technetium behaviour
  - i) Technetium behaviour under inert atmosphere
6. Long-term behaviour of leached radionuclides
  - j) Further elution data on Am
7. Colloid identification
  - k) Measure of colloid polydispersion in glass leachate
  - l) First filtration model available
8. Actinide complexes in natural water
  - m) Start of the study on Np carbonate complexes

## APPENDIX 2 - PLANNED ACTIVITIES AND IMPORTANT MILESTONES

Table III. Project 3: Actinide Separation

Activities		1	2	3	4	5	6	2nd semester 1982
		first semester 1982 (months)						
Plutonium separation from MLW	1		a					
Actinide separation from HLW	2				b			
Equipping of the ADECO hot cells	3			c				

1. Plutonium separation from liquid MLW
  - a) Completion of the tests on the application of OXAL; decision on the continuation of the activity
2. Actinide separation from HLW
  - b) Printing of the summary report
3. Equipping of the ADECO hot cells
  - c) Decision on the operation

**APPENDIX 2 - PLANNED ACTIVITIES AND IMPORTANT MILESTONES**

*Table IV. Project 4: Actinides Monitoring*

Activities		1	2	3	4	5	6	2nd semester 1982	
		first semester 1982 (month)							
Revision of the Guide	1							a	
Passive neutron Assay	2	b						d	
Experiments at DNPDE	3	e	c						f
Intercomparison Exercise	4								

1. Revision of the Guide
  - a) Publication of the revised version. chapter 1, 2, 3, 4
2. Reference Monitor
  - b) Theoretical assessment by Monte Carlo method
  - c) Experimental verification on the theoretical assessment
  - d) Preparation of coupling software
3. Experiments at DNPDE
  - e) Publication of final report part 1
  - f) Publication of final report part 2 - 3
4. Intercomparison Exercise

# PROJECTS

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## 1. Risk Evaluation

The project includes two main actions:

- Risk analysis of geological disposal of radioactive waste including seabed disposal.
- Assessment studies on alpha-waste management.

The project includes also the preparation of the final summary report of the assessment studies on nuclear transmutation of actinides.

Objective of the assessment studies on alpha-waste management is the optimization of the procedures to be adopted, taking into account mainly cost and benefit on the long-term risk. Thus the assessment studies on alpha-waste management have to be strictly connected with the studies of risk analysis of geological disposal.

### **Risk Analysis of Geological Disposal of Radioactive Waste**

This activity includes:

- The development of models for risk analysis of geological disposal and their application to a potential disposal site (Boom clay formation).
- Assessment studies on seabed disposal.

### **Development and application of models for risk analysis of geological disposal**

#### *Objectives*

Aim of this study is to develop and test a methodology for the assessment of the risk linked to the disposal of radioactive wastes into geological formations.

The starting point is the mathematical definition of the risk:

$$\text{RISK} = \text{Event Probability} \times \text{Event Consequences}$$

In accordance with this definition, risk analysis is split into two components:

I - Release Scenario Analysis.

II - Release Consequence Analysis.

where the first component accounts for the probability term, while the second one provides information on the expected consequences, if the release occurs.

On these bases, the methodology which at present is being developed consists of the following steps:

1. Assessment of release probabilities, through application of the Fault Tree Analysis.
2. Evaluation of release consequences, through modelling of the barrier system which is interposed between the waste repository and population.
3. Risk assessment, by combining points 1 and 2.

One critical point is due to the presence of large data uncertainties.

Models currently in use are often implemented in deterministic manner. In fact, both the variability of the system and the distribution of the input data are neglected; thus, the predictions generated consist of single values, which are scarcely realistic. Indeed, long-term risk assessments always imply a large degree of uncertainty, due to scarce knowledge of the values of the parameters utilized both in probability assessment models and in consequence assessment models.

The following way can be adopted to evaluate how uncertainties in input parameters are reflected in the model results: a probability distribution is defined for each uncertain input parameter to cover the range over which it may vary; as a result, a probability distribution is obtained for the quantity which is being assessed; this latter, in the present case, can be any type of release consequences, or release probabilities, or probabilistic risk.

The competences developed by the J.R.C. will be utilized in the coordinated study on the Geological Disposal Risk (GDR) to be carried out in the framework of the Community Plan of Action.

GDR has received the favourable advice of the ACPM Community Plan of Action on September 30, 1981.

Objective of this study is to obtain in due time (about 6 years) a harmonized evaluation of the principal waste disposal options presently under study in the Community (salt, granite, clay, sub-seabed).

The activity of the J.R.C. will particularly deal with the clay and sub-seabed disposal options.

Coordination of the study will be assured jointly by J.R.C. and indirect action programmes.

#### *Results*

**A.** The CEN/SCK of Mol (Belgium) is investigating the possibility of disposal of radioactive waste into the clay formation of Boom.

In the framework of a collaboration JRC - CEN/SCK, the above described methodology is being applied to a potential repository in the mentioned formation.

The probability assessment model utilized and the results obtained were already presented in the previous Programme Progress Report (1).

The study allowed to recognize the most important release scenarios; among them, the creation of a permeable fracture across the repository was identified as the most likely one, and therefore was chosen for consequence modelling. The preliminary results of this analysis were assembled in an interim report (2).

Np-237 could be identified as the most important isotope in governing the long-term risk; this fact is due to the concurrence of its very long half-life together with its large mobility, and large dose factor. Other isotopes of concern appeared to be I-129 and Tc-99, while plutonium isotopes are especially important for inhalation pathways (Figures 1 and 2).

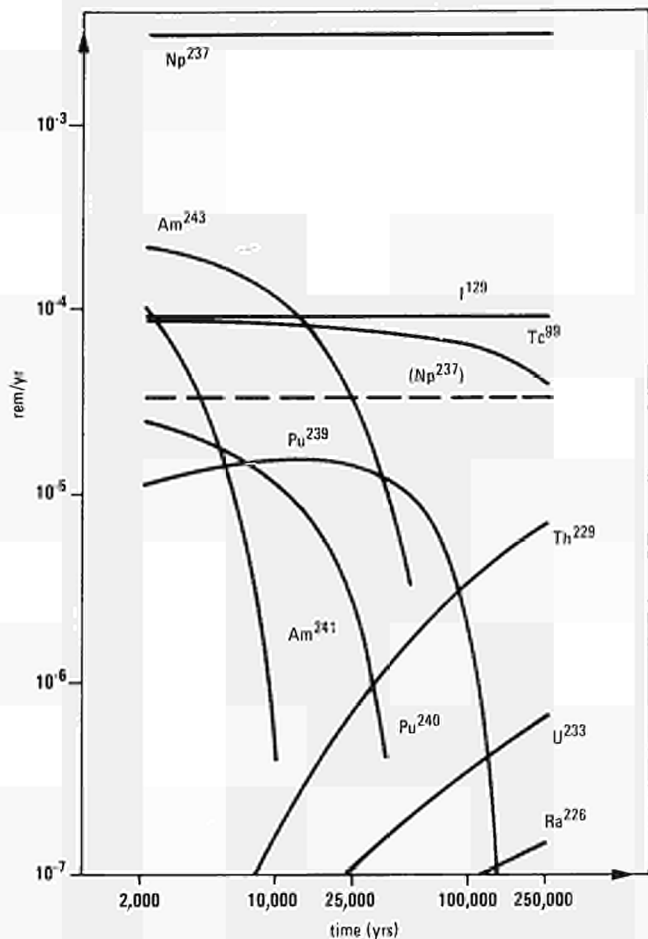


Fig. 1. Dose rates to a maximum exposed individual as a function of time of initial release. Release to the lower aquifer. Isotopes from VHLW and CIW (ingestion pathway).

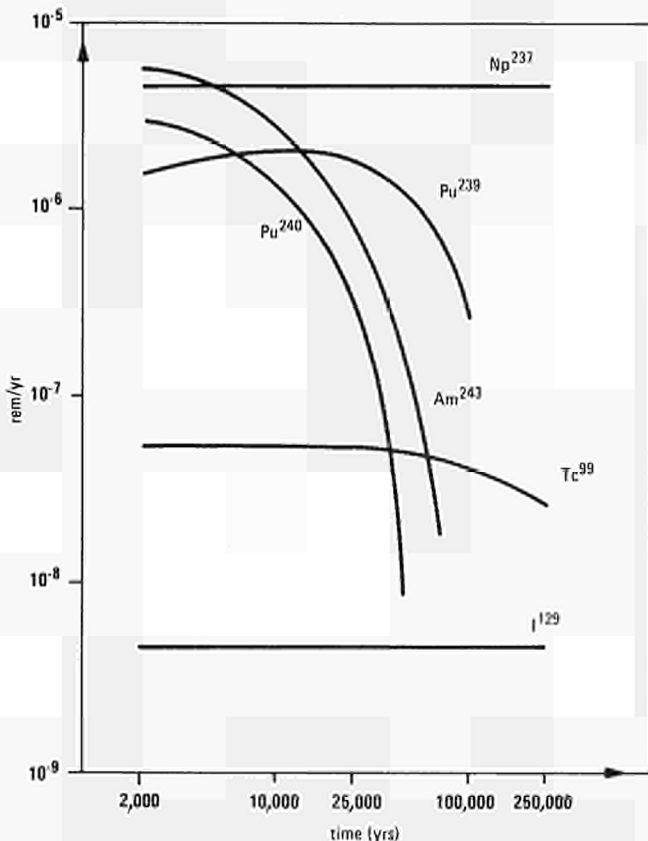


Fig. 2. Dose rates to a maximum exposed individual, as a function of time of initial release. Release to the lower aquifer. Isotopes from VHLW and CIW (inhalation pathway).

The uncertainties which affect input data were then taken into consideration, by using the above-mentioned methodology. The following steps were performed:

- The functional relations through which the model results are linked to the  $n$  input parameters were defined, as
 
$$Y = F \{ X_1, X_2, X_3, \dots, X_n \}$$
- For each uncertain parameter  $X$ , an adequate probability distribution over its variability range was specified, on the basis of the available information integrated with the necessary degree of subjective judgement.
- A computer code was developed to handle each parameter with its own ranges of values and corresponding probabilities, in order to obtain the model output in the form of a probability distribution. A Monte Carlo method has been utilized, but also analytical codes are available at JRC to perform the same task.

As an example of the results obtained with this approach, the probability distribution of the dose rate to the most exposed individual of an hypothetical critical group is shown in Figure 3: it may be seen that the uncertainty range of the results covers five orders of magnitude; however, more than 99% of the combinations fall in the range  $10^{-5} - 10^{-2}$  rem/year; by comparison with the dose due to the natural background (also shown in the Figure) it may be seen that the consequences fall in an acceptable range. Similar histograms were obtained for collective dose and detriment to the population and for the probabilistic risk, over 250,000 years (Figure 4).

This work is still under way; further developments are required to perform a statistical analysis of the results. The methodology has been described in a paper which will be submitted for publication (3).

**B.** A further examination of the results obtained from the probability assessment model (Fault Free Analysis) has shown the necessity to investigate more in details the consequences of a glacial erosion over the repository region, as the probability of occurrence for such a scenario is not negligible. This scenario appears to be characterized by some degree of uncertainty; it implies large changes in the radioactivity source term, as a fraction of the wastes may be displaced

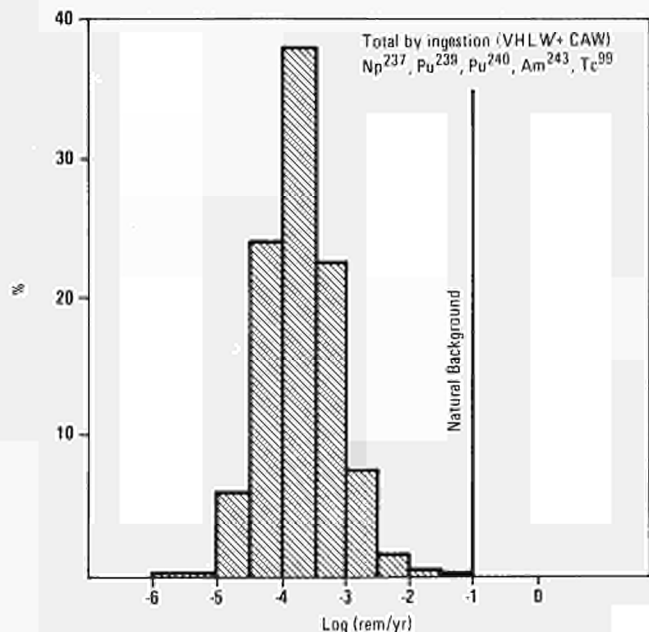


Fig. 3. Dose rate to a maximum exposed individual (rem/yr)

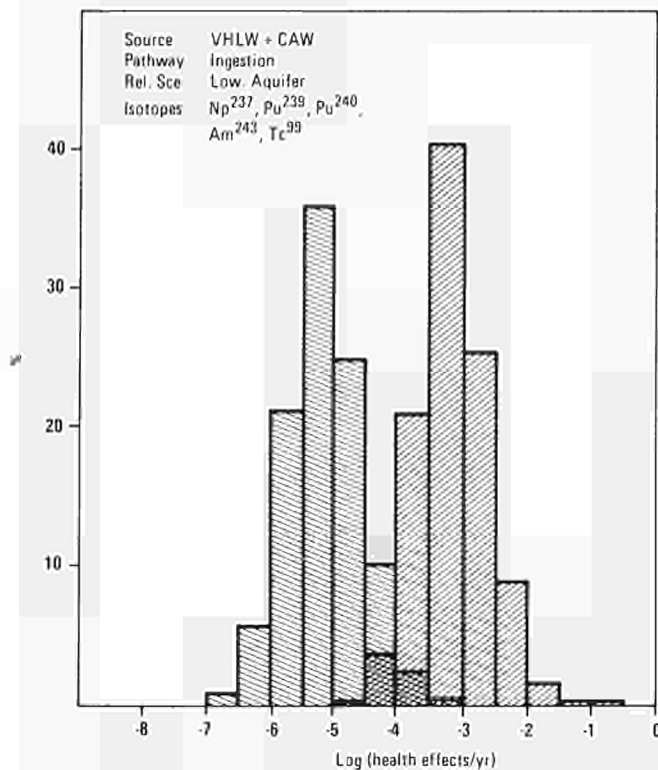


Fig. 4. Detriment to population ( // // // // ) probabilistic risk over 250,000 years ( / / / / / / / / )

from the repository while undergoing important mechanical actions; the availability of the radioelements to transport into the biosphere would be increased. Preliminary dose assessments seem to indicate that the consequences of this scenario could be of some importance and therefore require to be carefully weighed against the corresponding probabilities, in order to get a comprehensive view of the risk.

### Collaboration with External Organizations

Collaboration contract with CEN/SCK - Mol.  
Relations with organizations working in the indirect action programme.

### References

1. M. D'Alessandro: "Radioactive waste disposal into a plastic clay formation: probabilistic assessment of the geological containment". Topical report in Programme Progress Report January-June 1981.
2. G. Bertozzi and M. D'Alessandro: "Radioactive waste disposal into a plastic clay formation: a site specific exercise of consequence analysis". Technical note N.° 1.07.03.81.66 (1981).
3. G. Bertozzi and M. D'Alessandro: "A probabilistic approach to the assessment of the long-term risk linked to the disposal of radioactive waste in geological repositories". To be published.

## Assessment Studies on Seabed Disposal

### Objectives

The activities to be developed at present include three aspects:

- A. The participation of the Commission of the European Communities in the NEA International Seabed Working Group.
- B. Assessment methodology for disposal of high-level waste into the deep ocean floor.
- C. Development of a proposal for a marine disposal assessment programme for consideration in the next J.R.C. research plan.

### Results

**A.** The Commission participates as an official member in the NEA International Seabed Working Group (SWG). Three Commission's programmes are involved in the study of the seabed disposal option: indirect action Management and Storage of Radioactive Waste, indirect action Radiation Protection and direct action Safety of Nuclear Materials. At present five task groups of the NEA Working Group have been identified as of direct interest to the European Commission's programmes. These concern systems analysis, sediment and rock, waste form and canister, biology and engineering studies. Representatives from the Commission were designated for each of these task groups.

Two interim meetings of Engineering Studies (ESTG) and Systems Analysis (SATG) Task Groups were held in September-October 1981. In view of the importance attached to engineering studies by the Systems Analysis Task Group the Joint Research Centre and the Sandia National Laboratories were charged to act as liaisons between the two groups in order to facilitate and accelerate information exchange.

The meeting of the Engineering Studies Task Group was held in Delft, 21-25 September, 1981 at the Delft Soil Mechanics Laboratory. The main business of the meeting was the development of a detailed network analysis on the basis of the preliminary evaluation carried out during the Sixth Annual Meeting of the Seabed Working Group (SWG), Paris, February 1981.

Other items discussed were the following:

- 1) Progress relevant to engineering studies made in various national programmes since the Paris meeting.
- 2) Boundary Conditions and Scope of Work of the task group as previously defined at the Paris meeting.
- 3) The Draft II SWG Five-Year Plan and the deep ocean drilling proposed by Site Selection Task Group at the Paris meeting and expanded upon at their May 1981 meeting.

It was concluded, after discussion of the above points, that by the end of 1983 the ESTG will have selected a limited number of operations for preconceptual design studies. By 1984 one or more options will have been identified for detailed design and analysed for technical feasibility. Sensitivity studies should have been completed by 1985. Preconceptual designs of the preferred options will have been made by 1986.

The interim meeting of the Systems Analysis Task Group (SATG) was held in Antibes, Ecole des Mines, 28 September - 2 October, 1981. The main purpose of this meeting was to discuss the requirements for radiological assessment of operational failures before and during disposal and low probability post-disposal events as had been decided during the Paris meeting.

Other items discussed were:

- 1) Progress of work done by SATG members, in particular

the modelling being carried out by Sandia National Laboratories, USA and Whiteshell, Canada.

- 2) Report on Engineering Studies Task Group meeting in Delft.
- 3) Report on progress made in the field of radiological criteria for nuclear waste disposal.
- 4) Report on progress in the field of legal, social and international aspects.
- 5) Draft II SWG Five-Year Plan.
- 6) Draft paper to be submitted by SATG for publication. This paper summarizes the results obtained by the SATG in the initial modelling attempt presented at the Paris meeting.

The problems associated with various probabilistic approaches applied to sub-seabed disposal were considered to require detailed investigation.

It was decided to operate on the following lines:

- to evaluate the possibility to develop a probabilistic systems model using the Canadian SYVAC (1) methodology, using the simple set of submodels developed by the SATG for its first deterministic assessment (2).
- to identify operational failure scenarios using the base-case model and to calculate the consequences.
- to review probabilistic methodologies for low probability post-disposal events.

The first results of these studies should be available in 1982.

**B.** The development of assessment methodologies parallel to those used for terrestrial formations is being carried out in co-operation with the Systems Analysis Task Group. A simple overall system (deterministic) model has been developed and preliminary details and calculations were presented at the NEA International Seabed Working Group meeting in Paris (February 1981).

In a study carried out by the J.R.C. where a simple radiological methodology was also developed for the assessment of the feasibility of the disposal of high-level radioactive waste into deep ocean sediments, a number of conclusions similar to those of the preliminary Systems Analysis model could be drawn:

- The sorption of radionuclides within the sediment column plays an extremely important role in controlling the actual radionuclide concentration eventually reached in the water column.
- Under the conditions of the model and for the emplacement depth studied (100 m) retention times of between  $10^5$  -  $10^9$  years seem to be attainable.
- The recycling and downward transport of the actinides by biological or sedimentary processes may be of significant importance in the long-term in decreasing surface and mid-depth water concentrations.
- Due to the importance of the geochemical barrier for radionuclide migration, careful experimental study must be made of the properties of deep ocean sediments which control retardation processes. Further the effect of biological and sediment sorption at the sediment-water interface must also be investigated.

It is clear from this present study as well as the one of the NEA Systems Analysis Task Group that the future development of more realistic models will require a high degree of collaboration between modelling, experimental studies and engineering emplacement investigations, in order that con-

clusions concerning the feasibility of this option can eventually be drawn. The development of the necessary engineering studies (including modelling) of a number of different emplacement methods will be needed to show engineering capability for shallow and deep burial options.

**C.** In view of the development of a proposal for a marine disposal assessment programme for consideration in the next J.R.C. research plan, more detailed evaluations are under way on three main project areas.

They may be summarized as being:

- a) To increase modelling activity on risk analysis of the seabed disposal option. Two main aspects could be envisaged, the first relates to a continued collaboration with the Systems Analysis Task Group in developing deterministic and probabilistic methodologies for sub-seabed emplacement; the second aspect concerns developing (at the J.R.C. Computing Centre) the ability to use a methodology for evaluating the radiological consequences of radioactive effluent releases.
- b) To develop experimental studies on the barriers against radionuclide migration by including investigations carried out in conditions simulating the deep ocean, i.e. pressure up to 500-1000 bars, temperatures down to 2°C.

This project would possibly consist of four aspects:

- 1) Development of high pressure facilities including instrumentation and in-situ sampling systems/engineering studies.
  - 2) Increasing activity concerned with biogeochemical studies related to radionuclide migration, chemical speciation and bioavailability, under varying simulated deep ocean conditions.
  - 3) Studying the effect of corrosion and leaching processes under different thermal, radiation and pressure fields on various waste forms and canister materials.
  - 4) Increasing modelling efforts on thermodynamic and nuclide migration processes.
- c) For the European Commission to act as a focal point for multinational in-situ experimental activities.
- In view of fact that deep ocean studies are inherently complicated and expensive and of the increasing need for cost sharing of large scale projects, specially related to engineering studies and in-situ experimental systems, a co-ordinating role by the Commission could play an important part in getting major projects undertaken for the study of sub-seabed disposal feasibility.
- A number of areas could be of eventual interest: development of experimental platforms, study of emplacement techniques, large scale cruises/ocean current studies, deep drilling experiments etc.

Study contracts are being undertaken to define more clearly the needs and requirements of various aspects of these projects.

In the development of the programme proposal for the next research plan, the J.R.C. will take into consideration the need of a strict coordination with various international programmes:

- Indirect actions Management and Storage of Radioactive Waste and Radiation Protection.
- NEA International Seabed Working Group.
- Coordinated study on Geological Disposal Risk (GDR) to be carried out in the framework of the Community Plan of Action.



## Collaboration with external organizations

- Collaboration with various organizations participating in the NEA International Seabed Working Group.
- Further discussions have been held between the J.R.C. -Ispra, CNEN Fiascherino Laboratory and the D.G. XII Radiation Protection Programme concerning a joint programme on the biogeochemistry of technetium. A first shipment of Tc 95<sup>m</sup> has been sent from the J.R.C. to Fiascherino. Studies are proceeding on the chemistry of this element in natural waters.
- Contacts have been maintained with the IAEA Monaco Laboratory for studies concerned with transuranics in the marine environment.

## References

1. K.W. Dormuth, R. Sherman: "Syvac, a computer programme for assessment of nuclear fuel waste management systems, incorporating parameter variability". Report AECL-6814. (August 1981).
2. Systems Analysis Task Group, International Seabed Working Group, Report on the SATG Interim Meeting held at the National Radiation Protection Board. (November 1980).

## Assessment Studies on Alpha-Waste Management

### Objectives

Aim of the study is the optimization of the management of alpha waste streams produced both in reprocessing and fabrication plants.

In continuation of the assessment studies on alpha waste management, effort has been directed during the respective work period on the following:

- the completion of the reference waste treatment facility
- a report on the present status of waste classification
- proposal for the improvements in the Purex reprocessing scheme for irradiated nuclear fuel material by the integration of a routine waste streams rework process
- the design stage completion for a scale-up of a precipitation - denitration reactor.

During the reporting period it was also planned to continue the preparation of the final summary report on the nuclear transmutation of actinides.

### The Reference Waste Treatment Facility

The Baseline Waste Management Strategy (BWMS) adopted for the initial study phase on alpha waste management assessment studies (1) has proceeded by the completion of a reference waste treatment facility (RWF) (2). The need for

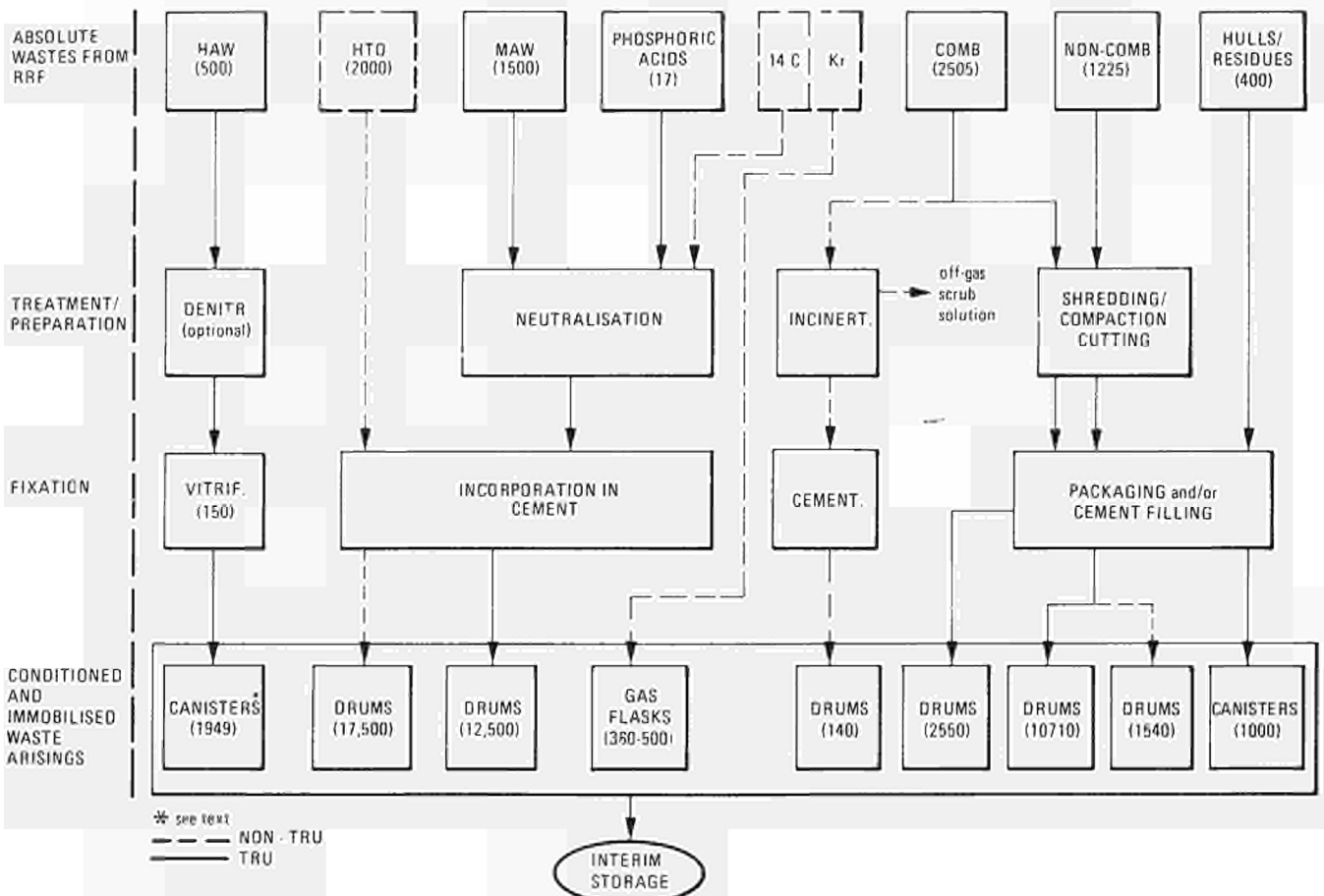


Fig. 1. Schematic representation of the functional operation of the reference waste treatment facility for the wastes arising in the RRF.

such a RWF became the next logical step in the assessment studies after the qualitative and quantitative analysis of the absolute wastes arising in the reference reprocessing and MOX fuel fabrication facilities (RRF and RFFP respectively).

The absolute wastes emanating from the RRF and the RFFP facilities are of various physical, chemical and radioactive compositions and are considered to typify the next generation commercial facilities.

The basic concept envisaged to solve the problems created by these wastes aims at immobilising them in suitable matrices and placing in suitable containers such that the necessary criteria for a particular disposal option can be satisfied. From the reference facilities (3, 4) it is clear that in contrast to the HAW arising the volumes of intermediate and low level waste arisings are much greater and in addition cover a range of radioactivity and actinide content.

These medium (intermediate) and low level wastes have therefore received closer attention over the past few years in view of their generation rate, conditioning and disposal, especially in function of their actinides content. Volume reduction and suitable immobilisation has therefore been the prime concern of many nuclear research facilities for these waste types. The main emphasis has been directed on the evaluation and improvement for final disposal requirements of cement and bitumen solidification techniques, which had been developed and implemented on an industrial scale already for many years. In recent years synthetic polymers, ceramics, mixed resin/cement, slags and improved bitumen matrices have been considered and represent still an ongoing research effort.

Establishing such a conceptual base case RWF within the BWMS requires for each absolute waste arising the implementation and selection of the following:

- treatment process
- matrix conditioning medium
- reference container
- controlled interim storage facility.

One common feature of all immobilisation techniques for all waste forms is the need for some form of container in which the waste and matrix are placed. Evidently the choice of a suitable reference container becomes the first real need for a RWF concept. Information in this respect was taken from INFCE (5) although by far the most usual container is the 55 gallon standard oil barrel.

For each of the absolute wastes arising from the two reference plants (reprocessing and fabrication) considerations have been given to the present day methods for their treatment and conditioning which are already implemented on an industrial scale or which are promising to reach maturity and reliability in the near future. For the various waste categories the selection has been as follows:

## HAW

For this waste, glass was adopted as the conditioning medium. The INFCE studies (5) assumed a volume of 0.15 m<sup>3</sup> of glass resulting from the reprocessing of one-MTHM fuel which corresponds to approximately 15% by weight of fission products assuming a concentration of 120 g/l fission products and a final glass density of 2.6 g/cc filled into stainless canisters of 20 cm diameter and 300 cm height.

## Hulls, spacers, dissolver residues

The INFCE studies assumed that the hulls, spacers and dissolver residues are suitably immobilised in HWR-type canisters without indicating the immobilising medium.

The present state of the art already implemented for the hulls treatment is simply cementation (WAK, EUREX) and is also envisaged for the future arisings at Cap de la Hague and Windscale. For some sites actually the hulls are placed in suitable containers and stored pending the decision on the conditioning medium. The dissolver fines are also envisaged as being placed in the containers with the hulls.

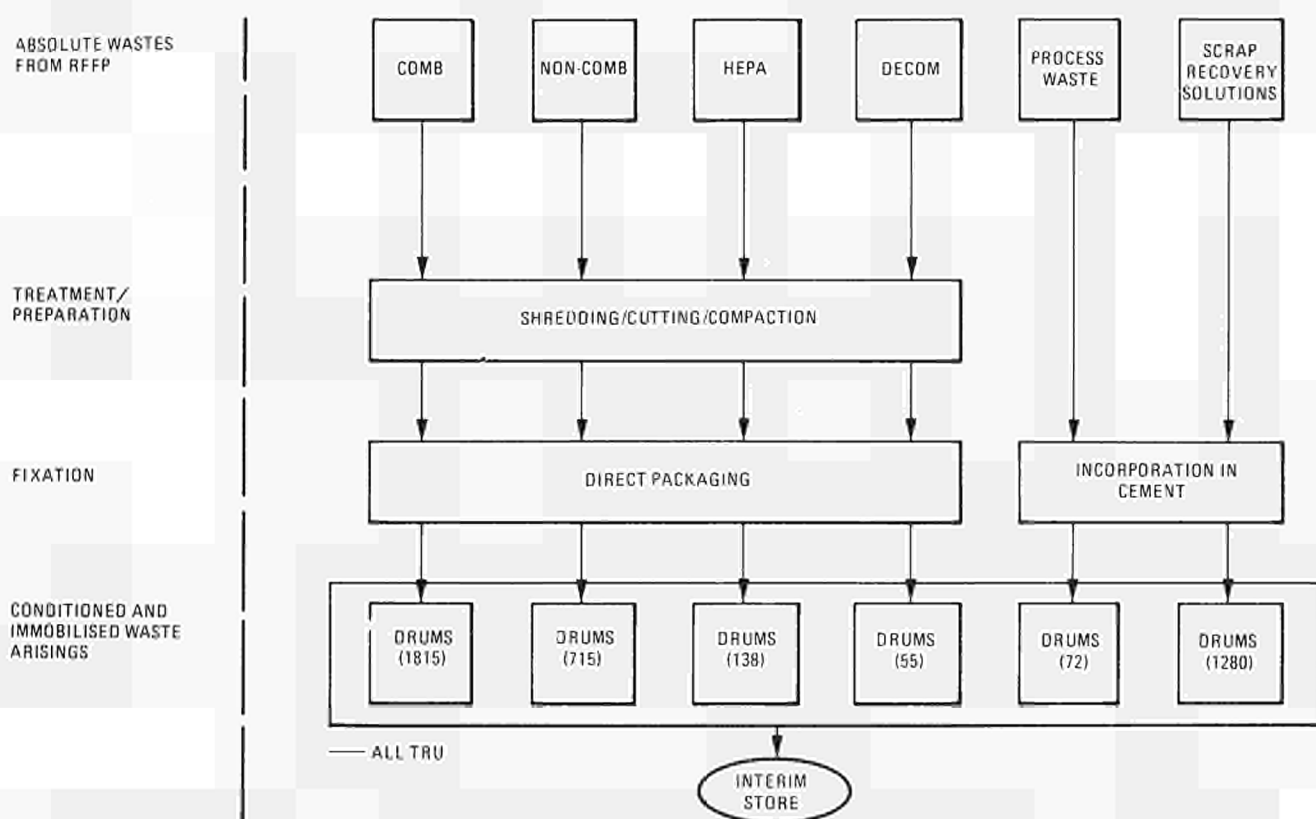


Fig. 2. Schematic representation of the functional operation of the reference waste treatment facility for the wastes arising in the RFFP.

This is usually accomplished by the use of remote handling replaceable centrifuge bowls or filter cartridges in the head-end plant.

For the RWF these wastes have been considered to be incorporated in cement and placed in these HWR type reference containers. Approximately one-thousand reference HWR canisters would be required for 1000 MTHM/a processed. The concern of the choice of cement however depends on its ability to contain the tritium content of the hulls which could eventually demand the need for a better tritium holding medium.

### MAW aqueous concentrates

The choice for the immobilising medium within the RWF falls on cement or bitumen. For the base case it has been decided to select cement on which ultimately comparisons of other matrixing agents will be made.

The reference containers are 55 gallon drums.

### Combustible solid wastes

For this waste type it has been assumed to place the shredded material in the containers (55 gallon drums) without any special compaction techniques and finally immobilise it by mixing with cement.

### Non-combustible solid wastes

This waste type is considered to be suitably immobilised in cement.

For some of the waste of this category it will be necessary to have techniques available for size reduction in order to place them in the 55 gallon drums.

In Figs. 1 and 2 the selected steps of treatment, fixation and conditioned waste arisings are indicated. These steps represent the selected choice for the RWF which however might not represent the best or most advantageous route or

Table I. Estimated volumes of the RRF fixated wastes destined to interim storage

ABSOLUTE WASTES	VOLUME OF RAW WASTE m <sup>3</sup> /1000 MTHM	FIXATED WASTES		No. OF CANISTERS/DRUMS /FLASKS(a)	CONTAINED Pu(kg)
		MATRIX/TREATMENT	VOLUME m <sup>3</sup> /a		
HAW	500	GLASS	150	848/1949	50
MAW (i) aqueous	1500	CEMENT	2500	12,500	15
(ii) phosphoric acids	17				
(iii) <sup>14</sup> C (t/a)	0.1				
HTO	2000	CEMENT	3500	17,500	—
COMBUSTIBLE (TRU)	1845	COMPACTION	461	2550	8.1
COMBUSTIBLE (non-TRU)	660	INCINERATION/CEMENT	25	140	—
NON-COMBUSTIBLE TRU	1071	PACKAGING	2142	10,710	29.9
NON-TRU	154		308	1540	—
HULLS/SPACERS etc.,	350	CEMENT	600	1000	15
DISSOLVER RESIDUES	50				
NOBLE GASES(Kr)	97	SEPARATION/STORED UNDER PRESSURE		360-1000	—

(a) assuming 500 m<sup>3</sup> STP/hr, DOG Kr air 1.14 ppm (~ 300 vpm)

Table II. Estimated volumes of the RFFP fixated wastes destined to interim storage

ABSOLUTE WASTES	VOLUME OF RAW WASTE m <sup>3</sup> /a	FIXATED WASTE		No. OF CONTAINERS	CONTAINED Pu (kg)
		TREATMENT	VOLUME m <sup>3</sup> /a		
COMBUSTIBLE	1320	COMPACTION	330	1815	130
NON-COMBUSTIBLE	260	CUTTING/COMPACTION	130	715	10.5
HEPA	100	COMPACTION	25	138	1.7
DECOMMISSIONING <sup>(1)</sup>	10	SIZE REDUCTION	10	55	see (1)
SCRAP RECOVERY SOLUTIONS	117	CEMENT	230	1280	115
PROCESS WASTE <sup>(2)</sup>	6.5	CEMENT	13	72	0.15
(Lab. misc.)					
SOLVENT (TBP) <sup>(3)</sup>	37				< 0.01%
ORGANIC (oils, lubricants etc.,) <sup>(4)</sup>	0.5				
EVAPORATOR OVERHEADS <sup>(5)</sup>	160				

(1) Pu content depends on DF achieved, process used etc.,

(2) It has been assumed that the RRF receives process waste solution from the MOX facility.

(3) Treatment can be performed in similar fashion or with the method as employed in the RRF.

(4) These cumbersome waste types have received very little attention up to now, probably a chemical or high temperature process can be applied.

(5) These are potentially alpha contaminated, therefore they would not appear in the absolute waste balance if recycled or if possible discharged. Alternatively they could be conditioned in a suitable matrix.

routes that definitely will be implemented within the overall framework of waste management and disposal.

The estimated volumes of fixated wastes, number of containers and plutonium content are indicated in Tables 1 and 2.

## Waste Classification

Most of the important types of radioactive waste arise from the "back-end" operations of the nuclear fuel cycle for which the BWMS is primarily concerned. As mentioned previously the absolute wastes arising vary in quantity and diversity. Classifying and categorising such waste streams produced is the first real task of the operator, firstly to achieve a safe and efficient operation and secondly to avoid any extra financial burden that would be incurred due to the "sentencing" of the waste into a category involving further treatment and conditioning operations which otherwise might be unnecessary.

Important factors in such a source route oriented consideration would therefore be:

- the physical and chemical state of the initial raw waste arising;
- the gross activity concentration and radiation dose which has a significant influence on the succeeding steps such as;
- the handling and treatment methods and technologies of such raw waste streams;
- the subsequent handling, treatment and conditioning processes to and of the final absolute waste form;
- the transport of the conditioned and immobilized waste;
- the disposal route of the immobilized waste.

In essence the full characteristics of the waste are required from the on-set of creation right through to the final disposal (or interim storage). The hazard posed by the disposed waste can be estimated for example on the basis of the maximum permissible concentration of the various radionuclides contained in the final immobilized and packaged waste form for a particular chosen disposal scenario, or better from the fraction of radionuclides that might be able to re-enter into the biosphere from the corresponding repository. Specification of the important properties and requirements of the conditioned waste thus relies also on informational feedback from these risk and radiological hazard assessment studies. The outcome of such a "disposal route" oriented classification must not necessarily coincide with the former source route classification.

For what concerns the establishment of criteria and classification of radioactive waste in function of their actinide contents, it has been seen that there are different criteria in a number of countries and furthermore discrepancies within individual countries (6). On the one side there are criteria which specify the alpha limit in function of the conditioned waste (e.g. the US limit of 10 nCi/g and ANDRA's limit of 1000 MPC (air), and on the other side in function of the raw untreated waste (e.g. U.K. 20 mCi (alpha)/m<sup>3</sup> after 100 years storage and France of 100 nCi/g or 0.3 g Pu-239/m<sup>3</sup>). These last two values provide guidance to the operator in allowing a functional operational sorting of the waste into TRU or non-TRU as it arises without taking into consideration possible implications of any further treatment steps before disposal.

In contrast however, ANDRA's and the US figures require the operator to have available well defined treatment and conditioning steps so that it is possible to determine whether a particular raw waste will meet the specified criterion or not.

It is recognised that there are wastes which can be characterised as definite TRU or definite non-TRU waste simply by

the "source-route" arising, however it is equally recognised that between these two extremes there is a region of a high generation rate of low level or suspected TRU waste. Economic penalties would naturally be incurred by sentencing non-TRU waste as TRU waste.

Anomalies can arise if one considers a raw waste which may be well defined as non-TRU but if a conditioning route is followed involving concentration such as compaction or combustion, the resulting activity per unit volume will be increased which may render the conditioned waste TRU. In contrast, a TRU waste could very well be designated non-TRU simply by dilution and therefore be subjected to a less severe disposal route.

The resolution of such conceptions probably lies in correlating the disposal requirements ("disposal route" oriented classification) with those of the conditioning requirements as suggested in reference 7.

Whatever the eventual criteria, however, the operator requires specific and clear guidelines to follow enabling screening of the waste into TRU or non-TRU which in turn needs precise routine monitoring equipment.

## An Integral Alpha Waste Management Strategy in the Nuclear Fuel Cycle

### Introduction

From the assessment and experimental work carried out up to date on the present program together with the added advantage and knowledge of actinides separation from HAW through the last programme of work there has emerged the real and practical possibility of integrating an alpha waste management strategy into the fuel cycle.

### General description of the method and incentives

The method can be applied for the recovery of actinides (except U) from all process liquid waste streams (Plutonium Contaminated Liquids-PCL) which result from the reprocessing and fabrication of nuclear reactor fuel and indeed potentially extendable to TRU solid waste arisings, leading to a practical process scheme for a fully integrated alpha waste management strategy highly compatible with the Purex process within the nuclear fuel cycle (see Fig. 3).

More specifically this scheme relates to a method which allows rework of re-ionised Pu (recoverable) from all PCL namely the "primary process specific wastes" (HAW, 2nd and 3rd cycle raffinates, exhaust solvent), and "management wastes" (decontamination solution, plant rinses etc., inclusive of complexants), together with the splitting of the actinides from the bulk of the FP and with slight adaptation the quantitative recovery of actinides from solids (dissolver residues, ashes, HEPA filters etc.).

The method in question concerns firstly a simple oxalate precipitation process (OXAL process) which can be applied to all the "technological" and "management" wastes that arise through nuclear fuel reprocessing and fabrication and secondly the use of an oxalic acid first cycle solvent wash allowing all the "lost" actinides (excluding U) to be concentrated into one process stream.

A process scheme for purification has been adopted which is highly compatible with present day Purex technology and furthermore provides the following advantages:

- a rework system of re-ionised Pu (and therefore recoverable) from normal and sub-standard process waste streams

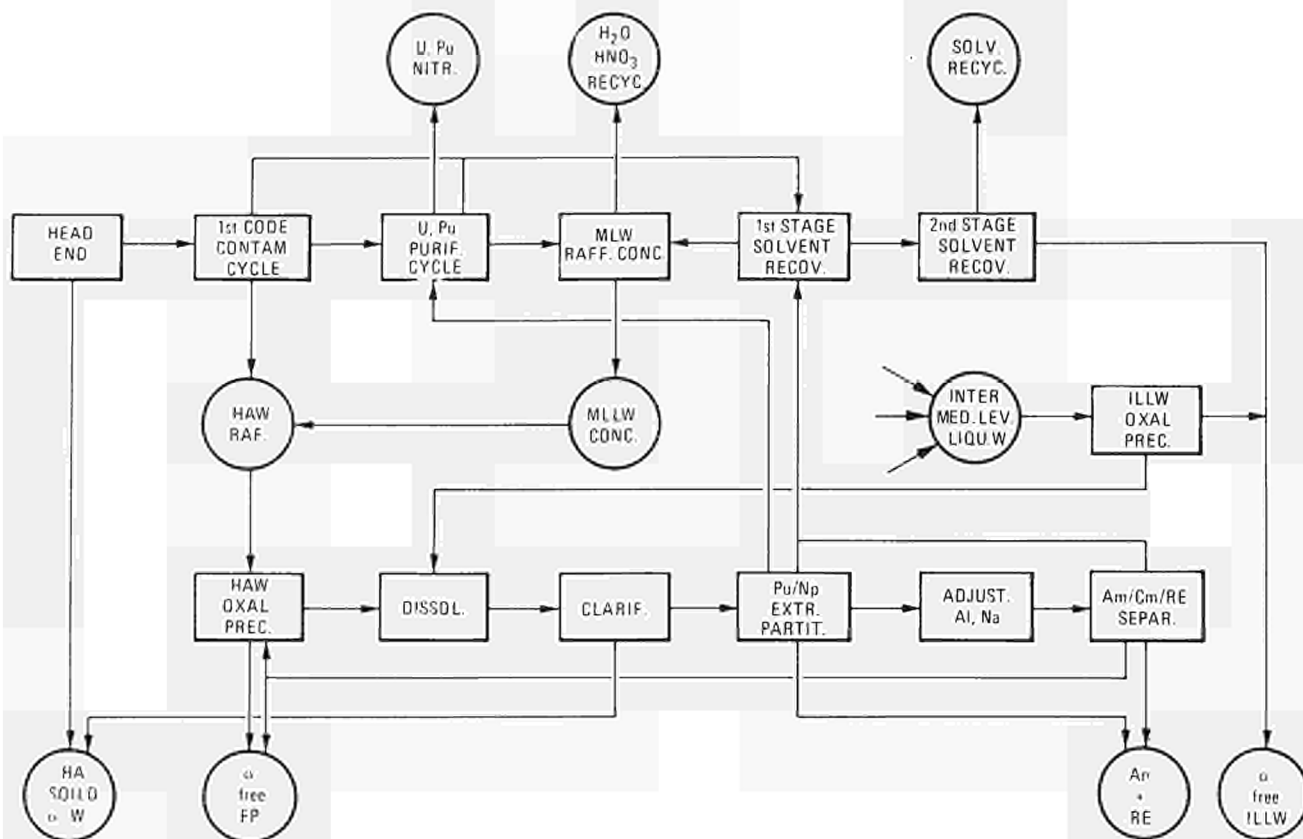


Fig. 3. Liquid alpha waste splitting scheme

- considerable relaxation in process set limits in view of the re-work system
- a continuous, uninterrupted smooth Purex operation
- increased load factor of the plant
- reduced quantity of fissile material lost definitely to waste
- reduction in the volume of TRU waste
- a consequent reduction in the hazard associated with the waste
- a reduced quantity of salt waste arising due to the implementation of the oxalic acid solvent wash
- considerable reduction in Ru volatility during concentration and vitrification of the FP solution
- the rework system is fully compatible with Purex
- oxalic acid solvent scrub stream can be considered "salt-free" since oxalic acid can be easily destroyed
- destruction of the oxalic acid by feeding it to the bottom of the purification cycle raffinate evaporator
- high burn-up fuel (LWR and in particular FBR) may be reprocessed at shorter cooling times due to the availability of the rework system itself and also due to the following
- reduction in column size (extraction device) i.e. elimination of unnecessary spare extraction stages by operating at a high solvent loading
- reduction in solvent flow rates per unit of fuel processed
- increased DF per process step
- lower fissile material hold-up (beneficial for safeguards and fissile material accountancy)
- shorter residence time (time of contact of solvent with radiation)
- reduction in solvent degradation
- reduction in possibility of risk of crud formation

- the rework system concentrates all the "lost" actinides (excluding U) into one stream
- the purification scheme splits the mixture into alpha and non-alpha fractions
- Np is confined to a unique stream
- isolation of all precursors of Np from the FP
- "tailor-made" conditioning of the actinides-RE fraction leads to a more stable matrix
- relaxation of FP conditioning and disposal specifications in view of the required confinement time of only a few centuries
- possibility exists of separate conditioning of the Np for which special disposal options may be considered.

With such advantages to be gained for the operator, for the Purex process itself and for the management and disposal of the wastes an integrated system can be optimised to produce:

- a vastly improved and flexible Purex process
- safer management and disposal of alpha contaminated wastes
- considerable cost savings aided overall with benefits for the nuclear fuel cycle.

#### Denitration - Precipitation reactor scale-up

The chemical feasibility of the denitration - precipitation reaction with formic and oxalic acids has already been demonstrated on a laboratory scale level. In order to provide further information on its large scale practical feasibility for denitration-precipitation, separation and dissolution a reactor vessel design of 20 - 30 litres capacity has been completed. The relevant pieces of equipment and parts have been ordered.

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## 2. Protective Barriers

In the concept of a multiple protective barrier against migration of radionuclides to the biosphere an important role is played by the long term stability of conditioned waste (waste conditioning barrier) and by the capability of retention of radionuclides by the surrounding geological media (geochemical barrier).

Typically the accident which is considered in the risk analysis is the failure of the geological barrier and the contact of the conditioned waste with water which then flows through the surrounding media.

The two problems are strictly connected. As a matter of fact the type of conditioning will define the rate and the mode of release (solute, colloids) of the radioactivity and then will influence directly the mechanism and the capability of retention of the surrounding media. In order to be able to evaluate the safety of the repository it is necessary to improve the knowledge of the mechanisms of leaching and retention and to obtain the necessary data for the model evaluation.

The leaching rate of the conditioned waste will be proportional also to the surface exposed to leaching.

In the model, then, it will be important to introduce possible effects on bulk integrity due to radiation damage of the conditioned waste.

### Long-Term Stability of Conditioned Waste

#### Objectives

The activities planned for 1981 are the following:

#### Radiation damage in borosilicate glasses

- Post-irradiation examination of the glass samples irradiated in the HFR reactor, Petten.
- Studies on damage effects and annealing in silica using optical techniques.
- Observation at the HV electron microscope of damaged borosilicate glasses.
- Studies on the mechanisms of density variation in damaged glasses.

#### Leaching and corrosion experiments

- Leaching and corrosion tests in montmorillonite/sand paste.
- Leaching tests on borosilicate glasses containing Pu and Tc.
- Modelling of the dissolution of a fissured block of borosilicate glass.
- Corrosion tests on punctured containers.
- Setting-up of an experimental facility for surface analysis.

#### Special matrix for conditioning of actinides + rare earths

- Exploratory investigation on the use of monazite type ceramics.

## Results

### Radiation damage in borosilicate glasses

During the first semester of 1981 a review of the status of the art on radiation damage in borosilicate glasses has been carried out. This review is presented in a Topical Report at the end of the present section.

Of all the activities planned for 1981 only the studies on the mechanisms of density variation in damaged glasses have not been undertaken and have been delayed to 1982 due to difficulties in the supply of the borosilicate samples with plane and parallel surfaces.

#### Post-irradiation examination of the glass samples (BONI III) irradiated in the HFR reactor, Petten

The results obtained with the capsules BONI I and BONI II have shown the validity of the damage simulation by fission fragments. The highest dose received by the samples was 0.36 dpa corresponding to a damage period for vitrified HAW of about  $10^5$  years.

It appeared convenient to use this simulation technique to reach an equivalent time of the order of 1 million years.

Previous experiments have shown that a source of error was the temperature distribution inside the cylindrical glass sample. In fact the glass cylinders ( $\varnothing = 10$  mm) with the highest U-235 content (1.7 w%) had a surface temperature of 50°C and a central temperature of about 75°C. In order to reduce the inhomogeneity in temperature, annular samples were used in the new irradiation experiments.

The irradiation in the HFR reactor, Petten, finished in December 1980. Due to delay in the transport the samples were available at Ispra only in July 1981. The samples will be used mainly to test possible leach rate variation due to irradiation. The capsules were introduced in the dismantling cell to retrieve the irradiated samples. After cutting the heads of the capsules it was realized that the samples were blocked. An additional tool is in preparation to cut longitudinally the capsules.

The leaching system has been tested and is ready for introduction in the cell.

#### Studies on damage effects and annealing in silica using optical techniques

The results previously reported were obtained using a single type of particle for each separate experiment. However, during storage of a nuclear waste, several sources of irradiation are acting simultaneously with a wide range of mass and energy, including electrons, alpha particles and the recoils of heavy actinides. The various effects of nuclear displacement, ionization and implantation of all these particles, on the concentration of the atomic defects and on the chemical bonding may be superimposed.

In order to acquire some information about the general pattern of the total damage produced by the combined actions of different particles, we have further measured the optical absorption spectra of silica glasses bombarded with light

and heavy radiations applied both separately and in sequence upon the same sample.

The result is shown in Fig. 1, where an optical spectrum of a proton reirradiated sample is compared with the spectrum of the original heavy ion irradiated sample. The  $B_2$  band, characteristic of heavy ion irradiation, decreases, while the  $E_1$ , present after all types of irradiation, increases. Two hypotheses can be made: i) the hydrogen atoms interact with the  $B_2$  centers destroying them; ii) the radiation annealing is very efficient for these types of defects. To better clarify this point double irradiation alpha + heavy ions are in course. In any case it can be deduced that the final form of the damage cannot be foreseen only on the basis of displaced atoms but it has to take into account preexisting defects, ionization effects and radiation annealing.

### Observations at the HV electron microscope

The systematic study of the growth of bubbles under electron irradiations in borosilicate glasses has been pursued in order to evaluate the swelling parameter and to associate it to the displacement process of single defects. In any case it is confirmed that this effect starts at dose rates much higher than those expected during storage of HLW.

A typical series of photos illustrating this phenomenon is shown in Fig. 2. The first picture shows the starting of the effect at a dose rate of  $7.10^{19}$  e/cm<sup>2</sup>. sec. The other two pic-

tures are taken after 30'' and 90'' of irradiation at the same dose rate. The vacancy production rate required to give the observed bubble swelling rate is  $1.4 \cdot 10^{21}$  per electron/cm<sup>2</sup> corresponding to a displacement cross section exceeding 1000 barns, which would necessitate that the energy for direct displacement be of the order of 2 eV. This is too low since the Si-O bond energy is about 6eV. Therefore either displacements are made indirectly (via ionization) or vacancies are preexisting.

In this second case only the oxygen atoms are released by the knock-on displacement processes. If sufficient vacancies are present and they are mobile at 600°K the displacement cross section for oxygen (calculated on the basis of the pressure in the bubbles of 250 dynes/cm<sup>2</sup>) would be ~ 5 barns, which correspond to an energy for displacement of ~ 68 eV. This is an effective value, the real value must be less. However, this value for displacement is more realistic than the 2 eV estimated in the hypothesis of vacancies creation.

Concerning phase separation effect, further experiments are necessary. In fact although the number of  $\beta$  decays during waste storage is much lower than the electron doses adopted in our in situ electron irradiation, the corresponding dpa is comparable to that occurring during the first 10-100 years of storage when all types of displacive particles are considered. Therefore it is necessary to ascertain whether the phase separation is related to the specific kind of irradiating particle (electron) or to the dpa values.

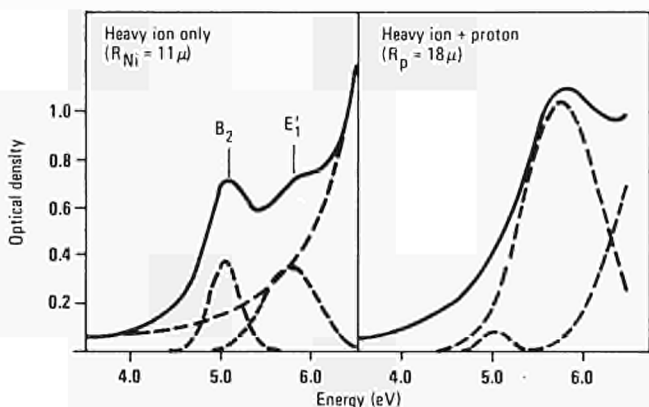


Fig. 1. Combined effect of heavy ion and proton irradiations on silica

### Leaching and corrosion experiments

#### Leaching and corrosion tests in montmorillonite/sand paste

A series of tests has been carried out to investigate the leaching behaviour of the glasses in conditions similar to those existing in a repository. In normal repository conditions the amount of water in contact with the glass is very limited so that the water composition is influenced by the glass leaching and by the surrounding materials.

If we assume that a sufficient time is passed so that the container is completely dissolved, the glass will be in contact with the backfilling material and the corrosion products of the container. The knowledge of the mechanism of corrosion and depolarization of the container is not sufficiently advanced to know if the corrosion products will be hydroxi-

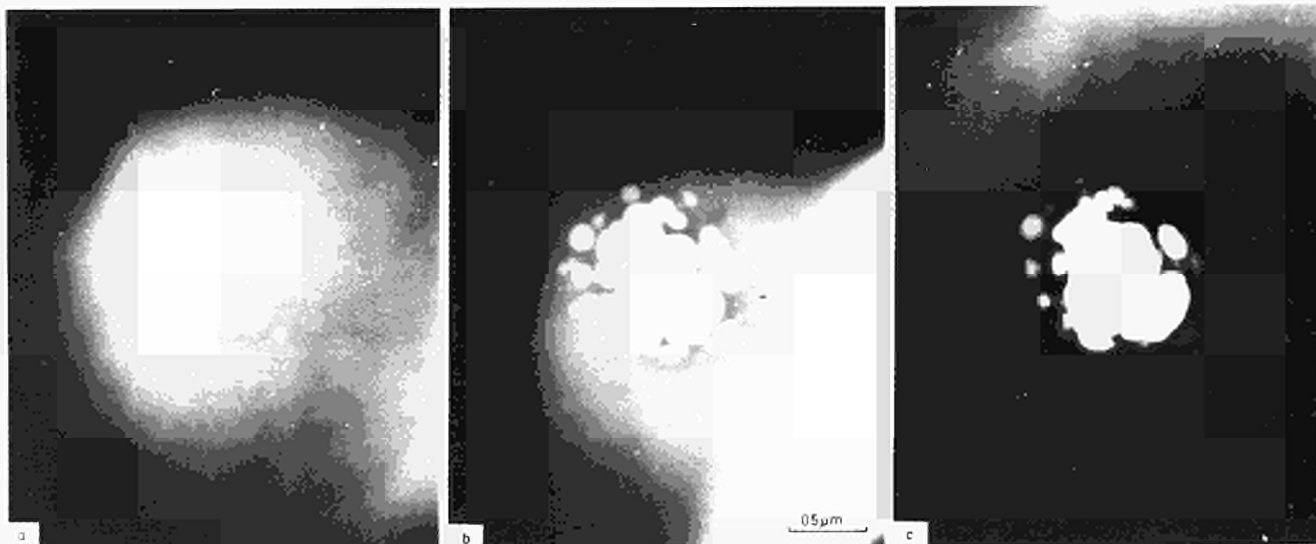


Fig. 2. Bubble formation in the electron irradiation of borosilicate glasses: observation at the HV electron microscope



des or sulphides. For the moment they have been simulated with  $\text{Fe}_2\text{O}_3$ .

With the exception of the salt repository, where the backfilling is the salt itself generally clay or mixture of clay and sand are proposed. Sand is added in order to improve the heat exchange. It was decided to utilize in the experiment a mixture of 20% sand and 80% montmorillonite and a mixture of 20% sand, 70% montmorillonite, 10%  $\text{Fe}_2\text{O}_3$  in order to evaluate the influence of the container corrosion products.

It has to be pointed out that in the previous Programme Progress Report we have erroneously indicated bentonite in place of montmorillonite as component of the mixture.

To take into account the slow penetration of the water in this mixture, the glass is immersed in a paste composed by 60% of water and 40% of the mixture sand-montmorillonite. Two types of water are utilized in the experiments: distilled water and water characteristic of the clay interstices. The experiments are carried out at 50° and 80°C.

The tests are performed in sealed glass capsules containing the paste, in which the glass is immersed, with a certain amount of supernatant water. The leaching rate is determined by means of weight loss measurements on glass samples extracted successively every three weeks. The surface is analyzed by the ESCA method.

Tests have been performed for 60 weeks.

The results reported in Fig. 3 and 4 show that, when distilled water is used, the weight losses for the samples immersed in the paste are similar to those measured in flowing water. When water typical of the clay interstices is used in the paste, the leaching rate is initially higher but after 30 weeks reaches a value similar to that measured operating with pure water.

Samples immersed in the paste containing 10%  $\text{Fe}_2\text{O}_3$  appear to have a more rapid saturation in the weight loss; a statistical analysis is in progress to verify this point.

A possible explanation of these results is that the various elements leached from the glass are trapped by the montmorillonite which acts as an ion exchanger.

In these conditions the composition of the water in contact with the glass is not modified by the element release so that the leaching rate is similar to that obtained in flowing water. Only when the ion exchange capacity of the montmorillonite is saturated, the water composition is modified by the element release with a consequent effect on the leaching rate.

Thus the leaching rate is controlled by the absorption capacity of the clay and by diffusion.

A similar experiment has been conducted under a gamma field in the cooling pond of the spent fuels of the Essor reactor.

The test lasted 6 months. The gamma field at the beginning of the experiment was 10,000 R/h and decreased exponentially being 1,000 R/h after 6 months. Nine samples were tested under different conditions at 50°C. As the results were similar to those obtained in the absence of a gamma field we can conclude that at this level of irradiation the effect of the gamma field is negligible.

A first series of surface analyses has been performed. The difference, in comparison with the composition of the layer in the case of leaching in a large amount of water, is remarkable. While at 80°C, in a large amount of water, iron hydroxide was the main constituent and silicon content was very low, the surface of sample leached in the paste has a very low content of iron and a very high content of silicon. It is possible that the layer developed in the paste has a better stability than the previous one. Other analyses are planned to determine the surface composition for the samples leached for 60 weeks.

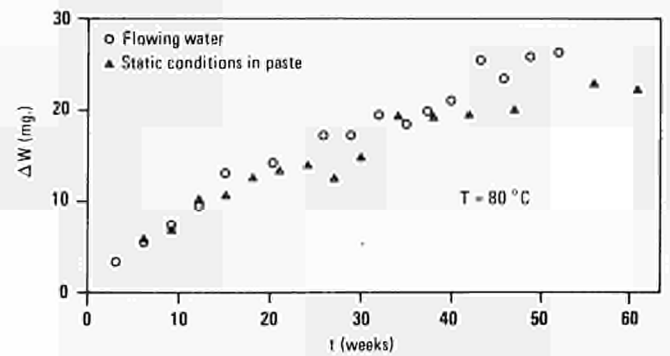


Fig. 3. Leaching of borosilicate glasses

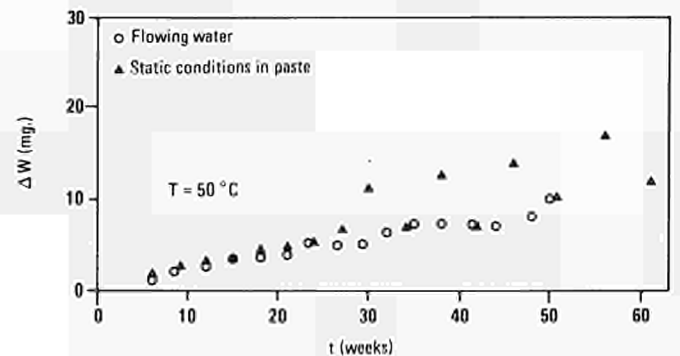


Fig. 4. Leaching of borosilicate glasses

From the results obtained it appears that it is not possible to separate the leaching of the glasses from the study of the backfilling or more in general of absorbent systems, like clay, in which the transport is controlled by diffusion.

For this reason we are setting up a test in which the glass leaching and the diffusion in clay are studied simultaneously. Fig. 5 shows the experimental arrangement. A piston presses a column of clay against a small block of glass casted in a steel crucible. The system is introduced in a thermostat. After due time the glass is removed and weighed; the diffusion of the elements in the column is determined by the analysis of various layers.

Preliminary tests have started on the system.

It is planned to operate initially using inactive glasses and later using glasses spiked with different radionuclides.

In the previous tests performed at 50°C and 80°C in the montmorillonite/sand paste, samples of stainless steel AISI 310 and AISI 430 have shown no detectable corrosion. The conditions were mild but, particularly for the 1 year tests at 80°C some corrosion and consequent weight loss were expected.

The absence of corrosion may be explained by the fact that the samples were immersed in a paste where the oxygen required for corrosion, was controlled by a diffusion mechanism.

One of the proposed solutions for waste containers is based on the use of large thicknesses of low cost corrodible materials. It appears interesting to study the behaviour of these materials in a porous system where the diffusion of oxygen may control the corrosion rate; to this purpose a test is being designed.

#### Leaching tests on borosilicate glasses containing Pu and Tc

The leaching tests on the borosilicate glasses loaded with plutonium and fission products, provided by CEA Marcoule,

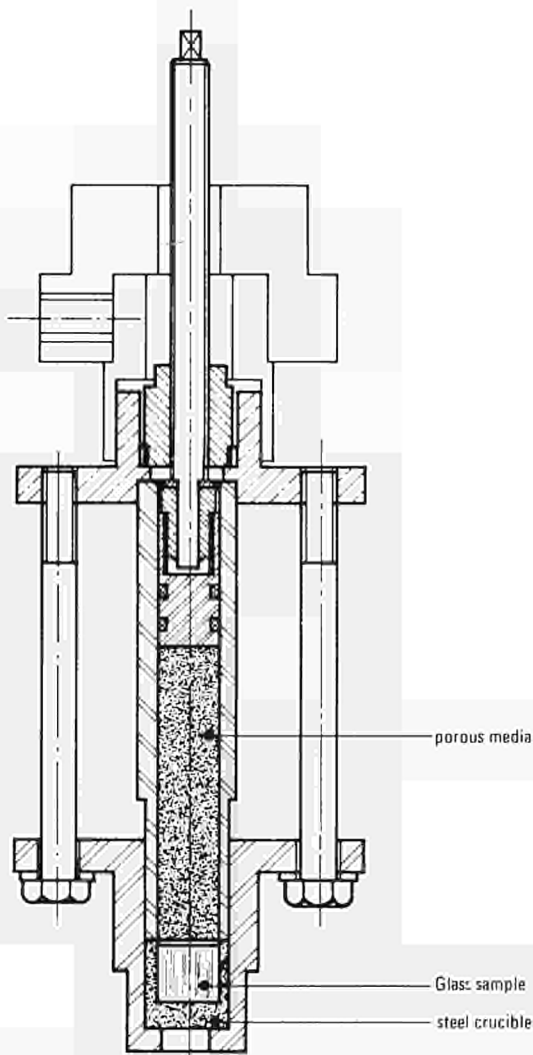


Fig. 5. Apparatus for the study of leaching and diffusion in porous media.

have been completed. The tests have been conducted following the procedure recommended by ISO. In the experiments a strong influence of the substitution time on the leaching rate was observed. The leaching rate of plutonium measured at 80°C was higher by a factor 4 than at 50°C. Analyses of the Pu content on the surface layer and on the base glass have been performed. The final report will be published at the end of 1981.

Glass samples containing 2% of Tc-99 have been prepared using a graphite crucible. The tests on this glass have been deleted waiting for the preliminary results of the leaching-diffusion experiments.

#### Modelling of the dissolution of a fissured block of borosilicate glass

Following the request of the risk analysis group a model of the dissolution of a fissured block is being set-up.

An increase of the surface by a factor 15 has been calculated due to the fracturing during cooling of the melted block in air.

The fissured block is treated as a sum of independent bricks, having a continuous distribution of dimensions, which dissolve gradually in time.

A comparison with the existing models shows that this model is particularly interesting when not only the initial release is requested but also the release as a function of time up to the complete dissolution.

A final report has been written and will be published shortly.

#### Corrosion tests on punctured containers

In normal engineering practice the localized corrosion is considered particularly dangerous as, with the attack of a limited amount of material, it can put out of operation the system considered. It seemed worthwhile to evaluate the importance of pitting in the case of a glass container.

Glass samples were melted in AISI 316 stainless steel crucibles. The upper part was cut and made smooth in order to offer a free surface to the leaching. In addition in the wall of the crucible a small hole, 1 mm. in diameter, was made.

Samples were introduced in autoclaves at 80, 100, 120, 150°C in order to compare the attack to the free surface with that at the bottom of the hole. Aim of the experiment was also to verify if at the interface between steel and glass a preferential attack was taking place.

Tests of 6 months duration have been completed. No particular attack is observed at the glass-steel interface. The observation of the glass at the bottom of the hole shows a negligible attack much lower than that occurring at the free upper surface. The weight losses of the samples with the hole were the same measured for the samples without hole. A new set of tests is in preparation without leaching of the upper surface in order to measure the leaching rate in the bottom of the hole.

#### Setting-up of an experimental facility for surface analysis

A better knowledge of the basic mechanisms of leaching is required to make possible correct evaluations of the long-term stability of borosilicate glasses for various repository conditions.

In this connection an experimental facility is being set-up at the J.R.C. Ispra for the measurement of the relevant surface quantities which determine the mechanisms of leaching:

- concentration profiles, bonding and valence state of the various elements and impurities at the surface of leached and unleached glasses;
- structural properties of the surfaces as a function of the leaching conditions.

The experimental facility for surface characterization will include Electron Spectroscopy for Chemical Analysis (ESCA), Auger Electron Spectroscopy (AES), Scanning Auger Microscopy (SAM).

The facility is expected to be installed in March 1982.

Meanwhile, some measurements involving these techniques will be performed at external laboratories.

A feasibility study is in progress on the possible use of measurements of X-ray absorption line structures for the determination of the valence state of technetium in borosilicate glasses.

The study is made in collaboration with the University of Strathclyde (U.K.) and the LURE Laboratory at Orsay (France).

First measurements carried out on two reference compounds,  $TcO_2$  and  $NaTcO_4$ , by a synchrotron radiation source (LURE, Orsay), have given promising results on the possibility to distinguish the valence states  $Tc^{+4}$  and  $Tc^{+7}$ .

#### Special matrix for conditioning of actinides + rare earths

In the course of the preparation of samples of ortophosphate of the monazite family it was realized that the main problem to be resolved was of technological nature. Monazite

by itself presents a low value of leaching rate. The real problem however is not the preparation of a material with a low leaching rate but the preparation of blocks of reasonable size having a low specific surface. The release rate of the radioactive material is in fact equal to the product of the leaching rate multiplied by the exposed surface.

It is this last parameter which imposes the most stringent requirements. In order to prepare a representative sample without porosities or cracks it is necessary to perform technological tests which require a large effort in personnel and budget.

Thus it was decided to stop the actual tests and to follow the development of synthetic minerals, like Synroc.

If simple method of preparation of large blocks of ceramic materials with a low specific surface will be reported in literature, the work on monazite type ceramics will be resumed.

### ***Collaboration with External Organizations***

Contract with AERE Harwell concerning irradiation experiments, electron microscopy examinations and theoretical investigations.

Collaboration with the University of Modena on theoretical aspects of the radiation damage.

Collaboration with CEA Marcoule on the leaching of glasses loaded with plutonium.

Collaboration with the University of Strathclyde and the LURE Laboratory at Orsay on application of measurements of X-ray absorption fine structure.

## **TOPICAL REPORT**

### **A Critical Review of Radiation Effects on Borosilicate Glasses**

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#### **Abstract**

A critical review of radiation effects on borosilicate glasses having the typical composition of those used for high-level nuclear waste storage is presented. In order to compare results obtained using particles of different mass and energy, a common dose unit based on the fractional number of displaced atoms is utilized (dpa) after some description of the fundamental damage processes which are taking place at atomic and electronic level during irradiation.

The results of measurements performed in various experimental conditions are thus compared including density changes, stored energy, microstructural changes and leaching.

Some comments are given about the conventional choice of 25 eV for the energy of atomic displacements which controls the assumed dpa values.

## **Introduction**

The radiation behaviour of glasses has been extensively studied both in the past and in more recent years in connection with various applications of these materials which require a high stability under different forms of radiation. We remember, for instance, the early works of Primak on radiation compaction of silica (1) and the review of Le Clerc (2).

A new interest appeared after 1975 due to the works on borosilicate glasses as possible matrices to incorporate high-level nuclear wastes. In order to act as a barrier against the dispersion of radioactivity, these glasses must be stable over very long times, at least of the order of one hundred thousand years, a period during which a relatively large dose of irradiation, consisting of  $\gamma$ -rays, high energy electrons and recoils of  $\alpha$ -particles is accumulated.

In view of such a large spectrum of masses, energies and charges, as well as of the complex composition of the waste glasses, it is not easy to correlate most of the previous work, aimed at characterizing fundamental quantities, with present studies in which most relevant quantities are density variations, storage of irradiation energy and leaching from water solutions. A suitable approach for the purpose of comparing the effects of the different particles is to define an appropriate unit for dose measurements. Such a quantity is also required in simulation experiments, where the desired accumulation of damage is reached much more rapidly than in real storage conditions, so as to reduce costs and times. The simulation, however, in order to be valid, must also indicate the dependence of the observed damage upon the rate at which it is produced. Such a necessity requires in turn a knowledge of the basic processes which take place during the irradiation of the glass at a microscopic and atomistic level.

In the following, we shall describe with some comments the results obtained in various laboratories, including our laboratory at JRC-Ispra, on density changes, stored energy and leaching of glasses irradiated with particles of various masses and energy, using the fractional number of displaced atoms (dpa) as a common dose unit.

The justification of such a choice will be given in terms of the fundamental damage processes. Some attention will also be devoted to microstructural changes such as recrystallization effects and the growing of defective aggregates which may alter the mechanical and thermal stability of the glasses and eventually the leaching rate.

When available, the effects observed in glass of simple composition will be reviewed so as to provide a basis of reference for the more complex systems. In this framework some data on pure  $\text{SiO}_2$  will also be included.

### **Defects in Glasses and Definition of Unit for Damage Measurements**

#### **Basic Defects**

At the microscopic level, the most prominent effects of exposure to irradiation and particle bombardment are the cleavage of atomic bonds and the direct displacement of atoms, with subsequent readjustment of local atomic and electron structures, and microstructural modification. Owing to the complex composition of glasses containing nuclear wastes, a large number of defect configurations can be generated from these elementary phenomena. However, a schematic analysis of the basic processes taking place in simple glasses, such as pure  $\text{SiO}_2$ , constitutes

a suitable framework of reference for the interpretation of radiation effects in more complex materials. A typical tool for the analysis of the defects in pure silica is optical spectroscopy (3, 7). Concerning the detection of defects two cases may be distinguished: a) defects for which it is not necessary to lose or to trap an electron to give an observable optical effect and b) defects that may be only visible after the loss or the capture of an electron.

In this most usual case a defect becomes observable after irradiation by ionizing radiation which in this case assumes the role, not of creating defects, but to allow to examine by optical means preexisting ones. This technique has been used in amorphous silica samples (8) after bombardment with  $\text{Ni}^{+6}$  ions (46.5 MeV) to produce a large number of atomic displacements as in the case of  $\alpha$ -recoils. A comparison has been made with other samples, having the same impurity content, which have been irradiated with electrons of 1.5 MeV.

Optical absorption spectra, induced with these treatments have been analyzed. The comparison between results obtained from heavy ion and electron irradiated samples indicates that the  $B_2$  band at 5.06 eV is related to displacement of atoms while the  $E'_1$  band at 5.76 eV is related to ionizing efficiency (Fig. 1).

The study of dose dependence shows saturation of colour centres for both types of irradiation: in the case of heavy ions saturation is attained when the dose exceeds  $10^{14}$   $\text{Ni}^{+6}/\text{cm}^2$  ( $\sim 0.01$  dpa); in the case of electrons, saturation begins at doses greater than  $10^{17}$   $\text{e}/\text{cm}^2$ .

The saturation level depends on irradiation temperature (a factor 2 lower at  $150^\circ\text{C}$  compared to room temperature). Isochronal annealing at various temperatures have been made on the irradiated samples.

Both centres annealed out at a temperature of  $\sim 500^\circ\text{C}$ . In order to distinguish between the annealing of the colour centre and the annealing of the defect causing the colour centre, identical samples, one pre-irradiated with heavy ions and the other unirradiated, were annealed at different temperatures up to  $1000^\circ\text{C}$  and subsequently irradiated with electrons. The analysis of the obtained spectra indicates that while the coloration effect was totally removed at a temperature of  $\sim 600^\circ\text{C}$ , the damage remained at temperature up to  $1000^\circ\text{C}$ .

Thus, experimental evidence has been obtained for the presence of defects of different nature in the irradiated silica glasses, as well as some information about their creation and annealing behaviour. It is thus opportune to examine how these defects may influence the physical properties determining the stability of glasses.

Fully displaced atoms may migrate to form agglomerates or to be captured at interstitial sites within the rather open structure of the amorphous network. Broken bonds may alter the local atomic configuration, leading to various effects such as, for example, density variations. In this case the number of introduced defects is a function of the number of displaced atoms (i.e. energy spent in elastic collision) and/or of the broken bond (i.e. total energy).

### Definition of a Dose Unit for Damage Measurements

In order to compare the damage produced by the different types of radiation it is necessary to have a common basis of measurements.

We have to choose between total dissipated energy and energy spent in displacements. Historically, the physical quantity which has been firstly examined, i.e. stored energy, seemed to depend upon displaced atoms (9) and not on total dissipated energy (10). Therefore, as a unit of damage measurement the number of displaced atoms is generally considered. However, when discussing the different technological implications of the radiation damage, it will be worthwhile also to discuss the influence of the ionizing radiation.

Many authors (9, 11) have indicated methods for the evaluation of the number of displaced atoms as a function of the mass and energy of the incident particle. For this computation we need to know the energy  $E_d$  required for a simple displacement. This value for glasses can be only estimated. In analogy with metals a value of 25 eV has originally been assumed by Jenks and Bopp (9). It should be recalled, however, that for quartz Gopal Das (12) has found a value 5.4 eV for Si and 9.5 eV for  $\text{O}_2$ . Experiments performed by bombarding a glass with a beam of accelerated electrons seem to indicate that the lower values (i.e. 9.5 eV) cannot be excluded. We have calculated the number of displaced atoms for different types of events for an  $E_d$  of 25 and 9.5 eV (see Table I).

It can be seen that in general such a number is inversely proportional to the displacement energy, with the exception of  $\beta$ -rays which become important only in the case of a low  $E_d$ . A calculation has been performed (see Appendix 1) in order to evaluate the total number of displacements in a typical HLW glass up to one million years. We can see that in the long term, even for low  $E_d$ -values, the role of  $\beta$ -rays is negligible. For this reason, while waiting for a confirmed value of  $E_d$ , we will assume the traditional value of 25 eV, and we will compare the different effects assuming as a unit of dose the dpa calculated in this way.

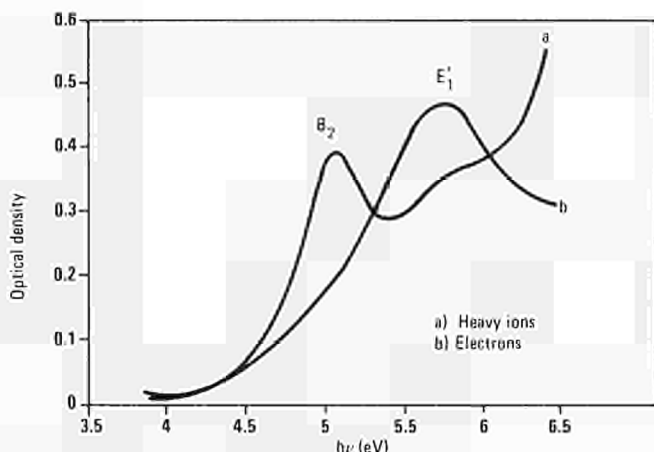


Fig. 1. Absorption spectra of irradiated silica

## Structural and Microstructural Modification

### Pure Silica Glass

A reasonable assessment of the effect of irradiation on the atomic and microstructural configuration of waste borosilicate glasses has to take into account that (notwithstanding the absence of long-range order) these compounds are characterized by a strong short-range order, owing to the covalent and ionic character of the Si-O atomic bonding.

In the case of amorphous silica an extensive densification and a large amount of stored energy is observed after irradiation. Silica densification occurs also under electron irradiation. W. Krättschmer (14) noted that under a 20 keV electron irradiation silica glass increases its density. The compaction becomes saturated at a dose of  $10^{15}$   $\text{erg}/\text{g}$  corre-

Table 1. Number of Displaced Atoms

Types of Radiation	Number of Displ. $E_d = 25 \text{ eV}$	Number of Displ. $E_d = 9.5 \text{ eV}$	Method Used
$\alpha$	134	365	Kinchin - Pease <sup>37</sup>
$\alpha$ - recoil 6 MeV 5 MeV	2,000 1,670	5,260 4,380	Kinchin - Pease <sup>37</sup>
fast neutrons	220	580	Dienes - Vineyard <sup>38</sup>
$\beta$ 0.5 MeV 1.0 MeV 2.0 MeV	0.8 1.2 2	4 6 9	O.S. Oen <sup>39</sup>
fission fragments	25,000	68,000	Bethe - Ashkin <sup>40</sup>
$\text{Ni}^{6+}$ (46.5 MeV)	8,000	22,000	M.D. Matthews <sup>41</sup>

sponding to a density increase of 2.4%. When the silica glass is bombarded with neutrons or ions an even larger densification occurs. As a matter of fact every allotropic form of silica submitted to radiation changes its density (either increasing or decreasing it) until it reaches a final state, which apparently is the same, irrespective of the initial state (1). The density of this final state is 2.26 g/cm<sup>3</sup> which, with respect to silica glass, corresponds to a density increase of 2.8%. The final state is reached only after a heavy dose of radiation, and it seems to show more short-range order than the initial amorphous one. Early measurements of X-rays and neutron diffraction seemed to indicate that small crystalline regions are formed after neutron irradiation, but more recent results obtained by Lorch (15) and Wright and Sinclair (16) have confirmed the original conclusions of Simon (17) that vitreous silica reached a new "metamictic structure", after irradiation, in which the values of the bonding angles and the bonding distances (Si-Si) are more widely scattered with respect to the unirradiated phase. We can therefore expect that, in general, irradiation of silica-based glasses generates a tendency toward a higher degree of disorder, which, however, does not strongly affect the SiO<sub>2</sub> unit. We can thus see that as far as density variation is concerned, not only displaced atoms, but also ionizing energy plays a role.

Experiments performed by bombarding amorphous silica with Ni-ions at an energy of 46.5 MeV have shown a stored energy of the order of 800 J/g (18). Such a value is too high to be attributed to single defects.

It seems that this is connected with the formation of a metastable structure which tends to return to the original state when heated to temperatures higher than 300°C.

### Borosilicate Glasses

The case of borosilicate glasses is more complex. As boron oxide is a glass former, a phase separation in borosilicate glasses is commonly observed after an appropriate heat treatment (19). Density variations are observed which seem to depend upon the initial composition. Shelby (20) has studied the variation in density of a series of borosilicate glasses under Co-60 irradiation. The density increase is roughly proportional to the boron content. For a B<sub>2</sub>O<sub>3</sub> content of 13.3% and a dose of 10<sup>10</sup> rad a density increase up to 1% is measured. Paymal (21) has studied the influence of a bombardment of thermal neutrons on a borosilicate glass containing 11.5% of B<sub>2</sub>O<sub>3</sub>.

B-10 reacts with neutrons giving Li-7 and He-4 which can badly damage the glass. Due to the very high neutron cross section of B-10 thin samples must be used to avoid inhomogeneities in the damage distribution. Densification occurs rapidly reaching a maximum of about 2% after 10<sup>18</sup> n/cm<sup>2</sup>, corresponding to 0.1 dpa.

### Borosilicate Glass Containing HLW

A borosilicate containing HLW is an even more complex system due to the presence of large amounts of different types of modifiers.

It should be noted that density variation can be an important effect from a technological viewpoint. When considering the behaviour of the waste container, a variation in glass density can induce variations in the stresses to which the container walls are subjected.

Density variations have been measured on borosilicate glasses loaded with Cm-244 or Pu-238 in the Battelle (22) and Harwell (23) laboratories. Measurements on samples damaged by fission products have been performed at Ispra. Fig. 2 gives the results obtained.

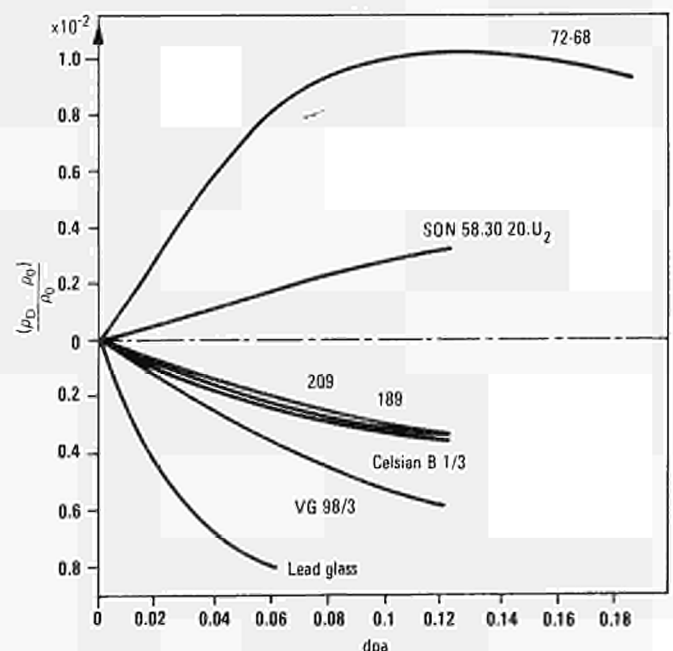


Fig. 2. Density variation as a function of the dose

We can see that some glasses show an increase of dimension while others show a decrease.

Marples (23) has analyzed the variation in density of a group of European glasses showing that the specific variation of density follows a law of the type:

$$\frac{\rho_D - \rho_0}{\rho_0} = A [1 - \exp(-\epsilon D)]$$

where  $\rho_0$  is the initial density,  $\rho_D$  the density at a certain dose,  $A$  the saturation value,  $\epsilon$  the fraction of the glass damaged by a unit dose  $D$ .

Experimental data are in good agreement with the proposed model.

It should be noted that the saturation values of complex glasses are lower than the value found for the amorphous silica. This can be explained by the presence of a large amount of metallic oxide which has no tendency in forming metastable states, so that even the silica present is sterically hindered in the transformations to the metastable state.

An attempt has been made (24) to evaluate systematically the dependence of the density variation at saturation on the glass composition, assuming that every glass will tend, under the effect of irradiation, to change its density towards an equilibrium value which can be calculated by averaging the densities of the different glass components.

Since preliminary results of the above study seem to be encouraging, it appears that a suitable choice of the glass composition might allow in the future to prepare a compound undergoing a minimum density change under irradiation.

As in the case of density variations the stored energy of complex glasses is also lower than in the amorphous silica. The energy deposition in the waste borosilicate glasses has been investigated using samples spiked with Pu-238 (23) or Cm-244 (22).

The stored energy measurements are around 50-70 J/g, and show a marked saturation for doses of the order of 0.1 dpa.

In order to rapidly reach a high level of damage, two different types of simulation have been tested (18). The first one makes use of the fission of uranium to produce the damage. The glass is doped with uranium and irradiated. The dpa obtained is limited by the need of avoiding too high a temperature inside the glass. A maximum value of 0.35 dpa has been reached. The second one consists of bombarding the glass with an external beam of highly energetic heavy ions. The sample must be very thin but the method has the advantage of reducing the time required to reach a heavy damage ( $\sim 1$  dpa) to the order of a few hours and to avoid the necessity of adding additional components. Stored energy values obtained in these experiments are in the same range as the values obtained in the actinide doping experiments. This has confirmed that as far as stored energy is concerned, the damage can be described by the number of the displaced atoms.

Between the uranium fission experiments and the accelerator experiments, a difference of 3 orders of magnitude exists in the dose rate. As no significant difference is noted, it can be concluded that stored energy is independent on the rate of damage.

If we compare the values obtained with the specific heat of the glass, the conclusion reached is that stored energy does not represent a problem in glass storing.

Stored energy depends strongly upon the temperature of irradiation; Roberts (25) found a decreasing linear relation between the near saturation value and the temperature. On

the basis of these results no stored energy is accumulated at the temperatures higher than 350°C.

## Microstructural Changes

When irradiation is present at a temperature at which point defects are mobile, defect clusters may be nucleated. The formation rate of voids and bubbles is controlled by the rate at which atoms can migrate (26).

As far as pure amorphous silica is concerned, no particular structure has been observed under electron bombardment even at high fluxes. Waste glasses containing 40% SiO<sub>2</sub>, 20% B<sub>2</sub>O<sub>3</sub>, and 20% waste products have been electron-bombarded and examined "in situ" by high voltage (1 MeV) electron microscopy by Gall et al. (27). At room temperature the tested glasses were unaffected by electron bombardment, even when subjected to particularly high doses. At 200°C and above, however, minute bubbles having a diameter of 200 Å were found to form.

This observation is partially confirmed by recent experiments performed with borosilicate glasses without HLW (13), where at 100°C large bubbles have been found after 1 MeV electron bombardment at a dose of about 10<sup>20</sup> e/cm<sup>2</sup>. This effect is, however, dose rate dependent and begins to appear at electron fluxes exceeding 10<sup>19</sup> e/cm<sup>2</sup>s. Moreover, at lower rates of electron bombardment, where bubble formation is not detectable, phase separation takes place forming planar regions which scatter electrons more than the matrix and give rise to a sharp contrast under electron microscope observation. Above 10<sup>21</sup> e/cm<sup>2</sup> these opaque regions begin to devitrify producing a diffraction pattern found to be consistent with that of high temperature tridymite SiO<sub>2</sub>.

A continuation of these experiments is needed to clarify the temperature influence and to see if similar effects are presented in borosilicate glasses incorporating HLW.

## Leaching of Radiation Damaged Glasses

### Early Etching Studies

Before the interest in borosilicate glasses as a conditioning matrix for radioactive wastes occurred, the effect of radiation on glass corrosion was studied by etching the glass with very aggressive systems, generally hydrofluoric acid solutions. Fleischer (28) found that fission fragment tracks, obtained by putting Cf-252 in contact with the glass surface, can be developed by etching with a hydrofluoric acid solution. Such an effect was observed in soda-lime glass, borosilicate glass and amorphous silica.

Krätschmer (14) irradiated amorphous silica with heavy ions and electrons. He found that by etching with a 40% hydrofluoric acid solution, the irradiated zone had an etching rate which was more elevated than the unirradiated one. Especially under electron bombardment there is a direct relation between density variation and increase in etching rate which reaches a maximum factor of 2.8.

In the case of ion bombardment, the maximum increase of the etching rate ( $\sim 10$ ) precedes the maximum of compaction and is probably due to the superposition of the various ion tracks.

When the borosilicate glasses began to be considered as a possible matrix, the resistance to leaching was considered the most important property and a large number of studies have been performed on the influence of radiation.

We note, however, that there is a fundamental difference between etching and leaching. While etching by a hydrofluoric solution is a direct dissolution process, leaching is a complex phenomenon.

In particular for multicomponent glasses the ionic exchange between alkalis and hydrogen ions can strongly modify the nature of the subsurface layer (29).

### Simulation with $\alpha$ -Emitters

Borosilicate glasses containing HLW have been tested under various types of irradiation conditions. A large number of tests have been performed on glasses loaded with actinides in order to produce an elevated number of displaced atoms. Table II summarises the results found in the literature. It can be seen that most of the results indicate no variation or negligible variation. Only for one glass was an increase of a factor 3 obtained. It should be noted that due to the cost for the preparation of the glasses and the time needed for the accumulation of the damage, no replication is generally undertaken, so that no indication of the statistical dispersion is available.

However, the totality of the samples indicates clearly that the radiation effect is small. Particularly interesting is the comparison of the Harwell results at room temperature and at 170°C. It must be remembered that stored energy, which can be directly related to the number of displaced atoms, decreases strongly with temperature.

Between values at normal temperature and values at 170°C a decrease in stored energy of a factor of 2 is noticeable (22). Nevertheless, as far as leaching is concerned, no sensible variation is obtained. Some doubt may exist concerning the conclusion that, as far as leaching is concerned, displaced atoms are the only damaging mechanism.

Following the suggestion of Krätchmer (14) we have tried to see whether there is a correlation between the variation in the leaching rate and the variation of density due to radiation. The available data are presented in Fig. 3. It is not possible to draw any conclusions, however it is remarkable to note that the largest variations in the leaching rate are observed for glasses which undergo compaction.

Table II. Tests with Glass Loaded with  $\alpha$ -Emitters

Laboratory	Type of Glass	$\alpha$ -Emitter	max dpa	Type of Test	Ki/K	Observations
Battelle <sup>22</sup>	72 - 68	Cm-244	0.066	IAEA modif.	2.1	Leachant pure water; measurement of potassium release
Karlsruhe <sup>42</sup>	Base borosilicate 98	Cm + Am	0.13	IAEA modif.	no effect	Leachants: carnallite solution and dilute salt solution; measurement of Cm and Am release; no increase with time
	98 + 16.6% HLW	Cm + Am	0.13	IAEA modif.	no effect	
	98 + 16.6% HLW + 9% Gd <sub>2</sub> O <sub>3</sub>	Cm + Am	0.13	IAEA modif.	no effect	
Marcoule <sup>30</sup>		Am-241 or Pu-238 or Cm-244	0.001	semistatic condition	no effect	Measurement of actinides release in tap water; no increase with time
Harwell <sup>23</sup>	189	Pu-238	0.11	Soxhlet	1.44-1.64	The leaching rate is obtained by measurement of the weight loss. The first data of Ki/K is referred to samples kept at room temperature during damage accumulation while the second is referred to samples kept at 170 °C
	209	Pu-238	0.11	Soxhlet	1.10-1.22	
	Son 58.30.20 U2	Pu-238	0.11	Soxhlet	3.05-1.63	
	VG 98/3	Pu-238	0.11	Soxhlet	1.32-1.07	
	Celsian B1/3	Pu-238	0.11	Soxhlet	0.81-0.97	

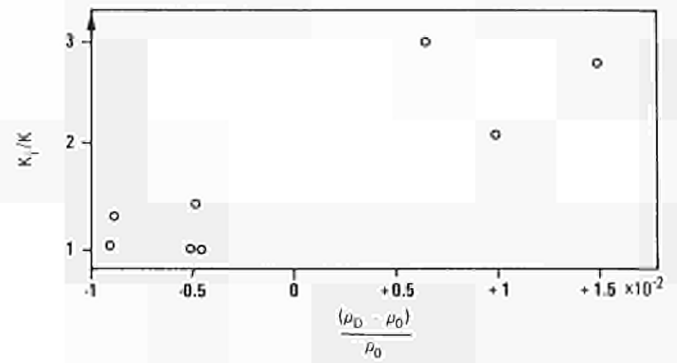


Fig. 3. Density variation vs leaching rate ratio

### Other Types of Simulation

Tests have been performed on samples which have sustained damage not by an emission of a particle but by some other sources of irradiation. It is obvious that under such a condition a comparison of damage with the real case is strictly connected to the evaluation of the damaging mechanism and the method of calculating the dose.

Irradiation with electrons up to  $1.2 \cdot 10^{11}$  rad (30) fails to show increase in the leaching rate by tap water.

Simulation experiments can be subdivided into two classes: bulk simulation studies and surface irradiation. A series of tests (31) have been performed loading a borosilicate glass (I 117) with various percentages of U-235 under a cadmium screen. Subsequent irradiation in a field of epithermal neutrons produced radiation damage up to 0.35 dpa. The glasses were tested using the Soxhlet method. No systematic variation of the leaching rate was observed. Surface irradiation has the advantage of accumulating rapidly high irradiation doses. However, there is the big disadvantage that the damage is only to a thin layer near the surface, and this gives rise to inhomogeneities which can introduce surface effects. J.C. Petit et al. (32, 33) have investigated the leaching properties of different types of glasses irradiated with a beam of lead ions having an energy of 1 keV/amu (208 keV).

The samples were covered with an electron microscope grid and irradiated with an integrated ion current of  $10^{10}$  up to  $10^{14}$  ions/cm<sup>2</sup>. The irradiated samples were subsequently leached with a NaCl solution (250 g/l) at 100°C. The leaching rate shows a strong increase around a dose of  $5 \cdot 10^{12}$  ions/cm<sup>2</sup> (0.03 dpa) which corresponds to the value at which the various tracks left by the incident ions start overlapping.

The first results presented by this worker (32) show a strong dependence upon the glass composition; the differential rate being as high as 2700 for low-level silica content glasses, but only 0.2 for pure silica.

Subsequent results show that the leaching rate also depends strongly upon the leachant used. For the glass I 117 the ratio of the leaching rates is 53 when salt brine is used, but goes down to 3 if pure water at 100°C is used.

It is difficult to give an interpretation to these results. It should be noted firstly that the critical dose corresponds, according to our calculations, to a displacement of 0.03 dpa, which is below the value obtained in experiments at Karlsruhe, Harwell and Ispra. No critical value of dose has been detected in those experiments.

Due to the fact that such an effect seems to be obtained with very high dose rates, it could be possible that dose rate plays a major role. In the discussion of the microstructural changes we have noted that the formation of bubbles is possible at high dose rate. It is possible that a similar effect occurs here with some sort of exfoliation when the samples are in contact with solutions which decrease the surface energy (34).

Moreover, this type of experiment only allows the measurement of the initial leaching process due to the fact that irradiation has damaged only a layer of 500 Å. The diffusion processes associated with the leaching phenomenon alter, in the long term, a subsurface layer which can reach a thickness higher than 500 Å. As a conclusion it does not seem that low energy ion bombardment can be considered as an acceptable method to simulate volume damage at low dose rates.

## Conclusions

The analysis of the data of the influence of radiation on the different properties shows that atom displacement is certainly an important mechanism causing damage. However, if the stored energy seems to depend only upon displaced atoms, for other phenomena such as, for example, density variation, ionization also plays a role; as far as leaching is concerned, the situation is not very clear due also to the uncertainty of the measurements.

The generally accepted value for the displacement energy of 25 eV seems to be too high and a more precise evaluation of this quantity and of its meaning in glasses, is strongly recommended.

The leaching of complex glasses, and particularly of glasses containing alkalis, in mildly aggressive media gives rise to compositional variation in the subsurface layer; a simulation of radiation damage by systems which interact with the entire volume seems therefore more realistic.

Microstructural variations consisting of bubble formation are possible but it seems likely that they will occur at doses rates higher than those expected in the real case.

The existing values for the examined properties seem to indicate that the effects of radiation will not greatly influence the stability of the glass at the doses and dose rates expected. An extension to higher doses could increase the confidence in the results obtained.

## APPENDIX 1

### Amount of Displaced Atoms Accumulated With Time

The relationship between the number of displaced atoms and the age of the glass depends upon many factors. Generally, calculations are performed assuming a standard PWR fuel element (burnup 33,000 MWd/t, U-235 enrichment 3.3%, change of fuel 1/3 every year) (35).

A major parameter is the amount of fission products which are present in the glass. We will assume that in order to incorporate the fission products and actinides coming from 1 THM of fuel 100 l of glass are used. In this case the glass will have a content of 15.1% of fission product and actinide oxides, which is probably a high value.

We note, however, that there is a direct proportionality between dpa in the glass and the fission product percentage in the glass.

As a first approximation, in order to calculate the number of displaced atoms, we will assume a glass density of 2.7 g/cm<sup>3</sup>, and for the elements constituting the glass a mean atomic mass and a mean atomic charge of 29 amu and 14, respectively.

Two series of calculations have been performed. The first one takes into account a displacement energy of 25 eV; the second uses an  $E_d$  of 9.5 eV. For the first series of calculations only the  $\alpha$ -emitters have been considered;  $\beta$ -rays and spontaneous fission under such conditions giving negligible contribution. In particular spontaneous fission after one million of years reaches only  $10^{11}$  fissions per gram of material (11). In the calculation the variation of the number of displaced atoms with the  $\alpha$ -emitters recoil energy has been taken into account. Five cases, have been analyzed:

- 1st Extraction of Pu and U with a yield of 99.5%. Fuel reprocessed after 1 year.
- 2nd Extraction of Pu and U with a yield of 99.5%. Fuel reprocessed after 10 years.
- 3rd Extraction of Pu and U with a yield of 99.8%. Fuel reprocessed after 1 year.
- 4th Extraction of Pu and U with a yield of 99.5%. Extraction of 80% of Np. Fuel reprocessed after 1 year.
- 5th Extraction of Pu and U with a yield of 99.5%. Additional presence of 1% Pu from other sources. Fuel reprocessed after 1 year.

The first case is generally considered the reference case. The second case underlines the effect due to the short life of Pu-241; the amount of Np-237 in the spent fuel increasing with time. The third case assumes a more efficient reprocessing, with U and Pu losses of only 0.2%. The fourth case assumes that 80% of the Np present in the fuel, is extracted together with Pu and U as is considered in the reference case of the coprocessing (36). The fifth case assumes that the glass is used also to condition wastes of different origin and thus has higher Pu-content.

The displacements per atom as function of time are expressed in Table III. We can see that in the long term the dpa's with the exception of the fourth case are practically the same for all the conditions considered. This is due to the fact that after 1000 years the number of disintegrations depends mainly upon the minor actinides and their daughters. In practice, with the exception of the Np-content, the only variable which influences the dpa is the volume of glass incorporating the waste. As a first approximation, as the relation between dpa and time is approximately linear in a dou-



Table III. Total Number of Displacements in the Glass as a Function of Storage Time

Time (years)	1st case	2nd case	3rd case	4th case	5th case
1	2.54 E - 3	8.58 E - 4	2.53 E - 3	2.54 E - 3	2.54 E - 3
5	7.18 E - 3	4.03 E - 3	7.16 E - 3	7.18 E - 3	7.21 E - 3
10	1.18 E - 2	7.46 E - 3	1.17 E - 2	1.18 E - 2	1.18 E - 2
50	3.16 E - 2	2.31 E - 2	3.13 E - 2	3.16 E - 2	3.19 E - 2
100	4.16 E - 2	3.20 E - 2	4.09 E - 2	4.15 E - 2	4.21 E - 2
500	8.06 E - 2	7.03 E - 2	7.83 E - 2	8.05 E - 2	8.25 E - 2
1,000	1.07 E - 1	9.64 E - 2	1.04 E - 1	1.07 E - 1	1.10 E - 1
5,000	1.62 E - 1	1.51 E - 1	1.56 E - 1	1.61 E - 1	1.68 E - 1
10,000	1.96 E - 1	1.85 E - 1	1.86 E - 1	1.94 E - 1	2.04 E - 1
50,000	3.08 E - 1	2.97 E - 1	2.98 E - 1	2.96 E - 1	3.24 E - 1
100,000	3.66 E - 1	3.55 E - 1	3.44 E - 1	3.32 E - 1	3.84 E - 1
200,000	4.70 E - 1	4.59 E - 1	4.46 E - 1	3.69 E - 1	4.90 E - 1
500,000	8.90 E - 1	8.77 E - 1	8.63 E - 1	4.95 E - 1	9.13 E - 1
1,000,000	1.65 -	1.64 -	1.61 -	7.19 E - 1	1.68 -

Table IV. Evaluation of the dpa in Glass. Displacement Energy 9.5 eV

Time (years)	dpa due to $\alpha$ -emitters	dpa due to $\beta$ -rays	Total dpa	% due to $\beta$ -rays
1	6.8 E - 3	1.7 E - 3	8.5 E - 3	22.0
5	1.92 E - 2	4.06 E - 3	2.33 E - 2	17.5
10	3.16 E - 2	5.47 E - 3	3.71 E - 2	14.7
50	8.49 E - 2	1.14 E - 2	9.63 E - 2	11.8
100	1.12 E - 1	1.38 E - 2	1.27 E - 1	11.6
500	2.16 E - 1	1.48 E - 2	2.31 E - 1	6.4
1,000	2.87 E - 1	1.48 E - 2	3.02 E - 1	4.9
5,000	4.34 E - 1	1.48 E - 2	4.49 E - 1	3.3
10,000	5.25 E - 1	1.48 E - 2	5.40 E - 1	2.7
50,000	8.27 E - 1	1.51 E - 2	8.42 E - 1	1.8
100,000	9.83 E - 1	1.54 E - 2	9.98 E - 1	1.5
200,000	1.26 -	1.59 E - 2	1.27 -	1.3
500,000	2.39 -	1.66 E - 2	2.41 -	0.7
1,000,000	4.44 -	1.78 E - 2	4.45 -	0.4

ble logarithm plot, we can write:

$$\log(\text{dpa}) = -0.351 - \log V + 0.413 \log t$$

where V is the amount of glass in litres produced to condition 1 THM of spent fuel.

A second series of calculations have been performed using a displacement energy of 9.5 eV. In this case also  $\beta$ -rays could contribute appreciably to the total number of displacements. Table IV shows the effect of the  $\alpha$ -emitters,  $\beta$ -rays and their relative importance for the reference case. For short times the influence of  $\beta$ -rays is important but with time decreases steadily, becoming less than 2% for times longer than 100,000 years.

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## Interaction of radionuclides with the environment

### Objectives

The objective of this activity is the quantitative description of the migration of radionuclides leached from conditioned wastes towards the biosphere, following an eventual release from the repository.

This activity involves the development of laboratory simulation techniques for studying natural environmental conditions, and the application of physico-chemical methods for investigating the speciation at extremely low concentrations.

The results of this activity should provide input data needed for risk assessment models.

For 1981 the following main studies were planned:

1. Behaviour of the colloidal forms.
  - Laboratory experiments on the retention and subsequent release of transuranics in various media.
  - Setting-up of microelectrophoresis instrumentation and photon correlation particle analyzer for the characterization of the colloidal forms.
  - Setting-up of a deep bed filtration model (under contract with a specialized laboratory).
2. Carbonate complexes.
  - Determination of stability constants of Am (III) and Np (V) complexes.
3. Technetium behaviour.
  - Determination of the chemical forms in the glass leachate.
  - Migration experiments in various media.
4. Chemical forms and bioavailability.
  - Development of methods for the determination of total quantities and chemical forms in environmental situations.
  - Studies of the relations between chemical forms and bioavailability for transuranics and technetium.

### Results

#### Behaviour of the colloidal forms

As reported previously the leaching of vitrified waste releases the radionuclides to the water vector partially by colloidal formation and partially by solubilization.

In the laboratory simulation experiments, the retention patterns of neptunium, plutonium and americium can be explained by the filtration effect of the media.

From characterization of the input distribution it has been shown that the soluble cationic species of these elements represent less than 3% of the total activity leached from the glass.

Thus the accumulation of transuranic nuclides within the first centimetres of the column must be due to a predominant filtration mechanism of neutral as well as negatively charged microcolloids and not to cationic fixation.

A further confirmation that the initial retention of the transuranics is mainly due to filtration of colloids, results from the examination of the profiles of activity as a function of percolation time.

In the Topical Report presented at the end of this section this particular aspect is discussed in detail.

The mathematical deep bed filtration model which takes into account the various retention mechanisms is under development by the Ecole di Mines de Paris (Armines) in the framework of a study contract started at the end of June.

In view of the clear importance of microcolloid behaviour during underground migration, an experimental study is being developed in order to characterize more clearly the colloids present in the vitrified waste leachate. Measuring techniques are being developed for the determination of their concentration, dimension and morphology as well as of their electrokinetic potential, and charge distribution.

The photon correlation particle analyser has been received during the month of June. This instrument uses the Brownian movement of particles suspended in a liquid for measurement of particle size. Illuminating the suspension with a laser, the scattered light from various particles will fluctuate due to their motion. The observation of these fluctuations with a photomultiplier, followed by an autocorrelation on the fluctuation of the photomultiplier out-put current yields a correlation function  $g(\tau)$ . This last is used to compute the particle size.

After assembly and optical alignment, a software programme has been developed to control the operations and parameters of the correlator and to elaborate the results.

Measurements on suspensions obtained from the leaching of a borosilicate glass in closed loops during some months at temperatures of 90°C, 40°C and 15°C show the same particle size for the three tests: 0.088 microns  $\pm$  0.003, and a monodispersed suspension. On the contrary, a large polydispersion and an average particle size from 2 to 6 microns are measured on the suspensions obtained from the leaching of glasses containing technetium or americium in the percolation system.

In parallel to the fixation phenomena, a migration of "soluble" species of the radionuclides has also been observed. For the transuranic elements, a small part of the anionic leached fraction is found continuously at the outlet of the column. This may be considered to represent the truly soluble anionic species of the nuclides and it is believed that this corresponds to the formation of anionic complexes with carbonate ions present in the groundwater.

A confirmation of the hypothesis of anionic complexes formation has been obtained when the loaded columns were washed with uncontaminated groundwater. In this case as well, the concentration of the actinides at the outlet of the columns maintained their initial value. This indicates an insitu formation of a soluble anionic species by dissolution of the previously retained transuranic colloids.

These results demonstrate the crucial importance of this solubilisation mechanism for the long term underground transport of the leached radionuclides. If this theory is demonstrated, the concept of use of distribution constant  $K_d$  will consequently require reconsideration.

In view of these facts, investigations are being developed at the Joint Research Centre on the characterisation of carbonate complexes and on the measurements of their stability constants.

### Complex stability determination

A solvent extraction method has been chosen for determination of the kind of carbonate complexes formed in condition similar to groundwaters and their respective stability constants. The complexing effect is indicated by the lowering of the distribution coefficient ( $K_d$ ) as bicarbonate concentration is increased in solution. In figure 1 are reported the results obtained by reverse extraction of americium with  $3 \cdot 10^{-2}$  molar di-benzoyl-methane in benzene as a function of pH and total carbonate concentration.

The experimental  $K_d$  values have been employed for the determination of the equilibrium constants of the reactions listed in Table I.

The use of these equilibrium constants together with the hydrolysis constants of americium (literature values) make possible the computation of the complex stability constants (Table II) and consequently the indication of the relative importance of the various complexes in water solutions (fig. 2). The apparent differences in the formulation of the complexes in Table I and II is due to the fact that the method used does not allow the distinction between complexes having different number of water molecules in their formula. The formula reported in Table II are, in our opinion, the most probable in the range of pH and carbonate concentration investigated.

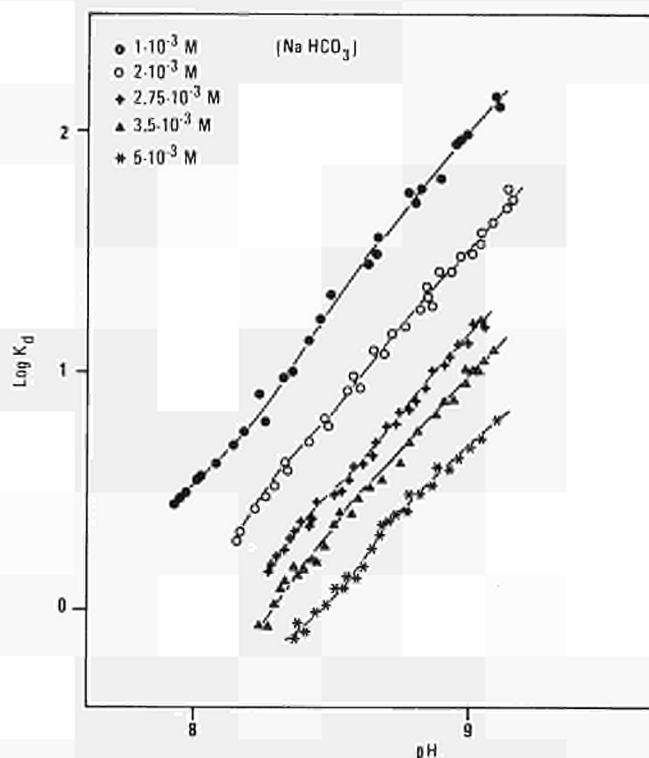


Fig. 1. Distribution coefficient at 22 °C of  $^{241}\text{Am}(\text{III})$  at various concentration of  $\text{NaHCO}_3$  ( $\Sigma\text{CO}_2$ ) as a function of pH. Organic phase = Di-benzoyl-methane  $3 \cdot 10^{-2}$  molar in benzene

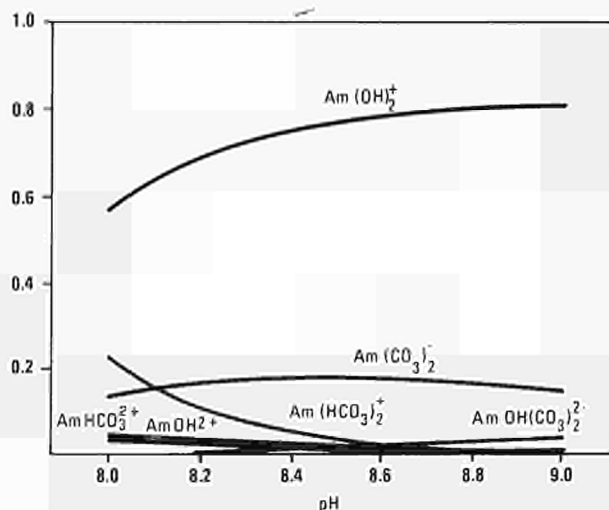


Fig. 2. Relative importance of the various soluble species of americium in groundwaters

Table I. Complexation reactions

	$k_{x,y}$	$\log k_{x,y}$
$\text{Am}^{3+} + \text{HCO}_3^- \rightleftharpoons \text{Am}(\text{HCO}_3)^{2+}$	$6.21 \cdot 10^4$	4.79
$\text{Am}^{3+} + 2\text{HCO}_3^- \rightleftharpoons \text{Am}(\text{HCO}_3)_2^+$	$1.41 \cdot 10^8$	8.15
$\text{Am}^{3+} + 2\text{OH}^- + 2\text{HCO}_3^- \rightleftharpoons \text{Am}(\text{OH})_2(\text{HCO}_3)_2^-$	$2.16 \cdot 10^{19}$	19.33
$\text{Am}^{3+} + 3\text{OH}^- + 2\text{HCO}_3^- \rightleftharpoons \text{Am}(\text{OH})_3(\text{HCO}_3)_2^{2-}$	$2.85 \cdot 10^{23}$	23.45

Table II. Stability constant of carbonate complexes

	$\beta_{x,y} = k_{x,y} \cdot k_w^\lambda (k_{\text{HCO}_3^-})^{-\lambda}$	$\log \beta_{x,y}$
$\text{Am}(\text{HCO}_3)_2^{2+}$	$6.21 \cdot 10^4$	4.79
$\text{Am}(\text{HCO}_3)_2^+$	$1.41 \cdot 10^8$	8.15
$\text{Am}(\text{CO}_3)_2^-$	$2.81 \cdot 10^{11}$	11.45
$\text{Am}(\text{OH})(\text{CO}_3)_2^{2-}$	$3.7 \cdot 10^{15}$	15.57

### Technetium behaviour

Technetium which is shown not to be retained by ultrafiltration, can be seen to migrate through the column with only a minimum of retention. Chemical analysis of input to the column showed that the species distribution was 85% anion and 15% cation respectively at the experimental redox condition adopted. At the outlet 100% of the activity was anionic, this represented over 70% of the total technetium leached from the glass.

These results are in contrast with the preliminary data presented in the previous progress report. The difficulties in obtaining reproducible results, for the case of technetium, is due to his huge tendency to be oxidized and to the difficulties in maintaining the percolation system out of contact of atmospheric oxygen.

In order to obtain proper results, during the reporting period a special experimental box under inert atmosphere has been set-up. A special measuring cell for dissolved oxygen determination has been designed making use of a membrane selective electrode. This device installed along the groundwater pathway has a detection limit of 20 ppb.

### Chemical forms and bioavailability

In the framework of the collaboration with DG XII Radiation Protection Programme a study has been developed to investigate the biogeochemical behaviour of plutonium and americium and the relations between chemical speciation and bioavailability.

The study is being carried out initially with the freshwater snail *Lymnaea Stagnalis* L.

In order to investigate the behaviour of plutonium further, particularly Pu (III) where little or no environmental data is available for comparison to Am (III), work on the stability of oxidation states is being carried out at the JRC. Experimental studies have been undertaken using the gamma emitting isotope  $^{237}\text{Pu}$  initially added in the III oxidation state, this being confirmed using thenoyltrifluoro acetone (TTA) solvent extraction procedures.

Fresh lake water in small volumes (100 ml) was used, with and without snails (*Lymnaea Stagnalis* L.), subsamples of the water being taken over a period of 29 days. By adding to these sub-samples  $^{236}\text{Pu}$  in the IV state and  $^{242}\text{Pu}$  in the VI state, to act as yield tracers, and by applying the method of

Lovett and Nelson for the separation of the reduced (III and IV) and oxidised (V and VI) species of plutonium, the variability of the Pu (III) form was monitored. These measurements were supplemented with further TTA extractions.

The experimental conditions and results are given in Figure 3 where the varying state of the plutonium species distribution with time is shown for the systems with and without snails. The figure shows that after two days, without any snails present, approximately half of the Pu (III) became oxidised to the V or VI states. Over the next 27 days this fraction then slowly decreased.

The TTA solvent extractions performed on the 13th and 29th day showed that the Pu (III) became slowly oxidised to Pu IV so that this latter form became the dominant reduced plutonium species. When snails are present no significant oxidation of the Pu (III) to the V or VI species is apparent, the plutonium staying in either III or IV reduced states.

Two points arise from these results. Firstly, the control experiment (without snails) demonstrated that changes in the chemical speciation of plutonium in-situ (and hence in its potential bioavailability) may be important. That transuranic chemical speciation is a dynamically active system must therefore be taken into account when estimating the environmental fate of transuranic releases and when subsequently making dose to man calculations. For these conse-

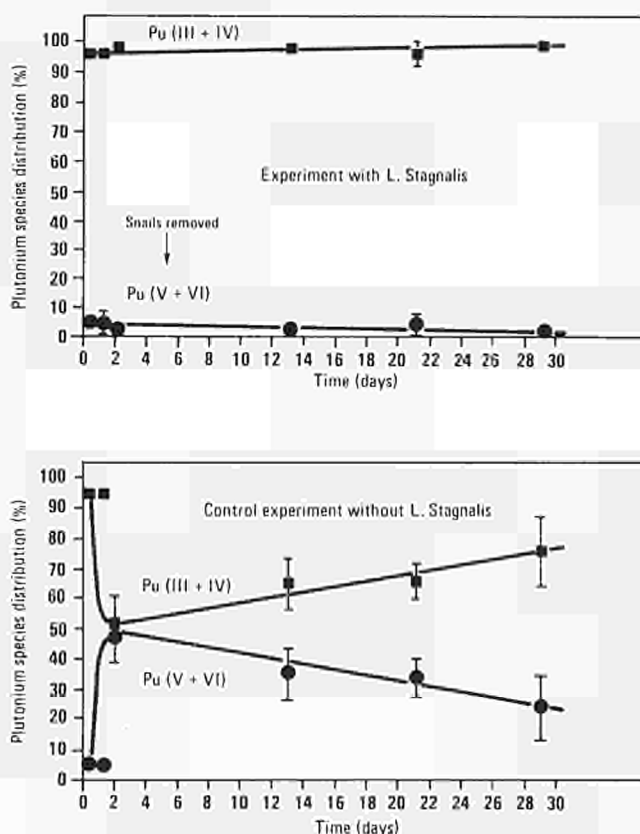


Fig. 3. Oxidation state distribution of  $^{237}\text{Pu}$  in time with and without the freshwater snail *L. stagnalis* (one sigma counting errors are shown).

Experiment with *L. Stagnalis* consisted of ten independent snail-water systems, 100 ml of natural lake water per snail. When sampling 10  $\mu\text{l}$  were taken from each system and combined into one 100  $\mu\text{l}$  sample.

Control experiment consisted of a single bottle of 100 ml natural lake water, 100  $\mu\text{l}$  sub-samples taken for analysis.  $^{237}\text{Pu}$  starting activity concentration in all systems was 2 nCi.ml<sup>-1</sup>. All experiments conducted at 21  $\pm$  1  $^\circ\text{C}$ .

quential effects to be accurately appraised not only must source terms be precisely characterized but also the behaviour of these elements in different environments be understood.

The second point is the ability of the snails themselves to effect the speciation of the plutonium. The apparent reducing effect of the snails compared with the control system may simply be an artifact of the closed experimental system; nevertheless, it indicates that under certain circumstances feed-back mechanisms from biota may be of potential importance in controlling the fate of transuranics.

### Collaboration with external organizations

Study contract with Armines for the development of a deep bed filtration model.

Collaborations have been established with laboratories working in the Radiation Protection Programme.

- Department of Radiobiology of CEN/SCK-Mol
- Biologische Anstalt, Helgoland, Hamburg
- Nantes University
- CNEN-Fiascherino

A collaboration has been established with the University of Padova concerning electrochemical analytical techniques for studying technetium behaviour.

Contacts are maintained with the IAEA Monaco Laboratory for studies on transuranics in the marine environment.

Collaboration will be established with laboratories working in the indirect action programme Management and Storage of Radioactive Waste, following the increase of the activity in the area of radionuclide migration.

## TOPICAL REPORT

### Underground Migration of Long-Lived Radionuclides Leached from a Borosilicate Glass Matrix

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#### Abstract

A programme on the safety analysis linked to the geological disposal of radioactive wastes is under study at the Joint Research Centre of the Commission of the European Communities at Ispra.

In relation with the migration of radionuclides in the terrestrial environment following an eventual release from the repository, specific experimental studies are being developed in order to provide the necessary input data for risk assessment models.

In the present paper the results of studies performed with neptunium, plutonium, americium and technetium isotopes leached from a borosilicate glass simulating the vitrified high level wastes are reported.

In order to simulate the expected conditions of glass leaching and underground transport in the laboratory, a water pathway is established which flows over the radioactive glass and then through columns containing typical soil samples. The columns are examined during the experiment by gamma scanning or cut into thin sections at the end of the run and the distribution profile of radioisotopes measured. Experimental results obtained on soil columns are compared with data obtained using filtering membranes and ion exchange resins. These experiments using borosilicate glass demonstrate the relative importance of colloidal filtration by the geological porous medium.

Following fixation it has been shown that slow rate processes probably account for the continuous small release of the radioactivity observed in the laboratory system. This long-term behaviour of colloids during the continuous percolation of groundwater is interpreted taking into account complex ion formation with inorganic ligands present in natural waters.

## Introduction

Schemes of management of the nuclear wastes involve their conversion to insoluble forms and subsequent storage in deep geological formations. Methods for long term safety analysis of geological disposal are therefore under study in many countries; at the Joint Research Centre of the Commission of the European Communities the barrier concept has been chosen (1).

This concept is based on the analysis of all the processes capable of causing the release of radioactivity from the repository and on the evaluation of the barriers which are present or may be interposed between the waste and mankind. The basis on which safety is evaluated (the "Barrier System") is represented in Figure 1.

Each barrier must be analysed on the basis of information available and a series of experimental studies are necessary to obtain better information on the controlling mechanisms and to furnish input data for the assessment models. These studies take into account — considering in particular the migration in the geosphere — retardation phenomena during the transport of radionuclides eventually leached from the repository.

The objectives of these experimental investigations can be summarized as follows:

- a) to assess the physico-chemical forms of radionuclides leached from vitrified wastes;

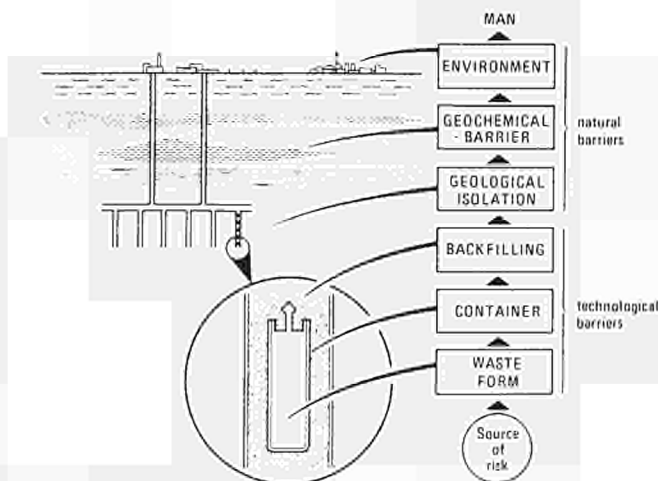


Fig. 1. The barrier system

- b) to describe their migration towards the biosphere following the eventual release from the repository;
- c) to study the environmental biogeochemistry of long-lived radionuclides;
- d) to provide the data base needed for safety assessment models.

As a matter of fact, the physico-chemical state of radionuclides governs their migration in the geosphere as well as their behaviour in the biosphere.

The source term of radionuclides in these studies is a borosilicate glass containing high-level waste origination from fuel reprocessing. This fuel cycle option is the one being most strongly supported by European countries. Contact of this vitrified waste with underground water represents the release mechanism that is considered in this study.

A number of release scenarios can be identified in a geological situation:

- 1) continuous contact of wastes with surrounding moisture (wet formation: clay, salt, sub-seabed) or with small quantity of nearly stagnant water (granite formation);
- 2) leaching of conditioned wastes due to accidental intrusion of a large quantity of groundwater;
- 3) continuous contact of wastes with moisture followed by accidental groundwater intrusion.

The released species are, therefore, a function of the release mode: in the first case the glass itself will cause a change in the chemical composition of the interstitial water surrounding the waste, giving rise in time to a gel-like source term. In the second case the glass comes into contact with a large amount of flowing water and the released species will be influenced by the composition of this water. In the third case the gel-like material will come into contact with a large volume of flowing water.

The different release mechanisms define the subsequent transport modes. In the wet formation scenario, transport will be mostly by diffusion processes through the stationary interstitial water of the media. This can be considered as the long-term normal behaviour of the geological repository. In contrast, the contact of the waste with a large quantity of water can be thought of as a consequence of an accidental event.

Depending upon the time in which this intrusion occurs, the water will come into contact with the borosilicate glass or the gel-type material mixture. The subsequent transport mode will be the migration of physico-chemical species through the porous or fractured media surrounding the repository.

The programme being undertaken by the Joint Research Centre, Ispra Establishment of the Commission of the European Communities, concerns the laboratory simulation of the accidental release corresponding to the second scenario considered.

In these studies, the conditions existing around the Boom clay formation in Belgium have been chosen as a reference case.

Since 1974 the CEN/SCK of Mol (Belgium) has been investigating the suitability of this formation as a potential disposal site for solidified radioactive wastes (2, 3). The long-term normal behaviour of the clay repository is under study by Belgian scientists; the contact of the waste with moisture and the eventual transport by diffusion processes in clay are considered in the repository evolution analysis.

The accidental failure scenario being considered by the JRC, consists of a faulting phenomenon causing radioactivity release to the overlying aquifer. The leached wastes are presumed to be high-level wastes conditioned as borosilicate glass, according to the AVM process (4). The experimen-

tal glasses containing 20% of simulated waste oxides and separately plutonium, americium, neptunium and technetium isotopes, have been produced in the laboratory. The concentrations correspond to the composition of vitrified high level waste after a storage time of 1000 years. The glasses are ground and sieved such that a material of fixed specific surface is used in the leaching and migration experiments.

In Figure 2 is schematised the experimental set-up adopted for the column migration studies. A water pathway is established which flows over the radioactive glass and then through columns containing samples of glauconitic sand which is the porous layer overlying the Boom clay formation. This sand layer has 34% porosity and permeability of about  $10^{-4}$  m/sec, and contains 20.0 wt% of glauconite. The synthetic water used has the typical composition of the aquifer where the glauconitic samples were collected (Table 1). The water reservoirs were always protected from contact with the atmosphere in order to control redox and pH conditions. The flow rate was controlled to give a linear velocity of 20 m/y corresponding to the natural groundwater situation. The radioactivity profile in the columns are measured by gamma scanning or by slicing the columns into thin sections followed by chemical separation and counting of the radionuclides. The physico-chemical forms of the radionuclides leached from the glass as well as those at the outlet of the columns are continuously monitored. This is undertaken using an analytical train consisting of an ultrafiltration system followed by ion exchange resins and a neutral fraction collector (5). The development of this laboratory simulation is considered to represent, reasonably well, the natural environmental conditions. This approach must, however, be evolved in the future to include considerations of the influence of container corrosion products and of eventual backfilling materials.

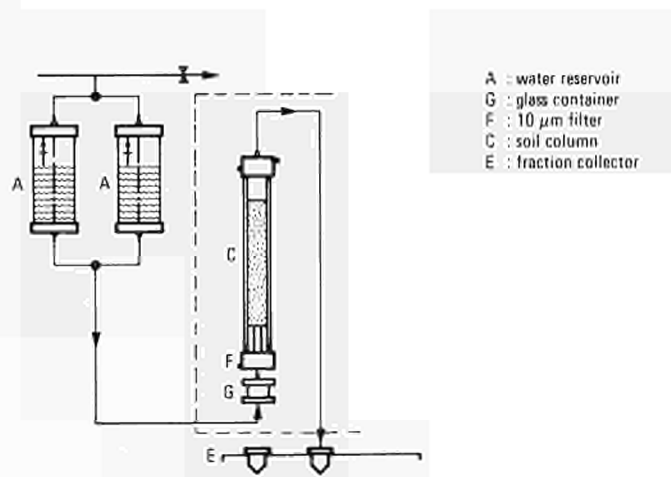


Fig. 2. Experimental set up for studying the interaction of glass leachate with deep soils

Table 1. Water composition (mg/l)

$\text{Ca}^{2+}$	= 3.03	$\text{Cl}^-$	= 6.4
$\text{Mg}^{2+}$	= 3.2	$\text{SO}_4^{2-}$	= 0.5
$\text{Fe}_{\text{tot}}$	= 0.1	$\text{CO}_3^{2-}$	= 201
$\text{Na}^+$	= 55.3	pH	= 8.35
$\text{K}^+$	= 7.71	Eh	= 150 mV

## Results and Discussion

Although the study of basic glass dissolution phenomena is not the main object of the present discussion, it is clearly necessary to understand them as they represent the initial source of the migrating species. Leaching of the glass can be assumed to be a homogeneous corrosion phenomenon where all the elements constituting the glass are leached at the same rate although not necessarily by the same mechanism (6). Two pieces of information support this apparent paradox: firstly the measurement of the leaching rate of the glass by weight loss of the sample gives the same value as is obtained by measuring the radioactivity released into the water ( $2 \times 10^{-6} \text{ gm cm}^{-2} \text{ d}^{-1}$ ); secondly it has been shown that in the case of plutonium, americium and neptunium, they leave the surface not only in soluble but also in colloidal form (5). That a different mechanism controls this release can be clearly seen in Figure 3, which shows the retention of these elements on membrane filters of different porosities. If their release was only related to the loss of the silica gel from the glass surface, all the elements would have shown the same retention patterns on the different filters. However, it can be supposed that a hydrated layer of silica is formed on the surface of the glass which will become slowly enriched in lower solubility elements. The subsequent loss of this layer to the water vector followed by the rapid dissolution of the siliceous material, releases the low soluble radionuclides partially by colloidal formation and

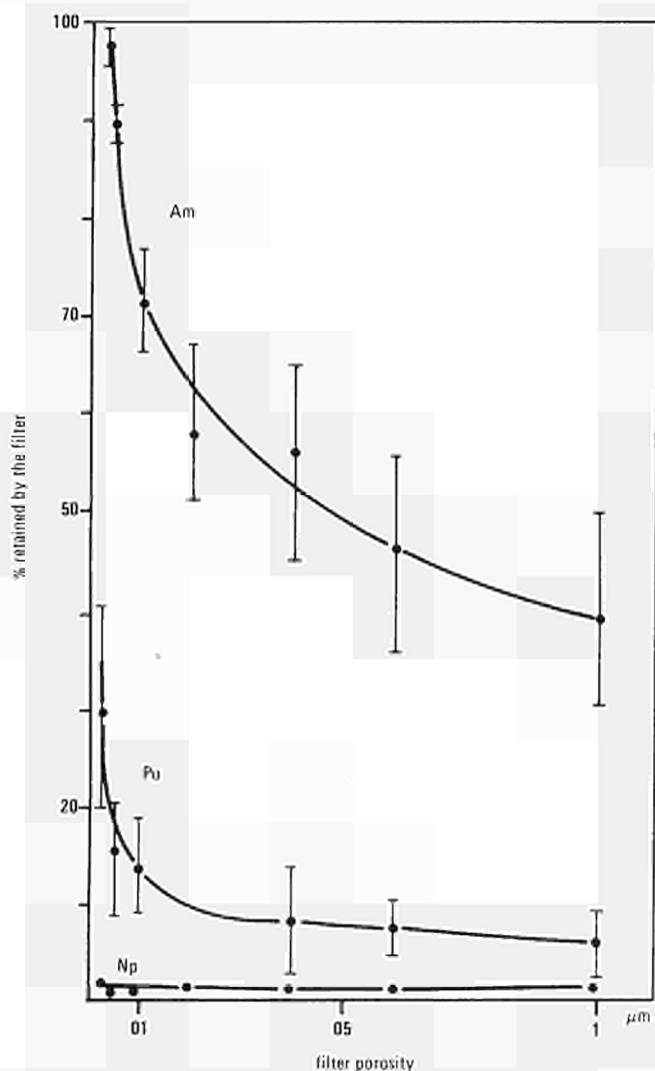


Fig. 3. Percentage retention of leached activity versus filter porosity (nuclepore membranes)

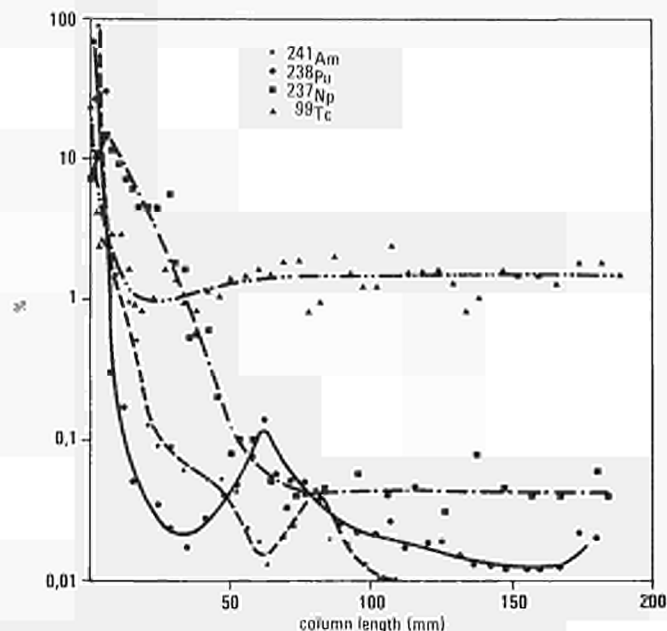


Fig. 4. Normalized activity profile in the glauconitic sand

partially by solubilization. It has been shown that under the present experimental conditions, the water is highly under-saturated with respect to silica.

Differing conclusions reached by other authors (7) might be explained by the fact that, if only soluble forms leached from the glass are measured, the actinides elements show release rates lower than that of silicon owing to their lower solubility in water.

The interaction with the geological media of these two leached fractions will determine the subsequent migration pattern of the radionuclides.

The results obtained in the laboratory simulation experiments for a number of long-lived radionuclides can be interpreted in terms of the relative importance of the soluble versus colloidal forms for each element. In Figure 4 are shown the normalised profiles of americium, plutonium, neptunium and technetium in the glauconitic sand columns after about 40 days experimental percolation.

A distinction can be seen of the retention of the various nuclides which it is suggested can be related to their different colloidal to soluble partitioning given previously in Figure 3. Technetium which is shown not to be retained by ultrafiltration, can be seen to migrate through the column with only a minimum of retention. The slight retention within the first 2 cm of the column is thought to be due to cationic fixation. The constant distribution over the remaining length may be considered to be the presence of pertechnetate species or anionic Tc carbonate complexes (8, 9) in the water filling the void fraction of the column, with the saturation of a very weak anion exchange capacity of the media. Chemical analysis of input to the column showed that the species distribution was 85% anion and 15% cation respectively at the experimental redox condition adopted.

At the outlet 100% of the activity was anionic, this represented over 70% of the total technetium leached from the glass.

In the case of americium and plutonium, their retention patterns can be explained by the filtration effect of the media. From characterization of the input distribution it has been shown (5) that the soluble cationic species of these elements represent less than 3% of the total activity leached from the glass. Thus the accumulation of americium and





dionuclides has also been observed. In the case of technetium, over 70% of the leached activity from the vitrified wastes passes through the column as  $TcO_4^-$  ions or carbonate complexes in true solution (8, 9). For the transuranic elements, however, only a small part of the anionic fraction shown in Table 2 is found at the outlet of the column. This may be considered to represent the truly soluble anionic fraction of the nuclides and it is believed that this corresponds to the formation of anionic complexes with carbonate ions present in the groundwater. Two reviews have recently been published on the geochemistry of selected radionuclides (11, 12) which form a useful data-base for the prediction of the thermodynamic behaviour in natural conditions.

A confirmation of the hypothesis of anionic complexes formation has been obtained when the loaded columns were washed with uncontaminated groundwater. In this case as well, the concentration of the actinides at the outlet of the columns maintained their initial value. This indicates an in-situ formation of a soluble anionic species by dissolution of the previously retained transuranic colloids.

In order to follow the evolution of the contamination profile during washing, a scanning system has been developed as shown in Figure 7. Profiles of americium-241 obtained with this set-up are given in Figure 8. Curve 1 is the profile at the end of the loading step of a glauconitic sand column after 30 days and curve 2 is the profile obtained on the same column after about 90 days of washing with uncontaminated groundwater. It can be seen that the activity peak has remained in the same position demonstrating the good filtering efficiency of the column. The decrease in the integral activity of curve 2 confirms the formation of a soluble species which must be neutral or anionic as it was not detected in the remaining length of the column. The total activity measured at the outlet of this column was found to be fixed on an anion exchanger; this activity corresponded very well to the decrease of the column peak.

As previously reported (5), the concentration of actinides at the outlet of the columns were found to be  $2 \cdot 10^{-13}$  molar for americium and plutonium and  $8 \cdot 10^{-10}$  molar for neptunium. These results demonstrate the crucial importance of this solubilisation mechanism for the long-term underground transport of the leached radionuclides. If this theory is demonstrated, the concept of the use of distribution constant  $K_d$  will consequently require reconsideration (13).

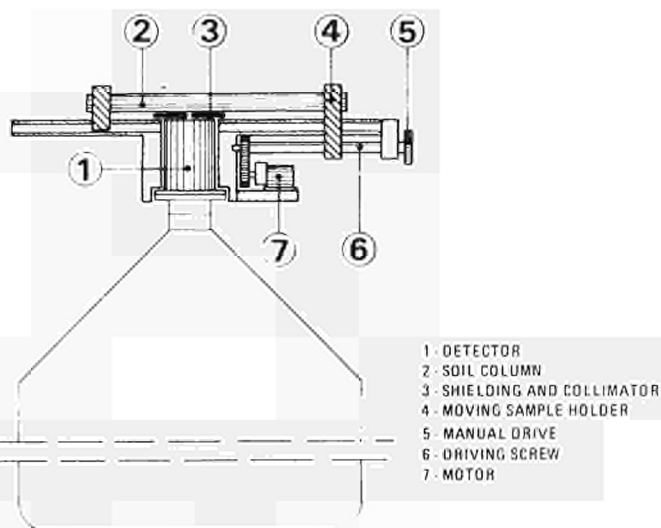


Fig. 7  $\gamma$  scanning device

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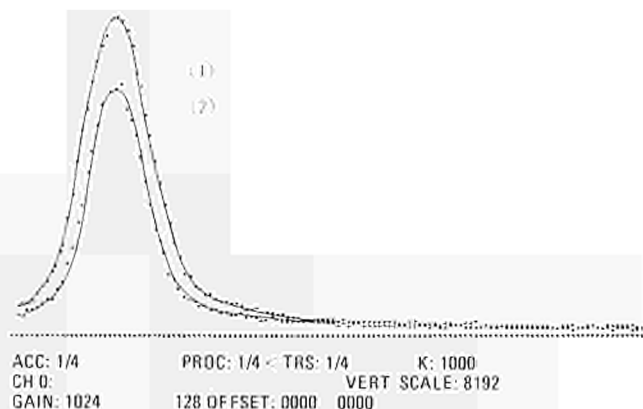


Fig. 8.  $\gamma$ -scanning of a glauconitic sand column  
 1 : after the loading step with  $Am^{241}$   
 2 : after a washing step of 90 days

In view of these facts, investigations are being developed at the Joint Research Centre on the characterisation of carbonate complexes and on the measurements of their stability constants.

## Conclusions

Results have been presented of an on-going study on the migration of some selected leached long-lived radionuclides through a porous geological formation. Although a large part of these results are specific for the reference study selected, they are a useful indication of the kind of processes that may occur in other geological systems. Two main processes have been identified which govern the migration phenomena: the retention of microcolloids present in the glass leachate by homogeneous deep-bed filtration mechanisms, and the formation of soluble anionic species which migrate with minimum interaction at the velocity of the water vector.

The first process is characteristic of the behaviour of the actinides in the short-term situation as the geological media effectively retain the leached nuclides. The second process may be viewed as the controlling factor over the long term. The formation of actinide soluble species in fact becomes the rate determining step in the subsequent dispersion of these elements.

In the case of technetium soluble anionic species are present immediately in the vitrified waste leachate under the simulated natural conditions adopted.

A number of environmental parameters have been identified which have been shown to effect these migration phenomena.

These are pH, Eh, chemical composition of groundwater and its flow rate through the selected media.

The present work has been carried out using fixed values of these parameters. In order to have a more general predictive capability, it is necessary to undertake a parametric study over the range of their possible natural variations. The redox potential, pH and chemical water composition will affect the physico-chemical states of the nuclides and will de-

termine their partitioning between the colloidal and soluble phases. The flow rate on the other hand controls the kinetics of the transport of the colloids and their subsequent dissolution.

The present studies have indicated that there is a clear need for increased research effort in the area of transport of leached activity in order to reach a better understanding of the different processes involved. The results of the experimental work at the JRC-Ispra should give information needed for the development of models on the mechanisms of formation of colloids during leaching, their subsequent filtration by the porous media as well as on the thermodynamic evolution of soluble migrating species. A realistic description of these mechanisms is required for the development of more precise risk analysis models.

These models are needed for the assessment of the long term feasibility of the different geological disposal options.

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### 3. Actinide Separation

#### Objectives

The project includes:

- the setting-up of chemical methods for the actinides separation from various medium level waste (MLW) streams in view of an optimization of the alpha-waste management procedures;
- the completion of the activity on the management of high level waste (HLW).

The main activities planned for 1981 are the following:

1. Actinide separation from MLW.
  - Application of the Oxal process to MLW concentrate.
  - Tests on the oxalic wash of exhausted TBP for the recovery of the residual plutonium.
  - Tests on the recovery of plutonium from fuel dissolution residues.
2. Management of HLW.
  - Analysis of the experiments in progress at Fontenay-aux-Roses.
  - Tests on the recovery of noble metals.
  - Preparation of the final report of the JRC activity on the chemical separation of actinides.
3. Setting-up of the ADECO hot cells.
  - Evaluation of safety and financial aspects.

#### Results

##### Actinide separation from MLW streams

The experimental work essentially consists in the application of the Oxal process, previously tested on HLW, for the plutonium separation from the concentrate of the various liquid effluents of the reprocessing plants. The purpose is to reduce the volume of the alpha waste fraction (the bulk of the material becoming alpha free) and possibly to recover the plutonium in view of its recycling.

Some experiments have also been performed on the plutonium recovery from exhausted TBP by oxalic washing and from fuel dissolution residues.

The experimental work is carried out in a strict connection with the Assessment Studies on Alpha-Waste Management (see Project 1. Risk Evaluation)

##### MLW/Oxal Process

The experimental work was started using a simulated MLW solution with composition defined on the basis of a preliminary assessment (1). The composition of the solution and the results previously obtained are reported in reference (2).

During the reporting period the work has been continued using this solution and has been directed to study the following points:

- a) influence of the complexing agents on the oxalic precipitation;
- b) recovery of plutonium from the precipitated oxalates.

In the meantime the assessment studies on alpha-waste management have defined a reference reprocessing facility and the composition of the related waste streams (3). The composition of the MLW solution, defined by the assessment studies, is considered as reference for the J.R.C. studies.

Thus, a new simulated MLW solution has been prepared and used in a set of experiments.

##### INFLUENCE OF THE COMPLEXING AGENTS ON THE OXALIC PRECIPITATION

The results given in the previous report were obtained from a MLW solution without the complexing agents. Several tests have been made to verify their influence on the oxalic precipitation and the successive neutralization at  $\text{pH} \geq 8.5$ . The simulated solution had the composition reported in reference (2) with in addition:

EDTA	: 2.7 E-3 M
Na citrate	: 1.9 E-2 M
Na tartrate	: 2.2 E-2 M

In order to precipitate the oxalates at higher acidity, the concentration of Ce carrier and oxalic acid was increased

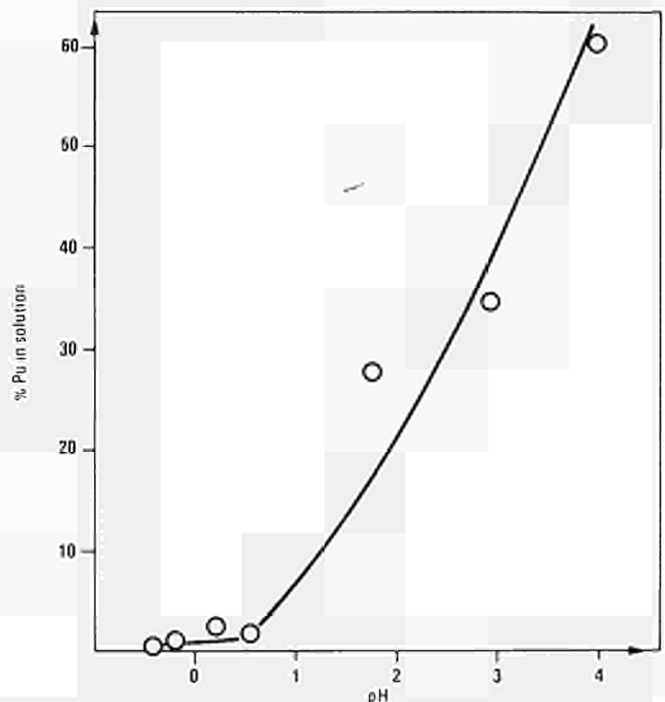


Fig. 1. Fraction of plutonium in solution after oxalate precipitation, as a function of pH.

by a factor of 10 compared to the previous tests. The concentrations adopted were the following:

- cerium 0.05 M
- oxalic acid 0.25 M

In this way, the addition of oxalic acid to the MLW solution containing Ce gave rise to an abundant precipitate which flocculated very well and was easy to filtrate.

For the filtration we used Millipore 0.8  $\mu\text{m}$  and the digestion time was 30 min.

Fig. 1 shows the fraction of plutonium in solution after oxalate precipitation, as a function of pH.

As shown in Fig. 1, the best precipitation is obtained at high acidity; when pH increases, the influence of the complexing agents becomes stronger and Pu is partially redissolved. About 99.5% of plutonium is precipitated in the best conditions while the contamination by elements such as Sr and Fe is limited.

The successive neutralization of the supernatant at pH about 9.0 left the solution very clear. Only after 1 hour a very slight precipitate, probably  $\text{Fe}(\text{OH})_3$ , was formed and Cs in presence of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  (4) did not precipitate.

Even after a 3 days digestion time, only 50% Fe and 40% Sr were precipitated.

In conclusion, the oxalic precipitation gives good DFs for Pu, even in presence of complexing agents, while the elimination of the  $\beta$ ,  $\gamma$  emitters at higher pH becomes questionable.

#### RECOVERY OF PU FROM THE PRECIPITATED OXALATES

The solids from the oxalic precipitation contain more than 99% of Pu but are contaminated by  $\beta$ ,  $\gamma$  emitters (Ce, Eu...) and by chemicals ( $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , F...) which make the dissolution quite difficult. Tests have been performed to investigate the feasibility of recovering Pu by extraction with TBP in the presence of these contaminants, after dissolution of the oxalates in a boiling mixture 6M  $\text{HNO}_3$ - $\text{H}_2\text{O}_2$  under reflux.

The nitric solution was contacted 3 times with equal volumes of fresh 30% TBP n-dodecane. Prior to each extraction, the TBP was pre-equilibrated with 6M  $\text{HNO}_3$  (O/A = 2). The following values for the extraction coefficients ( $E_{\alpha}^{\text{Pu}}$ ) at each step have been obtained (average values from several experiments):

$$\text{Step 1: } E_{\alpha}^{\text{Pu}} = 6.7$$

$$\text{Step 2: } E_{\alpha}^{\text{Pu}} = 3.6$$

$$\text{Step 3: } E_{\alpha}^{\text{Pu}} = 2.7$$

These experimental values are lower than the theoretical one which is higher than 21.5 (5) for the extraction of Pu in 6M  $\text{HNO}_3$  by 30% TBP kerosene. In any case, after the third step, less than 1% Pu was found in the aqueous phase. From the experimental  $E_{\alpha}^{\text{Pu}}$  values, we could calculate that about 6 extraction stages would be needed to recover more than 99% Pu by using a countercurrent device.

#### TESTS ON THE MLW REFERENCE SOLUTION FOR J.R.C. STUDIES

The composition of the MLW reference solution defined in the assessment studies on alpha-waste management (3), is reported in Table 1.

The quantities indicated in Table 1 are the highest expected

Table 1. Composition of the MLW reference solution for J.R.C. studies

Chemical composition	M	g/l	kg/1000 t HM
$\text{NaNO}_3$	4	340	5.1E5
$\text{Na}_2\text{HPO}_4$	3.5E-2	5.0	7.5E3
$\text{Na}_2\text{SO}_4$	5.0E-2	7.1	1.1E4
NaCl	7.5E-2	4.4	6.6E3
HCl	1.0E-2	4.0E-1	5.4E2
Al	8.2E-3	2.3E-1	3.5E2
Ca	3.8E-2	1.5	2.3E3
Cr	1.5E-3	8.0E-2	1.2E2
Cu	2.4E-3	1.5E-1	2.3E2
Fe	6.8E-3	3.8E-1	5.7E2
K	2.1E-3	8.0E-2	1.2E2
Mg	3.1E-2	7.5E-1	1.1E3
Mn	1.4E-3	8.0E-2	1.2E2
Mo	4.0E-3	3.8E-1	5.7E2
Ni	1.4E-3	8.0E-2	1.2E2
Ru	1.5E-3	1.5E-1	2.3E2
Zn	2.3E-3	1.5E-1	2.3E2
Zr	8.8E-4	8.0E-2	1.2E2
<b>Miscellaneous</b>			
Sodium oxalate	3.7E-2	5.0	7.5E3
Sodium tartrate	2.2E-2	5.0	7.5E3
Sodium citrate	1.9E-2	5.0	7.5E3
NaF	5.3E-2	1.0	1.5E3
EDTA	2.7E-3	1.0	1.5E3
Complexants/ surface active compounds	—	2	3E3
<b>Degradation enainment</b>			
TBP	7.5E-4	2.0E-1	3.0E2
HDBP	9.5E-5	2.0E-2	3.0E1
$\text{H}_2\text{MBP}$	3.2E-5	4.9E-3	7.3
Kerosene		2.0E-2	3.0E1
<b>Actinides</b>			
Pu	4.2E-5	1.0E-2	1.5E1
U	6.7E-3	1.6	2.4E3
Np	1.35E-5	3.2E-3	4.8
Am	1.4E-5	3.3E-3	5.0
Cm	5.5E-6	1.3E-5	2.0E-2
<b>Fission products</b>			
Ce	—	1.8E-3	2.65E3
Cs	—	1.8E-3	2.65E3
Eu	—	0.13E-3	1.96E2
Ru/Rh	—	1.6E-3	2.41E3
Sb/Te	—	0.4E-3	6.34E2
Sr/Y	—	1.0E-3	1.45E3
Zr	—	2.7E-3	4.02E3
<b>Radioactivity</b>			
Total	5.0E-1 Ci/l		
<b>Physical properties</b>			
Volume	1.5 m <sup>3</sup> /t HM		
Density range	~ 1200 - 1400 (kg/m <sup>3</sup> )		
Heat generation	~ 0.01 - 0.1 (w/l)		

in such a solution. For the experimental work, it was decided to use a solution diluted by a factor 2 in order to reduce the salt concentration so that the solution is chemically easier to handle.

The reference solution essentially differs from the previous one (2) as indicated in Table 2.

Due to the presence of elements such as Al, Ca, Cu... which form very stable complexes with EDTA, citrate... or can precipitate as oxalate (Ca), extrapolations from the previous experimental work seemed unrealistic. For that reason, a new series of experiments has been initiated by using the reference solution.

For each test, after addition of the Ce carrier in form of Ce (NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O and of the oxalic acid in solid form to 50 ml of simulated MLW solution, the acidity is decreased by adding 8 M NaOH to the stirred mixture. The pH and the temperature are continuously controlled. At determined pHs, samples are drawn and after centrifugation, the elements of interest measured by several analytical techniques, such as radiotracers, atomic absorption and optical emission spectroscopy.

### Ce behaviour

The first tests were aimed at determining the conditions for the Ce carrier precipitation.

Table II. Comparison of the MLW solutions

Compound	Previous solution (M/l)	Reference solution (M/l)
Na NO <sub>3</sub>	0.6	4
Al	n.a.	8.2 E-3
Ca	n.a.	3.8 E-2
Cu	n.a.	2.4 E-3
Fe	1.4 E-2	6.8 E-3
Ni	n.a.	1.4 E-3
Ru	4 E-5	1.5 E-3
Zn	n.a.	2.3 E-3
Zr	8 E-5	8.8 E-4
Surface active compounds	n.a.	2.0E0 g/l
TBP	n.a.	7.5 E-4
HDBP	1.0 E-2	9.5 E 5
H <sub>2</sub> MBP	3.4 E-3	3.2 E-5
Kerosene	n.a.	2 E-2 g/l

n.a. not added

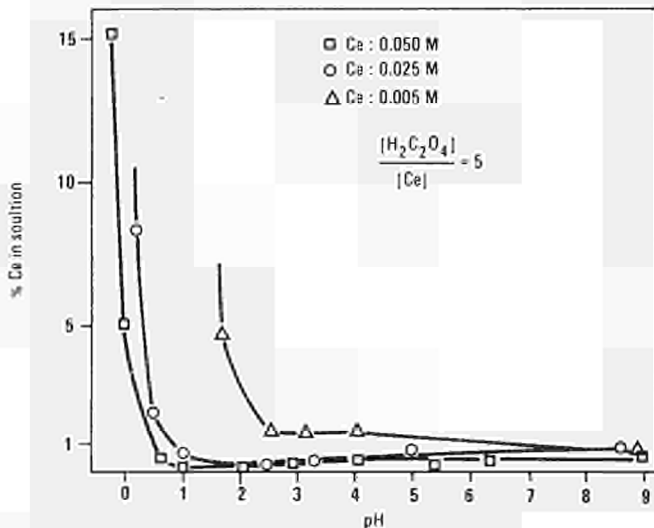


Fig. 2. Ce behaviour vs pH in the oxalate precipitation

Figure 2 shows the behaviour of Ce vs pH at various Ce concentrations; in each experiment, the ratio

$$\frac{[H_2C_2O_4]}{[Ce]}$$

was fixed to 5 (6).

Since contaminations are lower at high acidity conditions, for the successive tests we always used 0.05 M Ce and 0.25 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. These concentrations produce a precipitate which settles very quickly; after a few minutes the supernatant appears very limpid.

### Pu behaviour

Until now, only ionic Pu, as Pu nitrate from a stock solution of 13 g/l has been added to the MLW solution so that the final concentration was 13 mg/l. Figure 3 shows the Pu behaviour vs pH.

The slight differences which appear in the figure probably can be attributed to different experimental conditions.

For example, in test 1 sampling was made at higher temperature than in 2 and 3, while in test 2 digestion time was longer than in 3. More than 99.5% Pu is precipitated at a pH about 0.6.

In all the tests, when pH was increased, Pu slowly redissolved due to the action of the complexing agents. Up to 25% Pu were found in solution at pH about 3.5. The behaviour was not highly reproducible at high pH and a more careful analysis of experimental conditions is probably needed.

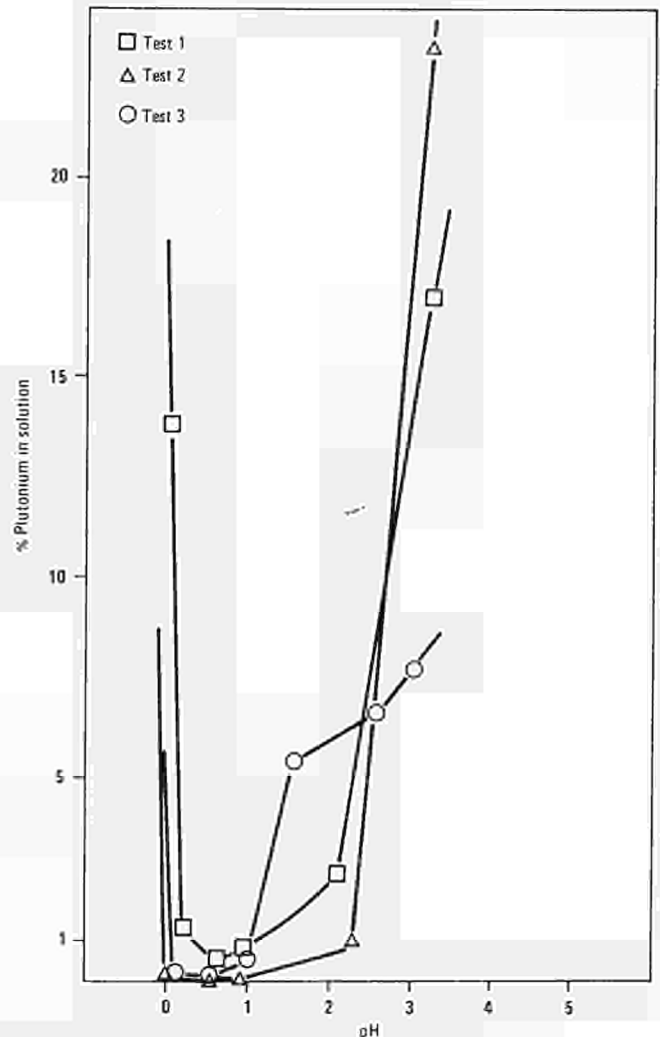


Fig. 3. Pu behaviour vs pH in the oxalate precipitation

## Behaviour of the other elements

Figure 4 is relative to the behaviour of Ru, Cs and Table 3 gives some results for Mo, Mn, Cr, Fe, Ba, Ca and P.

Figure 4 and Table 3 show that the oxalate precipitate is slightly contaminated by several non-radioactive species even at pH about 1.0.

Concerning Cs and Ru, specific carriers are needed for their precipitation. One test has been made as follows: after filtration of the oxalic precipitate at pH 0.6, the acidity of the supernatant was fixed at pH 1.5 and  $K_4(-Fe(CN)_6)$  added; afterwards, the pH was increased to 9.14 and  $CoSO_4$  and  $Na_2S$  added to coprecipitate Ru. After centrifugation, the supernatant still contained 8.2% Ru but only 0.2% Cs; these values are in good agreement with those reported in reference (4).

## CONCLUSIONS

At the present time, the following conclusions can be drawn:

- independently of the MLW solution tested, good DFs were obtained for Pu and by operating near pH = 0, contaminations can be quite reduced without important efficiency losses.
- oxalate precipitation is compatible with current precipitation methods (4) which become less efficient in pre-

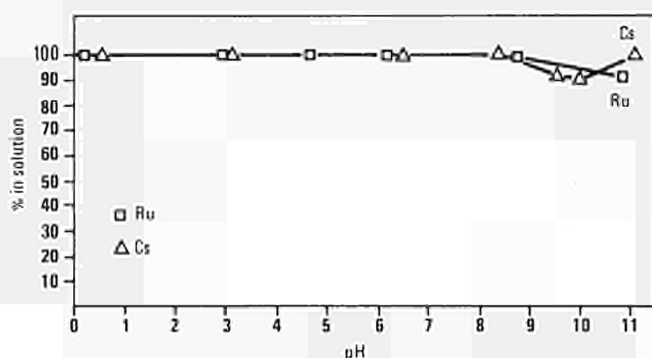


Fig. 4. Ru and Cs behaviour vs pH in the oxalate precipitation

Table III. Mo, Mn, Cr, Fe, Ba, Ca, P behaviour % in solution

Element	pH 0.92	pH 2.86	pH 9.80
Mo	61.9	56.5	60.5
Mn	76.6	56.6	13.1
Cr	78.6	65.1	36.6
Fe	91.0	83.4	20.5
Ba	78.0	0.7	0.7
Ca	86.6	1.7	0.6
P	~ 100	80.3	22.7

Table IV. Residual activity in TBP (in % after the successive washes)

Element	HNO <sub>3</sub> I	HNO <sub>3</sub> II	HNO <sub>3</sub> III	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
Pu	73	49	36	≅ 0
U	82	38	20	≅ 0

sent of complexing agents unless elements such as Al, Cu... prevent their action.

- the results are quite promising but some experimental work is still needed to study the behaviour of elements such as Np, Am, Tc, polymeric Pu, Sr etc.

## Exhausted TBP oxalic wash

Fifty cm<sup>3</sup> of 30% TBP n-dodecane have been stirred with an equal volume of real HLW: the radiation dose was about 20 wh/l and at the end of the irradiation the HDBP concentration was 0.11 mole/liter.

The irradiated TBP has been first washed with 0.02 M HNO<sub>3</sub> to decrease the activity of the fission products: in this way, it became possible to make the tests in a glove box but H<sub>2</sub>MBP was back-extracted too.

The TBP was successively contacted with a nitric aqueous phase containing <sup>239</sup>Pu and <sup>233</sup>U and used as starting solution for several tests.

TBP was first washed 3 times with equal volumes of 0.02 M HNO<sub>3</sub>. Then it was divided into 2 fractions: one was treated with 0.9M oxalic acid (O/A = 1) and the second with 0.2M Na<sub>2</sub>CO<sub>3</sub>.

The residual activity of U and Pu in the TBP after the various washes is reported in Table 4.

The oxalic wash does not back-extract HDBP but is very efficient for U and Pu ( $E_{\alpha}^U$  and  $E_{\alpha}^{Pu} < 10^{-4}$ ).

In the same conditions, 0.2M Na<sub>2</sub>CO<sub>3</sub> gave rise to a slight third phase which prevented a precise determination of the activity distribution. The carbonate treatment is still needed after the oxalic wash to remove HDBP but it will produce in this case a plutonium-free aqueous solution. The oxalic acid, which contains Pu, can be sent to the aqueous MLW treatment previously described.

## Recovery of plutonium from fuel dissolution residues

As reported in the previous Programme Progress Report (2) in presence of noble metals HCOOH may be expected to dissolve plutonium by its reduction to the more soluble trivalent state, providing that it is not trapped in the solid residues.

Two tests have been made on the dissolution residues corresponding to about 250 g of irradiated fuel (OBRIGHEIM, burn-up 30,000 MWd/t, decay 5 years). For each test, about the half of the residues was used.

### Test 1

In the first test, the successive washings were as follows:

- reflux in boiling 8M HNO<sub>3</sub> - 3 hours
- reflux in boiling 3M HCOOH - 5 hours
- reflux in boiling 8M HNO<sub>3</sub> - 1.6M HCl, 0.01M HF 4 hours.

After each step, the cooled mixture was filtered on Millipore 0.22 μm and a liquid sample was taken for activity measurement.

The third washing left a black residue: its activity was roughly estimated.

Table 5 shows the activity of some elements in each washing solution and in the final residue.

Table V. Activity expressed in cpm of the solutions of test 1

Element	8M HNO <sub>3</sub>	3M HCOOH	8M HNO <sub>3</sub> - 1.6M HCl-0.01M HF	Solid residues
Eu	7.99 E + 5	n.d.	n.d.	n.d.
Ce	2.67 E + 5	n.d.	n.d.	n.d.
Sb	1.10 E + 6	1.44 E + 5	1.23 E + 6	1.51 E + 5
Ru	2.52 E + 7	7.53 E + 6	7.47 E + 6	1.07 E + 6
Cs	1.36 E + 7	4.84 E + 5	2.57 E + 5	4.97 E + 4
<sup>239</sup> Pu	3.07 E + 7	3.36 E + 5	3.14 E + 5	8.16 E + 4
<sup>238</sup> Pu - <sup>241</sup> Am	9.36 E + 7	1.87 E + 6	1.13 E + 6	3.23 E + 5
<sup>244</sup> Cm	3.18 E + 7	1.63 E + 6	4.92 E + 5	1.46 E + 5

n.d.: not detected

## Test 2

It differs from test 1 for the fact that 3 HCOOH washings in place of 1 were performed and at the last step only 8M HNO<sub>3</sub> was used. The activity in the successive solutions is indicated in Table 6.

Both the tests show that the formic treatment is not so efficient as expected and even 8M HNO<sub>3</sub> seems to be a better leaching agent than HCOOH.

The low efficiency could be attributed to various reasons such as:

- too low concentration of the noble metals
- physical form of the noble metals not suitable
- insufficient disaggregation so that Pu remains trapped in the solid particles.

As the results are not very promising, thus no further experiment has been planned.

## Actinide separation from HLW

The continuous countercurrent experiments (mixer - settler batteries) performed at CEN laboratories of Fontenay aux Roses (CEA) in order to verify the HLW partitioning flow-sheet based on the HDEHP process scheme have been completed.

A detailed report on the results of these experiments is in preparation and will be available at the end of 1981.

Some of the most significant results illustrating the Pu and Am distribution in the different streams resulting from the HLW denitration and the washing and dissolution of denitration precipitate are anticipated in Table 7. As shown in this table the cumulative volume of the HCOOH solution used for washing the denitration precipitates is within the proportion (18%) indicated in the process flow sheet for its recycling to the actinide extraction step.

After two washing steps the residual Pu and Am still present in the precipitate represent 1.6% and 0.09% of the Pu and

Table VI. Activity expressed in cpm of the solutions of test 2

Element	8M HNO <sub>3</sub>	3M HCOOH I	3M HCOOH II	3M HCOOH III	8M HNO <sub>3</sub>
<sup>239</sup> Pu	1.04 E + 7	2.33 E + 5	7.92 E + 4	3.98 E + 4	1.98 E + 5
<sup>238</sup> Pu - <sup>241</sup> Am	6.39 E + 7	2.50 E + 6	5.77 E + 5	2.33 E + 5	1.08 E + 6
<sup>244</sup> Cm	5.25 E + 7	3.00 E + 6	4.97 E + 5	1.84 E + 5	4.72 E + 5

Table VII. Distribution of Pu and Am in various streams resulting from the denitration of an actual HLW solution and treatments of denitration precipitate

	Volume (l)	Pu		Am	
		(mg/l)	(%) (1)	(mg/l)	(%) (1)
Acid HAW solution	48.0	16.9	0.65	80.3	100
Denitrated HAW (pH 2.25)	48.0	16.0	0.61 (94) <sup>(2)</sup>	80.2	> 99
1st ppt wash (0.5 M HCOOH)	4.2	7.76	0.026 (4)	2.75	0.3
2nd ppt wash (0.5 M HCOOH)	4.4	1.44	0.0052 (0.8)	0.44	0.05
ppt solution (8 M HNO <sub>3</sub> , 0.1 M HF)	1.0	6.46	~ 0.01 (1.6)	1.73	0.09

(1) % values referred to the amount of nuclide initially present in the spent fuel solution

(2) % values in brackets are referred to the amount of Pu initially present in the HAW solution

Am initially present in the HLW solution (i.e. 0.65% and 100% of Pu and Am present in the spent fuel).

The above results concerning Pu are in fairly good agreement with some results previously obtained at ISPRA laboratories.

The retention of Am appears on the contrary to be lower than previously observed.

As to the removal of Pu and Am from the denitrated HLW solution more than 99.9% of Pu and about 99.9% of Am have been separated by continuous countercurrent mixer-settler extraction tests using HDEHP. No alpha activity has in fact been detected in the output aqueous raffinate from the extraction section of the mixer-settler battery. A back extraction yield of 99.7% has been attained for Am using a DTPA-glycolic acid solution.

Due to unforeseen delays in the preparation of the 5 liter batch of concentrated HLW the start of continuous countercurrent experiments for verifying the TBP process flow-sheet has been postponed. Anyhow the set of verification experiments will be completed at CEN laboratories before the end 1981.

The typing of the final version of the summary report of the J.R.C. activity on the chemical separation of actinides from HLW has been started. The report is expected to be ready for distribution during the first semester of 1982.

## Setting-up of the ADECO hot cells

In order to test on a larger scale the processes developed at the J.R.C. the possible utilization of the ADECO hot cells is being considered.

During the reporting period the discussions with the safety authorities have progressed on the modifications to be introduced in the hot cell system.

An engineering firm has been charged to perform a cost evaluation for the setting up of the hot cells on the basis of a preliminary design prepared by the J.R.C.

Concerning operational costs and implications on the services of the establishment evaluations are in progress.

The decision on a possible setting-up of the hot cells has been postponed to the beginning of 1982 in coincidence with the decision on the orientations of the next J.R.C. plan.

## Collaboration with external organizations

Collaboration contract with CEA, Fontenay-aux-Roses, aiming at a large scale verification of the solvent extraction processes developed by J.R.C. for HLW partitioning purposes.

Relations with national laboratories working on chemical treatment of MLW in the framework of the indirect action programme.

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## 4. Actinide Monitoring

### Objectives

The objective of this study is to develop methodologies and instrumentation for the monitoring of plutonium contaminated waste streams by means of non-destructive assay techniques.

The J.R.C. operates as an advisory laboratory in this area. The main activities planned for 1981 are the following:

- Continuation of the experiment at DNPDE-Dounreay.
- Developments in the area of passive neutron assay.
- Revision of the Guide on "Monitoring of Pu-contaminated solid waste streams".

### Results

#### Integral Experiment at DNPDE Dounreay

The collaboration between JRC and DNPDE concerns the evaluation of the various NDA systems applied at Dounreay for the monitoring of plutonium contaminated solid waste streams.

DNPDE provides the operational data and JRC provides the mathematical modelling and interpretation.

In agreement with the planning, Part 1: Interpretation Models and Calibration Methods, of the final report has been drafted.

It is planned to publish this paper as an EUR-report (contributions from DNPDE, JRC and University of Lyon).

It deals with the following subjects:

- 1) Performances of the DNPDE solid waste measurement system.
- 2) Preliminary results from PR3 fuel reprocessing campaign.
- 3) Interpretational models.
- 4) Calibration methods.

Points 3) and 4) are treated in details while points 1) and 2) are summarizing descriptions of the problems to be dealt with.

Interpretational models are given for the utilized NDA-techniques, hence generally applicable. The given models for high resolution gamma spectrometry are covering gamma assay methods in various sample detector geometries, such as cylindrical sample-point detector / partial scanning /  $4\pi$  scanning / segmented scanning. Numerical results are displayed as tables and graphs.

Calibration procedures are given for the utilized "Segmented Gamma Scanner".

The general interpretational model for the passive neutron technique, as given in the chapter IV of our Guide has been numerically evaluated by neutron transport calculations (ANISN-P3, S8). Tables and graphs have been elaborated describing in a 3 energy group model the neutron leakage rates from various samples as functions of sample properties and neutron source locations. Interaction effects of leaking neutrons with detector materials are also evaluated and summarized as tables and graphs. The influences of

detector design parameters on the detector efficiencies are also described in the form of tables and graphs. Calibration procedures are given for the various utilized passive neutron monitors of the DNPDE.

Mathematical models for the active neutron technique by delayed neutron measurements after irradiation with a 14 MeV neutron generator are also presented. Numerical results from neutron transport calculations (TRIPOLI 02) are presented as tables and graphs. Detailed calibration procedures for this technique are given.

Comparison of the available experimental results with those from radiation transport calculations and the developed interpretational models are quite satisfactory. The implementation of the theoretical work in an industrial environment will certainly require a software for online (or off line) data processing. In this view we envisage an extension of the current collaboration agreements with the University of Lyon, which disposes of the required qualified staff.

#### Passive neutron assay

A detailed programme for an assessment of the various systems for passive neutron assay has been elaborated during the reported period. The main features and the present status of the activity are the following:

- a) A coherent consideration of the various systems has been introduced; that is, the systems to be analyzed are compared on a common theoretical basis. According to the developed theory the detected pulse train is completely described by the decay constant  $\lambda$  and by the number of singlets, doublets (two correlated neutrons), triplets (three correlated neutrons), ...per second. Being  $\lambda$  a pure instrumental constant, the quantities S (singlets) D (doublets), T (triplets)... and only these give information, via a time correlation analysis of the pulse train, on the neutron emitting isotopes. The response of any type of the various instruments are well defined functions of S, D, T,... Consequently a common interpretation method will be applied to all the various time correlation analyses.
- b) The different types of time correlation analysis will be considered in the assessment, and realized by the Plessey minicomputer. These are the:
  - Variable Dead-Time Counter method
  - Autocorrelation analysis
  - Pulse to pulse time correlation analysis
  - Variance methodThe pulse to time converter associated to the Plessey minicomputer has been completed and the corresponding software is under development.
- c) Three detector heads will be used.
  - Ring Detector:  $\varnothing = 20 \text{ cm}$   $\epsilon \sim 30\%$   $\lambda = 50 \mu \text{ sec}$
  - Octagon:  $\varnothing = 68 \text{ cm}$   $\epsilon \sim 8\%$   $\lambda = 32 \mu \text{ sec}$These detection heads have been used for many years in our laboratory.
  - Reference Monitor:  $\varnothing = 68 \text{ cm}$   $\epsilon \sim 15\%$   $\lambda = 32 \mu \text{ sec}$



Fig. 1. Detection head of the reference monitor

The mechanical part of this detection head has been completed, (see Fig. 1); the associated electronics is under construction.

- d) The measured data to be used for determination of the Pu content, at the present time will be punched on paper tape for following data-elaboration by the J.R.C. computing center, and in the future will be elaborated by a PDP 11/23 minicomputer.  
The two minicomputers (Plessey and PDP) will be connected in the near future. For software development a study contract has been established.
- e) A complete theoretical assessment of the various systems for passive neutron assay will be carried out by means of Monte Carlo simulation; especially a parametric study for determining the sensitivities relative to matrix effects ( $\epsilon$ ) and multiplication probability (P) will be performed.  
The computer programme for the pulse train simulation has been completed.
- f) Experimental verification of the assessment is planned by using:
- J.R.C. plutonium samples

- plutonium samples prepared for the planned interlaboratory tests
- future field experiments.

- g) Continuous information flow to J.R.C. staff is foreseen for the whole period of the planned assessment in form of discussions, demonstrations and eventually collaborations.

#### Revision of the guide

- A draft of the revised version of chapter 1 has been prepared. As it contains substantial modifications with respect to the first version, it is actually submitted to a careful assessment before being published, together with the revised version of chapters 2, 3 and 4.

#### Interlaboratory Comparison

The preparation of the synthetic waste drums is in course in the laboratory of the CEN Cadarache. An information meeting is planned for December 1981 to make the status of the different actions related to this experiment. It is to be noted that in order to optimize the measurement sequence between the various participating laboratories, the planning for the JRC has been modified. The measurements should take place in Ispra at the beginning of 1983. This time schedule has been confirmed in December 1981.

#### Collaboration with external organizations

- Collaboration contract with DNPDE Dounreay for the Integral Experiment.
- Study contract with the Institut de Physique Nucléaire (University of Lyon) for theoretical investigations and software development.
- Relations with AERE-Harwell, CEA-Cadarache and CNEN-Casaccia on various aspects of non-destructive assay.

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CDNA08775ENC