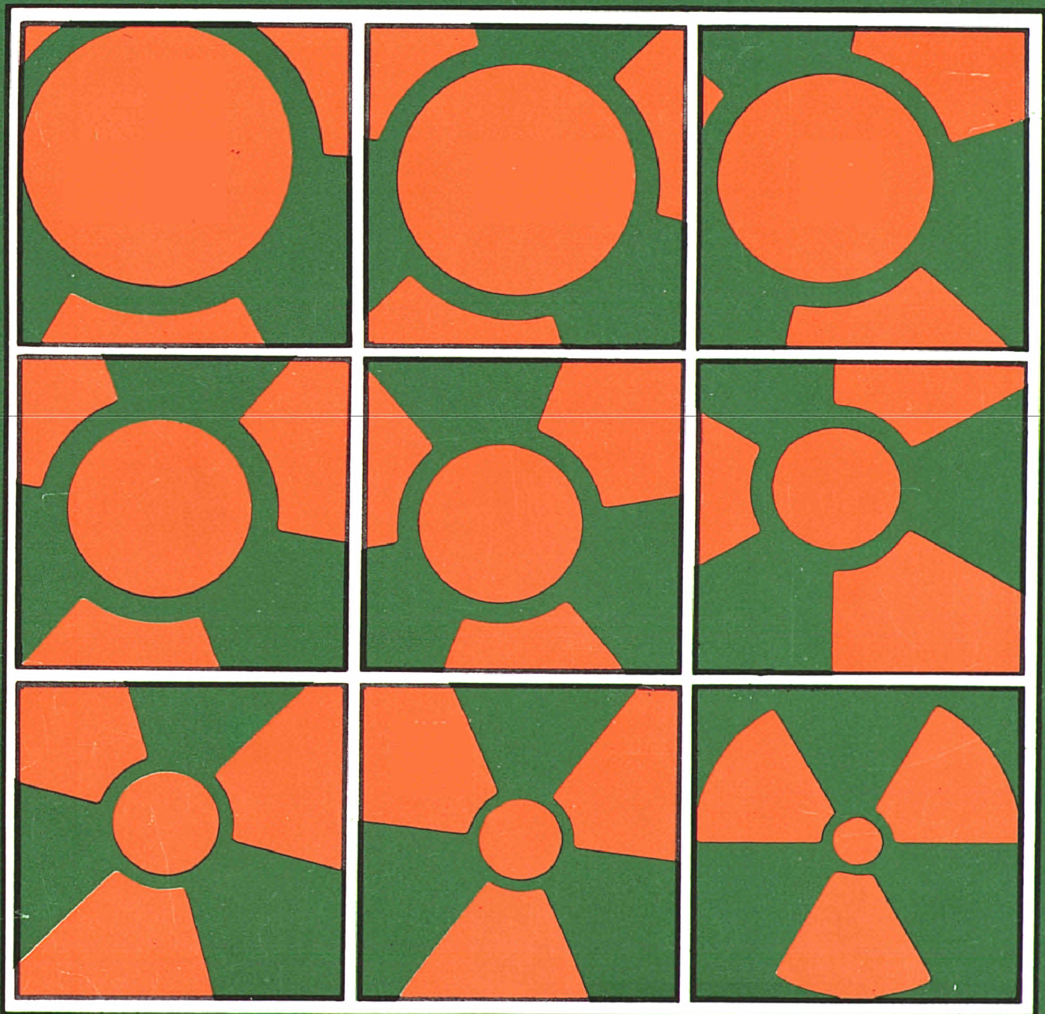
Commission of the European Communities

nuclear science and technology

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

Shared cost action

ANNUAL PROGRESS REPORT 1987



Report

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Edited by:

J.M. Gandolfo

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Directorate-General
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FOREWORD

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

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

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

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

A. WASTE MANAGEMENT STUDIES AND ASSOCIATED R & D ACTIONS

TASK 1 : SYSTEMS STUDIES

TASK 2 : IMPROVEMENT OF RADIOACTIVE WASTE TREATMENT AND CONDITIONING TECHNOLOGIES

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

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

TASK 5 : SAFETY OF GEOLOGICAL DISPOSAL

TASK 6 : JOINT ELABORATION OF RADIOACTIVE WASTE MANAGEMENT POLICIES

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

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

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

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

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

The Commission is responsible for managing the programme.

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

At the beginning of the 1985-1989 programme, the Commission issued a first call for research proposals dealing with tasks 2, 3, 4 and 5. Over 250 research proposals have been received at the closing date (15th June, 1985), trespassing in total several times the available budget, and only a fraction thereof could be accepted for negotiation. A second call for research proposals has been issued in 1986 with 31st October, 1986 as a closing date, over 160 research proposals have been received and 146 contracts have been signed on the 31.12.1987.

This report describes the work to be carried out under the research contracts already concluded before end of 1987, as well as the work performed and the results obtained.

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

S. ORLOWSKI
Head, Nuclear Fuel Cycle Division

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

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

(3) Radioactive waste management and disposal, proceedings of the 2nd European Community Conference, Luxembourg, April 22-26, 1985
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PART A : WASTE MANAGEMENT STUDIES AND ASSOCIATED R & D ACTIONS

PART A

WASTE MANAGEMENT STUDIES AND

ASSOCIATED R & D ACTIONS

CHAPTER 1

TASK No 1

Systems studies

CHAPTER 1
TASK No. 1: SYSTEM STUDIES

A. Objective

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

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

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

- Solid plutonium contaminated waste
- Alcaline liquid wash waste, arising during spent fuel reprocessing operations.

C. 1985-1989 programme

The system studies carried out are related to three subjects:

- Assessment of management alternatives for reactor waste
- Assessment of management alternatives for hulls
- Comparison of waste management implications of spent fuel disposal and reprocessing.

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

- Comparative weightings for cost and radiological parameters in the assessment of radioactive waste management options
- Accounting method of radiation doses due to long-lived natural radionuclides and daughters

D. Programme implementation

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

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

ASSESSMENT OF DECONTAMINATION AND VOLUME REDUCTION TECHNIQUES FOR CLADDING HULLS AND FUEL HARDWARE WASTES

Contractor: CEN/SCK, Mol, Belgium
Contract N°: FI1W-0123
Working Period: November 1987 - March 1990
Period Covered: November 1987 - December 1987
Project Leader: Mr P. de Regge

A. Objectives and Scope

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

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

The management routes treated by CEN/SCK are compaction/conditioning/packaging for the first route, and decontamination/cementation/packaging for the second route.

B. Work Programme

2.1. Waste characteristics and arisings. CEN/SCK participates in defining the reference waste composition.

2.2. Drawing up of basic management routes. CEN/SCK will extensively define two basic routes for hulls and caps management as input data for the subsequent cost and radiological impact assessment. Basically, these two routes will comprise the following intermediate management steps:
Route No. 1: hulls compaction/conditioning/packaging/interim storage prior to geological disposal;
Route No. 2: hulls decontamination/cementation/packaging/interim storage before disposal by shallow land burial.

2.3. Sensitivity studies. Once the two basic management routes extensively described, sensitivity studies will be performed in order to determine the impact of some important parameters on:
- the waste product characteristics and arisings;
- the total volume of the treatment/conditioning facility buildings.

2.4. Assessment of the occupational exposure. For the two basic routes of concern, the occupational exposure will be determined for routine operations including manual operations for repairs and maintenance. This will consist in calculating the annual individual dose and the collective dose for 30 years operation.

COMPARATIVE ASSESSMENT OF MANAGEMENT ALTERNATIVES FOR LWR WASTE

Contractor: Belgatom S.A., Brussels, Belgium
Contract N°: FI1W-0124
Working Period: November 1987 - January 1990
Period Covered: November 1987 - December 1987
Project Leader: Mr C. Renard

A. Objectives and Scope

The objective is to contribute to the implementation of a joint study on management options for LWR wastes by drawing up one basic route emphasizing the treatment/conditioning and packaging aspects.

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

Belgatom will take care of a basic management route corresponding to Belgian concepts and practices.

B. Work Programme

2.1. Definition of primary waste inventories. Belgatom will define reference primary waste inventories resulting from normal operation of 900 MWe PWR's including:
- gaseous wastes
- liquid wastes (concentrates, sludges, ion exchange resins, decontamination liquors)
- filters
- technological solid wastes.

2.2. Definition of discharge limits, waste acceptance criteria and transport regulations. Discharge limits for the release of gaseous and liquid effluents into environment (inland site) will be proposed. As for waste acceptance criteria for disposal, it will be made use of the regulations already fixed or envisaged for shallow land burial in Belgium.

2.3. Drawing up of the basic management route. Belgatom will define one basic management route for reactor wastes according to the Belgian practices, considering a 20 GWe nuclear park (100% PWR's) and grouping of reactors by 4 units. The description of the basic management route will be sufficiently detailed to subsequently enable their costing and the assessment of their related occupational exposure.

2.4. Sensitivity studies. Once extensively described the basic management route, sensitivity studies will be performed in order to determine the impact of some important parameters on:
- the conditioned waste product characteristics and quantities;
- the major cost components.

2.5. Assessment of radiological impact. For the basic management route, occupational exposure and radiological short-term impact to the population, both individual doses to critical groups and collective doses will be estimated.

COST EVALUATION OF ALTERNATIVE MANAGEMENT SCHEMES FOR LWR WASTE

Contractors : TASK Ricerca & Sviluppo S.r.l. - Kraftanlagen AG
Contract N° : FI1W-0125
Duration of Contract: from 01.10.87 to 31.12.89
Period Covered : from 01.10.87 to 31.12.87
Project Leaders : G. THIELS (TASK R&S), F. STENERSEN (KAH)

A. OBJECTIVES AND SCOPE

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

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

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

B. WORK PROGRAMME

2.1 Scope of the programme

2.2 Cost evaluation
- 2.2.1 List of possible intermediate management stages
- 2.2.2 Cost assessment procedure
- 2.2.3 Results
- 2.2.4 Sensitivity studies

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

To perform the cost evaluation, a procedure is being elaborated, which consists of:
- Determination of the various elements entering into the capital and operating costs of each management option;
- Actualisation of the costs and their conversion into an annual cost per unit volume;
- Scaling of costs with changing plant capacity.

COST EVALUATION OF ALTERNATIVE MANAGEMENT SCHEMES FOR ZIRCALOY HULLS

Contractors : TASK Ricerca & Sviluppo S.r.l. - Kraftanlagen AG
Contract N° : FI1W-0126
Duration of Contract: from 01.10.87 to 31.12.89
Period Covered : from 01.10.87 to 31.12.87
Project Leaders : G. THIELS (TASK R&S), F. STENERSEN (KAH)

A. OBJECTIVES AND SCOPE

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

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

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

B. WORK PROGRAMME

2.1 Scope of the programme

2.2 Cost evaluation
- 2.2.1 Management options to be costed (provisional)
- 2.2.2 Cost assessment procedure
- 2.2.3 Results
- 2.2.4 Cost scaling

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

To perform the cost evaluation, a procedure is being elaborated, which consists of:
- Determination of the various elements entering into the capital and operating costs of each management option;
- Actualisation of the costs and their conversion into an annual cost per unit volume;
- Scaling of costs with changing plant capacity.

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

Contractor: Initec S.A., Madrid, Spain
Contract N°: FI1W-0127
Working Period: December 1987 - May 1989
Period Covered: December 1987
Project Leader: M. Sanchez Delgado

A. Objectives and Scope

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

The main goals of this project are:

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

B. Work Programme

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

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

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

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

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

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

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

Contractor : National Radiological Protection Board, Chilton, Didcot, UK
Contract No. : FI1W-0128
Duration of contract : 1 August 1987 - 31 December 1989
Period covered : 1 August 1987 - 31 December 1987
Project leader : Dr A D Wrixon

A. OBJECTIVES AND SCOPE

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

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

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

B. WORK PROGRAMME

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

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

Contractor: National Radiological Protection Board, Chilton, UK
Contract No.: FI1W-0129
Duration if contract: November 87 - December 89
Project leaders: M D Hill, S F Mobbs (NRPB), and R Dodds (BNFL)

A OBJECTIVES AND SCOPE

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

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

B. WORK PROGRAMME

The study will be carried out jointly by the National Radiological Protection Board (NRPB) and British Nuclear Fuels plc (BNFL), acting under contract to NRPB. BNFL will be responsible for specifying the radionuclide content of all wastes and the design of waste treatment and storage facilities, together with estimates of financial costs. NRPB will carry out the assessments of radiological impact.

2.1 Direct Disposal of Spent Fuel

The quantity of fuel to be considered will be that arising in a hypothetical 20 GW(e) reactor park, consisting of PWRs, over a period of 30 years. The fuel will be assumed to be stored in a specifically constructed facility, prior to packaging and disposal in a granite formation. The type of packaging assumed will be typical of those under consideration in countries with large research programmes on spent fuel disposal in granite. The financial costs of packaging, transport and disposal will be estimated. The components of radiological impact which will be calculated will be: individual and collective doses to the public during routine packaging; transport and disposal operations; risks to individuals in the post-disposal period; collective doses to local, regional and global populations in the post-disposal period, as a function of time and level of individual dose. The probability of occurrence of collective doses will also be considered. All the radiological impact calculations will be carried out using existing models. For the post-disposal period, care will be taken to ensure consistency with the methods, models and data used in the PAGIS project and results will be given separately for naturally occurring radionuclides.

2.2 Reprocessing

The quantity of fuel considered will be the same as that assumed in the assessment of direct disposal. Reprocessing will be assumed to occur 5 years after discharge of fuel from the reactor, and vitrification to occur after a period of several years storage of the liquid high level waste. The vitrified waste will be assumed to be stored for 50 years prior to disposal in a granite formation.

Detailed radionuclide inventories will be provided for all wastes, and financial costs will be estimated for all of the waste management operations involved, ie, treatment of liquid and gaseous effluents arising during reprocessing and vitrification; immobilisation, packaging and disposal of low and intermediate level wastes arising during processing and vitrification; storage of liquid and vitrified high level waste; transport and disposal of vitrified high level waste. For all of these operations, individual and collective doses to workers and the public will be calculated, including doses form potential accidents. Radiological impact in the post-disposal period will be calculated using the same general method as for disposal of spent fuel, again ensuring consistency with previous PAGIS work and on-going PACOMA studies. Vitrified waste will be assumed to be disposed of in a granite formation. Low and intermediate level waste will be assumed to be disposed of in a deep clay formation.

2.3 Sensitivity Analysis and Additional Calculations

The sensitivity of the results of the cost and radiological impact assessments to variations in key parameters and assumptions will be investigated. The variations considered will include:

i) quantity of spent fuel to be disposed of or reprocessed;

ii) delaying reprocessing for at least 30 years;

iii) varied periods of storage of spent fuel and vitrified high level waste prior to disposal.

In this part of the work, all the results of the radiological impact calculations by NRPB and other contractors will be reviewed in the light of the requirements for the comparison between direct disposal and reprocessing, and any additional calculations which are necessary will be undertaken.

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

Contractors : GNS, Essen, F.R.G. and FRAMATOME, Paris, France.
Contract N° : FI1W - 0130
Duration of contract : from January 1988 to April 1990
Period covered : December 1987
Project Leaders: K. Janberg, Y. Huet.

A. OBJECTIVES AND SCOPE

During the last years, reactor waste management practices have taken advantage of many improvements as far as processes, organization and safety are concerned. Within the framework of the EC programme, GNS and FRAMATOME takè part in the present joint study the purpose of which is to characterize various overall management schemes resulting from these new developments. The complete describing and analysis of each scheme will permit to evaluate its feasability and availability and optimizing its radiological and economic features.

The assessment of the different european management alternatives will make up basic data for the study. The identified schemes will be applied to a hypothetical 20 GWe reactor park consisting of light - water cooled reactor (PWR's and BWR's) and to low and intermediate radioactive waste issued from normal operating. After having analysed the base-case, sensitivity analysis will be carried out varying the most important parameters such as disposal criteria, waste characteristics, size of the nuclear park and discharge limits acting both on cost and radiological impact.

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

B. WORK PROGRAMME

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

In this connection, FRAMATOME/GNS will take in charge partly tasks 2.2, 2.3 and 2.7 and wholly tasks 2.4, 2.5 and 2.6 for two basic management routes relying on the German and Italian concepts and practices.

WASTE MANAGEMENT SCENARIOS FOR LWR FUEL CLADDING AND HULLS

Contractor : CEA - VALRHO - MARCOULE - FRANCE
Contrat n° : FI W-0131
Duration of contract : 28 months
Period covered : September 1987 - December 1988
Project leader : C. SOMBRET

A. OBJECTIVES AND SCOPE

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

The corresponding study is part of the joint study which aims at assessing management routes for hulls and caps generated during reprocessing of spent fuel on the basis of economic and radiological criteria.

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

Basic assumptions are :

- Light water reactors stock : 20 GWe
- Yield : 600 $t.y^{-1}$
- Conditioning on production site
- 2 geographical sites : coastal and non costal

B. WORK PROGRAMME

The study directed towards 2 management routes based on direct cementation and on melting, will take in charge the following tasks :

Definition of the characteristics and arisings of hulls and caps.

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

Sensitivity studies on each basic management route.

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

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

Contractor : SGN - St Quentin-en-Yvelines, France
Contract No : FI 1W - 0132
Duration of the contract : September 1987 - December 1989
Period covered : September 1987 - December 1987
Project Leaders : B. de Wavrechin, C. Jaouen

A - OBJECTIVE AND SCOPE

The objective is to contribute to the implementation of a joint study on management options for LWR waste by drawing up two basic routes emphasizing the treatment/conditioning and packaging aspects. The assessment of management routes on the basis of economic and radiological criteria is based on the French and Spanish concepts and industrial practices.

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

B - WORK PROGRAMME

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

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

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

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

2.1.5. Assessment of the occupational exposure.

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

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

Contractor	:	CAP Scientific
Contract No	:	FI1W/0133
Duration of Contract	:	September 1987 to March 1987
Period covered	:	September 1987 to December 1989
Project Leader	:	R S Laundy

A. Objectives and Scope

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

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

The goals of the project are:

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

B. Work Programme

B.1 Evaluation of radiological and economic impacts.

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

C. Progress or Work and Obtained Results

State of advancement

Work started on the project in December 1987. A data requirement paper has been produced and work is proceeding on designing the model.

Progress and results

A number of processes involved in direct disposal and reprocessing have been identified. These are shown schematically in figures 1 and 2. The costs and environmental impacts that will be of concern have been assessed and a data requirements paper has been written. This paper proposes a set of impacts to be taken into consideration and describes the data to be collected.

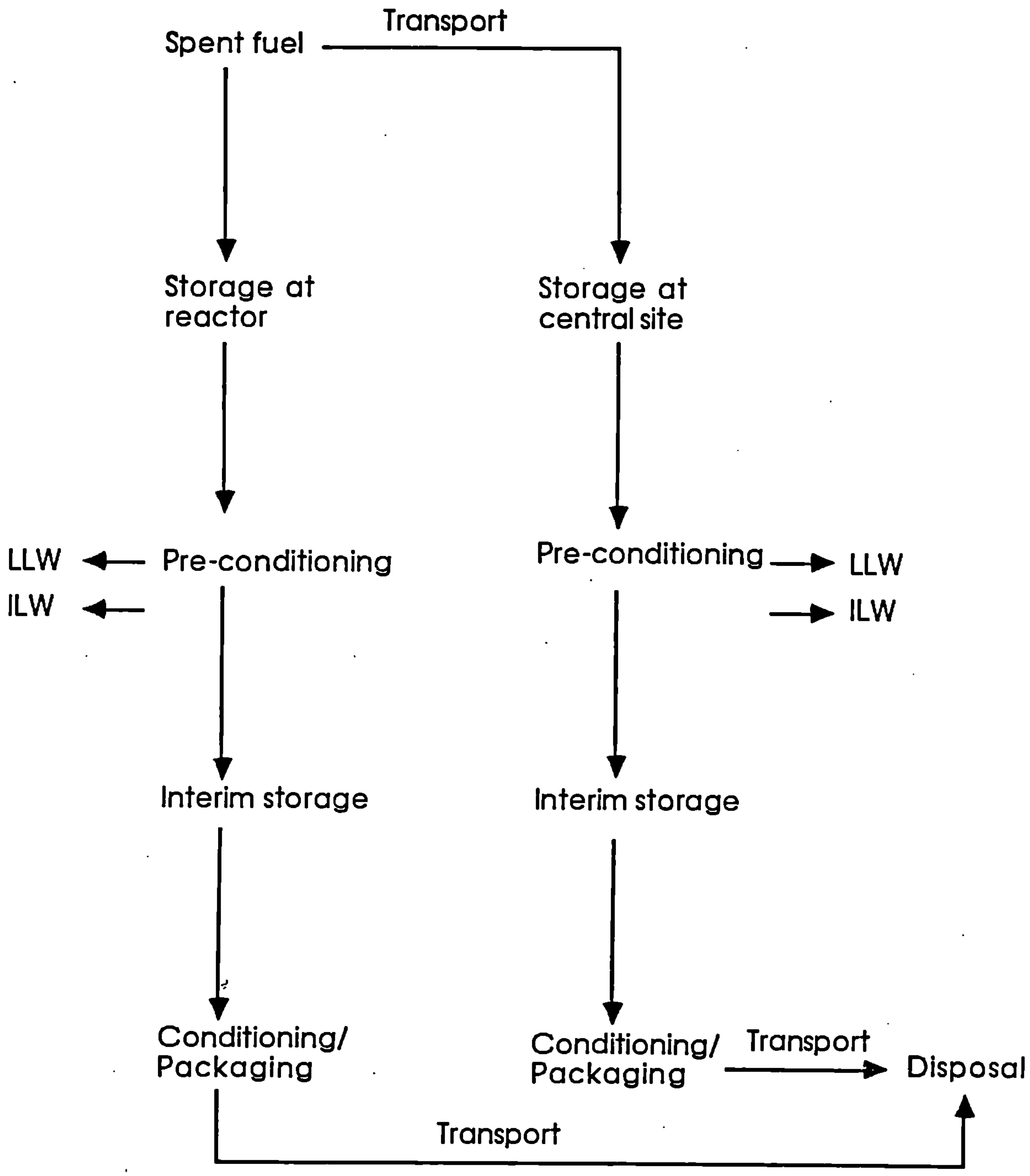


Figure 1 Schematic diagram of direct disposal options

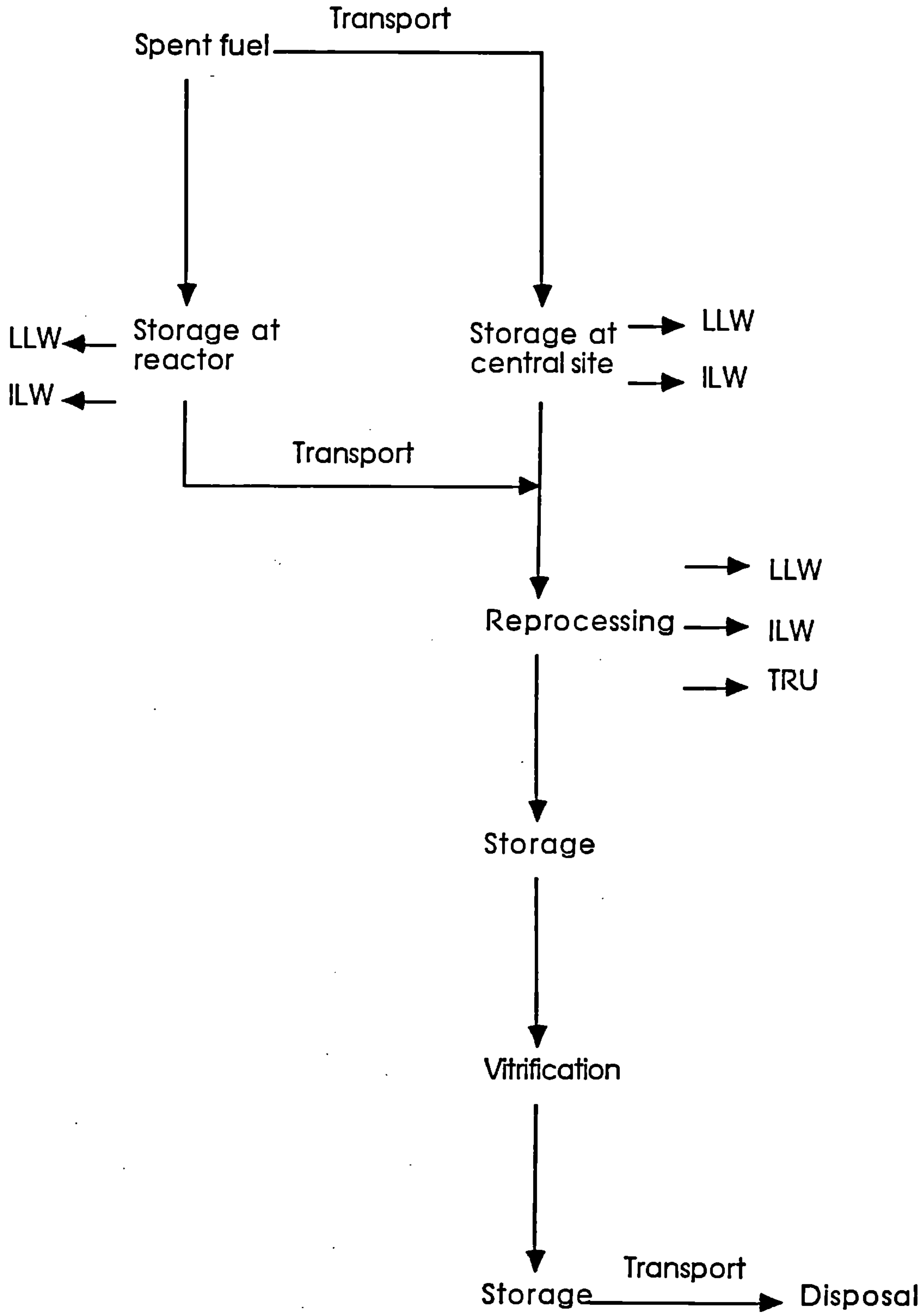


Figure 2 Schematic diagram of reprocessing options

COMPARISON OF WASTE MANAGEMENT ASPECTS OF DIRECT DISPOSAL

OF SPENT FUEL AND REPROCESSING

Contractor : CEN FONTENAY AUX ROSES - CEA - FRANCE

Contract : N° FI 1 W.0134

Duration fo contract : September 1987 - Décember 1989

Period covered : September 1987 - Décember 1987

Project Leaders : G. MALET - J. MALHERBE

A. OBJECTIVES AND SCOPE

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

Three main management routes are considered :

- immediate reprocessing of spent fuel after 3 years of cooling in ponds : that is the French solution in operation at La Hague (UP.2 and later on UP.3) ;
- delayed reprocessing after a rather long time in intermediate storage (up to 50 years) ; storage in ponds, in cask or in a dry storage is possible ;
- no reprocessing : immediate disposal after short cooling time and possibly rod consolidation.

In the part of the project covered by this study the aim is to compare immediate reprocessing and delayed reprocessing according to the following points of view :

- technical ;
- economical ;
- and radiological impact on population.

B. WORK PROGRAM.

The quantity of fuel to be considered will be that arising in a hypothetical 20 GW(e) reactor park consisting of PWRs, over a period of 30 years. The fuel is to be reprocessed either after a short cooling time, or after an interim storage time of up to 50 years in a plant with a 600 MTHM/year capacity.

The CEA study will only deal with the reprocessing option. The main items of the programm are as follows :

1. Data base and waste inventory

The 20 GWe nuclear park is assumed to consist of standard PWR reactors, the burn-up of the fuel being 33.000 MWd/MTHM.

The activities and thermal decay power of actinides, fission and activation products will be given in a first stage. Inventory of waste arising from reprocessing will also be determined.

2. Extended storage (work performed by SGN)

This part takes into account two successive steps : the first one is a storage at reactor (AR) and the second one is a centralised storage (AFR = away from reactor). For the AR concept only storage in ponds with dismantling under water will be studied (for consolidated and non-consolidated fuel).

3. Liquid waste treatment scenarios.

The inventories of reprocessing waste products will be determined taking into account the site characteristics (discharge limits) and the waste treatment scheme selected. Regarding this, three waste treatment schemes relying on the French, German and British concepts will be looked into as well as two sites (inland and coastal) for the location of the reprocessing plant of concern. Therefore, 6 variants of inventories will be studied. The British concept will be defined in co-operation with BNFL/NRPB.

4. Final disposal

Following these main scenarios, the conditioned waste arisings are classified in :

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

5. Transport (work performed by COGEMA)

The casks for transport of the conditioned waste are those in use by COGEMA. All characteristics like costs, occupational exposure and risk linked to transport will be, as far as possible, those of effective transport operations by COGEMA, BNFL and DWK according to the reprocessing plant considered.

6. Cost evaluation

The cost data concerning the different scenarios will be composed of costs from existing facilities or estimated costs from various projects (costs provided by SGN for the intermediate storage for exemple).

7. Radiological impact

The radiological impact to the public will be assessed in accordance with the methodology developed by CEA/IPSN. This study will largely rely on the experience obtained in the different French facilities.

8. Sensitivity studies

The sensitivity studies will deal with variation of burn-up (up to 45.000 MWd/t), variation of the size of the nuclear park, the treatment of MOX fuels, the variation of the disposal criteria and discharge limits (coastal and inland sites) and the type of packaging.

COST AND RADIOLOGICAL IMPACT ASSESSMENT FOR THE DISPOSAL OF REACTOR WASTE BY SHALLOW LAND BURIAL

Contractor : CEN FONTENAY AUX ROSES - CEA - FRANCE

Contract : N° FI 1 W 0135

Duration of contract : September 1987 - Décember 1989

Period covered : September 1987 - Décember 1987

Project leader : G. MALET - J. MALHERBE

A. OBJECTIVE AND SCOPE

The study is part of a joint study aiming at assessing management routes for LWR wastes on the basis of economic and radiological criteria.

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

In the frame of these large programme, CEA is mainly involved in the final part of management routes : definitive storage. In cooperation with INITEC we shall develop two concepts of disposal for these reactor wastes : shallow land burial (French and Spanish storage) and mine disposal (Konrad mine type).

B. WORK PROGRAMME

In this context, the CEA-FAR will perform the following studies :

. definition of criteria acceptance in the case of a shallow land burial, with reference to ANDRA specifications ;

. drawing up of basic management routes

On the basis of inventories and criteria acceptance, we will define all the subsequent disposal operations by shallow land burial. Disposal flow-sheets for each relevant category of LWR waste products and engineered flow diagrams will also be provided.

. Sensitivity studies

Sensitivity studies will be performed in order to determine the impact of some important parameters on cost and doses ; particularly, the impact of the package type on the volumes of waste to be disposed of will be assessed.

. Cost assessment.

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

We will try to perform scaling of costs with changing disposal site capacity corresponding to variations of the nuclear park.

. Assessment of the occupational exposure.

The radiological impact assessment will consist in calculating the annual individual dose and the collective dose for 30 year operations and if possible, doses will be estimated for each working place.

. Assessment of the radiological impact to the public.

Disposal site environment will be defined and the different pathways and scenarios through which doses to population could occur in the near or far future will also be determined with reference to ANDRA experience.

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

Contractor: Dornier System GmbH
Contract No: FI1W/0136
Duration of contract: October 1987-March 1988
Project leader: Armin-Dietmar Karpf

A. OBJECTIVES AND SCOPE

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

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

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

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

B. WORK PROGRAMME

(i) Assessment of natural scenarios: Abundance of natural radionuclides, mechanisms of deposition, mechanisms of mobilisation, pathways to population and collective doses, future developments, validitation.

(ii) Assessment for use of natural radionuclides: Total needs, produced waste, fuel cycle scenarios, failure of repositories, hazards to population.

(iii) Global comparison of natural and used uranium: Collective dose comparisons.

(iv) Local comparisons for scaling purposes.

(v) Probabilistic extension due to uncertainties in parameters.

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

Contractor: NUKEM GmbH, Hanau, Federal Republic of Germany
Contract N°: FI1W-0137
Working Period: October 1987 - December 1989
Period Covered: October 1987 - December 1987
Project Leader: Dr H.J. Wingender

A. Objectives and Scope

The study investigates management options for LWR hulls and caps by drawing up the two routes emphasising treatment/conditioning and packaging aspects.

The main objectives are to evaluate both management routes on technological, economical and radiological criteria. Therefore, the determination of operational and investment costs, the assessment of safety parameters like occupational exposure, effluents, incidents and material behaviour, and a detailed description of basic information concerning data and methods have to be provided. In order to compare the two management routes, the result of the study will be traced back and recalculated for variations in key assumptions. The study takes into account the overall discharge limits arbitrarily imposed to the two different sites for an hypothetical 600 t/a reprocessing plant.

B. Work Programme

This part of the study will investigate the management routes of hulls and caps generated during the reprocessing of spent fuel, comprising treatment, conditioning, packaging, interim storage, transport and disposal operations.

2.2. NUKEM will partially take into charge task 2.2. and is only asked to discuss the data provided by another organisation participating within the joint study, so that a reference waste composition can be defined.

2.3. NUKEM will define two basic routes for hulls and caps management as input data for the subsequent cost and radiological impact assessment.

2.4. The sensitivity study will be performed to determine the impact of some important parameters on:
- waste product characteristics and arisings,
- total volume of the treatment/conditioning facility buildings.

2.5. NUKEM will provide data on the related disposal costs as far as disposal of conditioned and packaged hulls in the Gorleben salt dome are concerned.

2.6. For the two basic routes concerned, NUKEM will determine the occupational exposure due to routine operations including normal operations for repair and maintenance.

C. Progress of Work and Obtained Results

First activities at the beginning of a project have to deal with collecting and inspection of basic information and data, in order to make the investigation fitting into previous and parallel activities. Due to the simultaneous preparation and elaboration in parallel groups, information necessary for evaluation of the amounts and radiological data of the hulls and caps has not been achieved in the reporting period. Needed data sets were discussed.

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

Contractor: NUKEM GmbH, Hanau, Federal Republic of Germany
Contract N°: FI1W-0138
Working Period: October 1987 - December 1989
Period Covered: October 1987 - December 1987
Project Leader: Dr H.J. Wingender

A. Objectives and Scope

The study investigates the waste management aspects of spent fuel storage in engineered structures, the final disposal in a salt dome repository and the disposal of low- and intermediate-level waste in the Konrad mine.

The main objectives are the determination of investment and operational costs, the assessment of safety parameters like occupational exposure, effluents, incidents and material behaviour, and the provision of detailed description of basic information concerning data and methods. In order to compare the reprocessing of Light Water Reactor fuel with direct disposal by emplacement in a deep geological formation, the study will provide the results in such a way and detail that they can be traced back or recalculated, and sensitivity analysis of the results to variations in key assumptions can be possible.

The study will follow the main basic scenario and variations, as specified for the joint study concerned with a hypothetical 20 GW(e) PWR park of 30 years operation period.

B. Work Programme

This part of the study will cover direct disposal. The program items are:

2.2. Spent fuel storage and preconditioning consists in evaluating basic data, storing prior to preconditioning, preconditioning (3 options), interim storage.

2.3. Conditioning for final disposal consists in determining the final conditioning procedures, installations, waste and safety aspects, transport to the final repository and repository features with respect to the spent fuel.

2.4. LLW/MLW disposal. The secondary waste is defined and compared with Konrad repository acceptance criteria. Repository structures, costs and safety aspects are treated.

C. Progress of Work and Obtained Results

First activities at the beginning of a project have to deal with collecting and inspection of basic information and data, in order to make the investigation fitting into previous and parallel activities. Due to the simultaneous preparation and elaboration in parallel groups, information necessary for evaluation of the amounts and radiological data of the spent fuel has not been achieved in the reporting period. Needed data sets were discussed.

CHAPTER 2

TASK No 2

Improvement of radioactive waste treatment and conditioning technologies

CHAPTER 2

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

A. Objective

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

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

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

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

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

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

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

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

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

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

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

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

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

C. <u>1985-1989 programme</u>

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

a) Waste from light water reactors

- Reduction at source of radioactive waste and of discharges of radioactivity into the environment by better management of effluents and the possible use of alternative treatment processes

- Development of new waste/matrix formulae in order to keep in step with safety regulations

- Analysis of the industrial operating conditions of waste conditioning installations with a view to setting up or improving quality assurance

- Development of new methods of conditioning incineration ashes.

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

- Decontamination of low- and medium-activity liquid waste by means of chemical precipitation with new, highly selective precipitants (for example, organic compounds). This activity will have to include active tests on real waste

- Development of processes alternative to those already developed under the 1980-1984 programme for the decontamination of reprocessing concentrates

- Conditioning of residues or concentrates rich in actinides (and possibly in fission products) in matrices of long-term stability

- Operation of pilot installations, functioning under active conditions, for the treatment of low- and medium-activity liquid waste by means of advanced processes (membrane and electrochemical processes, etc ...)

- Operation of pilot installations, functioning under active conditions, for the decontamination of solid waste and the recovery of plutonium

- Pilot-scale application of processes, under active conditions, for the conditioning of claddings.

c) Optimization of waste management at source

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

D. <u>Programme implementation</u>

23 contracts have been signed and the available information is listed thereafter. However information has not been received as far as contracts n FI1W/0005, FI1W/0012, FI1W/0013, FI1W/0019 are concerned.

2.A. Waste from light water reactor

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

Contractor : AEE Winfrith
Contract No.: F1 1W.0006.UK(H)
Work Period : January 1987 - December 1987
Project Leader : D J Lee/C G Howard

A. OBJECTIVES AND SCOPE

The overall objective of the programme is to identify a suitable cement matrix to dispose of organic ion exchange resins contaminated with decontaminating agents.

For the last five years, Low Oxidation state Metal Ion reagents (LOMI) have been used to decontaminate the 100 MW(e) Steam Generating Heavy Water Reactor at Winfrith. The use of these reagents has resulted in a dilute ionic solution containing activation products which are produced by corrosion of metallic components in the reactor. It has already been demonstrated that the amount of activity in solution can be reduced using organic ion exchangers, for example Purolite C100, a crosslinked polystyrene with sulphonic acid functional groups.

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

B. WORK PROGRAMME

B.1 Identify suitable simulant ion exchange resin waste.
B.2 Development of formulation using a range of waste simulant to cement ratios at Laboratory scale.
B.3 Demonstrate formulation is still acceptable after scaling up to 200 litres. If necessary the formulation will be adjusted.
B.4 Investigate the effects of decontamination reagent's components on cement hydration.
B.5 Investigate the effect of additives to improve the properties of the cemented product.
B.6 Establish waste volume reduction factors.
B.7 Compare and contrast methods used by other LWR Operators in Europe for decontamination of their reactor circuits and disposal of the solutions generated.
B.8 Establish a satisfactory process flow sheet for encapsulating ion exchange resins in cement.

C. SUMMARY

Purolite C100 ion exchange resin (a crosslinked polystyrene with sulphonic acid functional groups) in the sodium form can be successfully immobilised in blended cement systems. The formulation which appears acceptable is manufactured from a 9 to 1 blend of Blast Furnace Slag and Ordinary Portland Cement containing 40% ion exchange resin by weight in the form of a slurry. The product has adequate strength for handling and shows little dimensional change with time.

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

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

To improve the properties of the product microsilica was added. The result was a stronger and more durable product.

Small scale experiments showed that additions of acids found in decontamination reagents (LOMI), eg, picolinic and formic, retard the hydration of 9:1 BFS:OPC. Other experiments have shown that anion resin in the OH form has a similar effect on cement hydration to the cation resin.

In conclusion, laboratory scale work has shown that cation resin and resins treated with LOMI can be successfully immobilised in cement containing microsilica and produce a product with acceptable properties.

INTRODUCTION

In 1980 a pilot plant was constructed at Winfrith to demonstrate that organic ion exchange resins could be used to remove radioactive nuclides from the decontaminating agent LOMI. Using a strong cation exchange resin like Purolite C100, most of the activation products, eg, Fe^{59}, Cr^{51}, Mn^{54}, Zn^{65} and Co^{60} plus the vanadium from the LOMI and some of the fission products Cs^{137} and Sr^{90} can be removed from solution. Results also showed that some of the picolinate and formate from LOMI were also trapped in the resin.

FORMULATION DEVELOPMENT

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

1. The product in the mixing stage must be fluid enough to give a homogenised product.
2. The product must not have free water (bleed) on the surface of the product at 24 hours.
3. The product must have undergone initial hydration within 24 hours.
4. The product must have adequate strength for handling.
5. The product must be sufficiently dimensionally stable to ensure durability with time.

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

- Dimensional stability.
- Compressive strength.
- Pulse Velocity (Non-destructive determinations of compressive strength).
- Conduction Calorimetry (heat output at constant temperature).
- Viscometry.

Preliminary calculations show that a volume reduction factor of 4 is obtained by taking the active LOMI effluent, removing the activity onto the Purolite C100 and then immobilising in cement.

SMALL SCALE TRIALS

A number of experiments were undertaken to determine the effects of Purolite C100 resin on the properties of the cemented matrices. Most of the experiments were undertaken using the sodium form of the resin as a slurry containing 30% water. For determination of the water/cement ratio the total amount of water in the system was used.

Earlier experiments had shown /1/ that using pure OPC as the matrix to immobilise the resin resulted in excessive swelling of the product. This swelling caused the waste form to disintegrate after about a week if the waste loading exceeded 20% damp resin.

To improve on the product's properties and the waste loading, BFS was blended with OPC. BFS hydrates very slowly; however, when blended with OPC it acts as a latent hydraulic binder. Using a blend ratio of 9:1 (BFS:OPC) at least 50% resin can be incorporated into cement without incurring expansion which causes the product to fail.

A number of 20 litre scale mixes were undertaken and the resulting products are being tested for long term stability. The results of compressive strength determinations are given in Table I and show that increasing the resin loading results in a decrease in the compressive strength of the product.

THE USE OF MICROSILICA TO IMPROVE PRODUCT PERFORMANCE

Having increased the waste loading at the cost of reducing the compressive strength, a method of improving the physial properties was investigated.

Microsilica is a mineral composed of ultrafine solid, amorphous spheres of silicon dioxide and is used widely in the construction industry to improve cement and concrete systems.

When microsilica is dispersed through a cement matrix each cement grain is surrounded by thousands of reactive microspheres of microsilica. This results in all voids within the matrix being filled with strong hydration products. This causes changes in the physical properties of the cement matrix including:

1. An increase in the compressive strength of the product is achieved by adding 6% microsilica.
2. The pore filling effect of adding the pozzolanic microsilica to cement grouts drastically reduces the capillary porosity and grout permeability. This may result in a lowering of leach rates of radionuclides from cemented wastes.
3. A reduction in the amount of free calcium hydroxide as it is consumed by the pozzolanic action of the microsilica. This also reduces the susceptibility of the matrix to chemical attack from sulphates, chlorides and carbon dioxide.

As a result of adding microsilica to a mix, the water/cement ratio has to be increased to cope with the higher water demand of microsilica.

Two mixes were performed with microsilica as an additive. Both mixes contained 6% Microsilica, 84% BFS and 10% OPC. One contained resin in the sodium form and the other contained resin treated with a LOMI simulant. Both mixes produced acceptable products with compressive strengths of the products containing microsilica having greater values than those without (Table I).

EFFECTS OF PICOLINIC ACID AND FORMIC ACID

The hydration processes which occur during the hardening of cement can be affected by the chemical components present in the mix water. Salts of most short chain water soluble organic acids, eg, acetic and formic, are known to retard the hydration of cementitious material at certain concentrations.

A series of experiments showed that at concentrations of 3 w/o picolinic acid and 8 w/o formic acid results in a large increase in mix viscosity making mixing impossible. At 6 w/o picolinic acid or 9 w/o formic acid, flash sets result from the high heat output of the acid base reaction.

In reality the amounts of free picolinic and formic acids will be very low as anion exchange resins will be used to remove them from solution before cementation.

VOLUME REDUCTION FACTOR

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

TABLE I: MIX DETAILS AND COMPRESSIVE STRENGTH OF RESIN LOADED CEMENT SAMPLES

Cement:Binder	Duolite Loading (by wt of slurry)	Duolite Form	Additive	Compressive Strength N mm^{-2}		
				7 days	28 days	90 days
9:1 BFS:OPC 0.33 w/c	40%	Sodium	None	2.9	7.1	10.0
9:1 BFS:OPC 0.40 w/c	50%	Sodium	None		5.2	5.4
9:1 BFS:OPC 0.5 w/c	50%	Sodium	6% micro-silica	4.5	6.6	7.6
9:1 BFS:OPC 0.45 w/c	-		6% micro-silica (control)	14.9	17.2	35.6
9:1 BFS:OPC 0.45 w/c	50%	LOMI simulant loaded	6% micro-silica	10.5	13.6	14.5

REFERENCE

/1/ HOWARD, C. G., LEE, D. J., AEE WINFRITH REPORT M 2469 (1987).

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

Contractor : Laborelec (Belgium)

Contract N° : FI 1 W - 0007 - B (GDF)

Duration of contract : 18 months (from June 1, 1986 to November 30, 1987)

Project leader : R. Roofthooft

Second annual report (1987)

A. Objectives and scope

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

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

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

B. Work program

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

C. Progress of work and obtained results

State of advancement

In 1987 the study of the procedure to precipitate Co-58 and Co-60 has continued and been applied to an important volume (720 m^3) of borated waste that had to be treated in a very short time.

The influence of different pollutions has been examined. Decontamination factors are decreased principally by citric acid, oxalic acid and EDTA. These elements can be absorbed on activated carbon.

Centrifugation tests have been performed on lab scale.

Progress and results

Floc-recycling : it has been possible to recycle flocs up to 15 times. The activity of the treated water remains below the specified limit of 18,5 MBq/m^3. A small improvement is realized when 10 ppm Fe^{+++} are added at each treatment.

Treatment of a borated waste (720 m^3) : the floculation with $Ca(OH)_2$ and Fe^{+++} has been realized in batches of 35 m^3. The average time per batch is about 6 hours. Twenty-four batches have been treated and the sludge has been removed 5 times giving a volume of settled sludge of 5 m^3. The activity of the treated water has always been below 18 MBq/m^3. The main activity after treatment is formed by Cr-51 and Sb-124, when present in the influent. The settled sludge has further been concentrated by a thin film evaporator to 0,5 m^3 giving a total volume reduction factor of 1440. If this waste had been treated by evaporation the volume reduction factor would have been limited by the boric acid to a maximum value of 20. The cost of the treatment (reagents) is about 25 BF/m^3. The results for Co-60 are given in fig. 1. The activity of the sludge taken after the fifth batch is given in table 1.

Influence of chemical composition on the floculation

Different products, normally used in nuclear power stations, have been added to an effluent before treatment.

These products are : RBS-5C (non foaming detergent) Sator 2+ (detergent without phosphates) SU 388 (peroxide), citric acid, oxalic acid and EDTA.

The influence of a concentration of 50 ppm of these products on the decontamination factor is given in fig. 2.

Tests to eliminate the products on activated carbon have been performed. Some good results have been obtained on Hydraffin 300.

Lab tests on centrifugation

Centrifugation tests have been performed on a laboratory centrifuge. The influence of the speed of the centrifuge, the injection of polyelectrolyte and of $Ca(OH)_2$ have been examined.

A centrifugation at 1000 rpm is sufficient to obtain good results on the lab scale.

Pilot-plant centrifuge

Due to local problems in Tihange 2 it has not been possible to install the continuous centrifuge system. The installation is scheduled for the beginning of 1988.

Table 1 : Sludge activity after 5 treatments of borated waste (MBq/m^3)

^{110m}Ag	644
^{57}Co	24
^{58}Co	3315
^{60}Co	1961
^{51}Cr	559
^{54}Mn	190
^{95}Nb	62
^{124}Sb	186

Figure 1

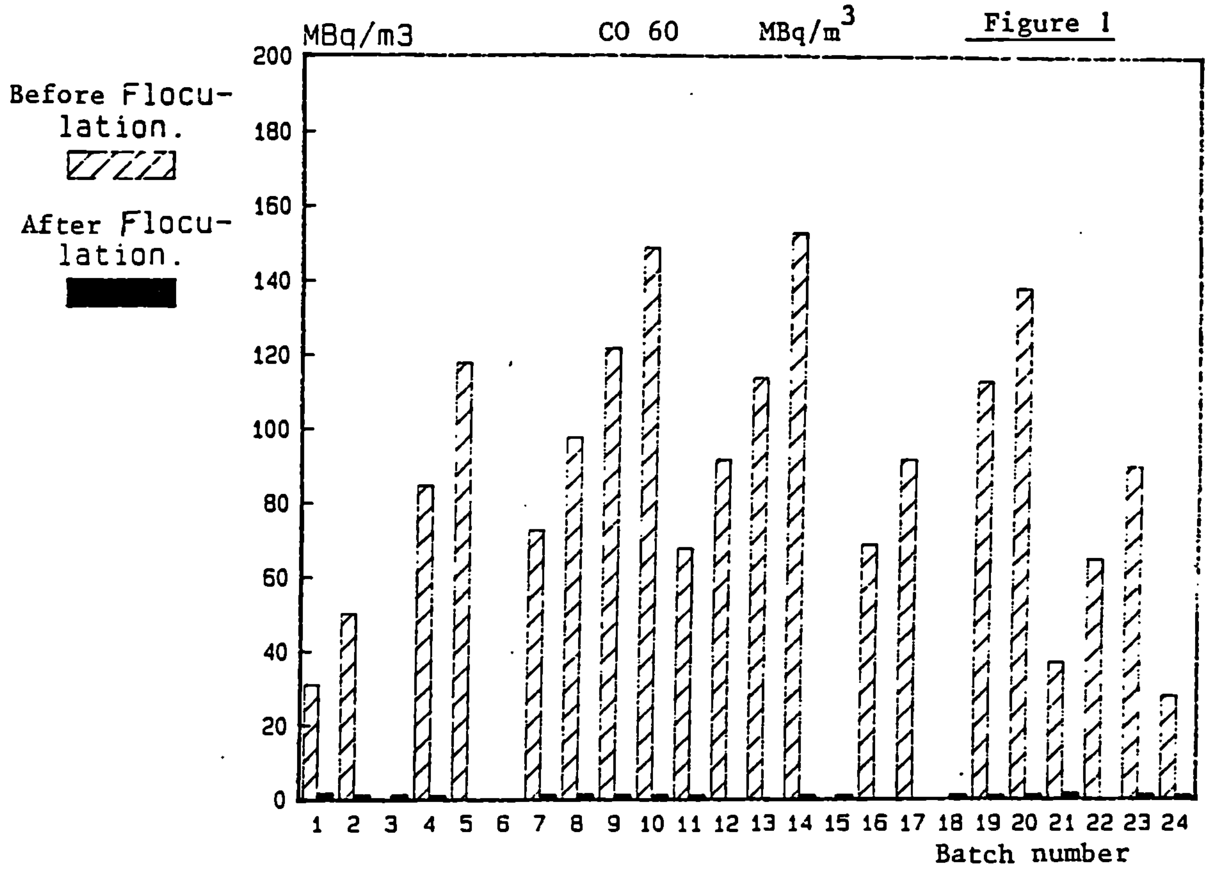
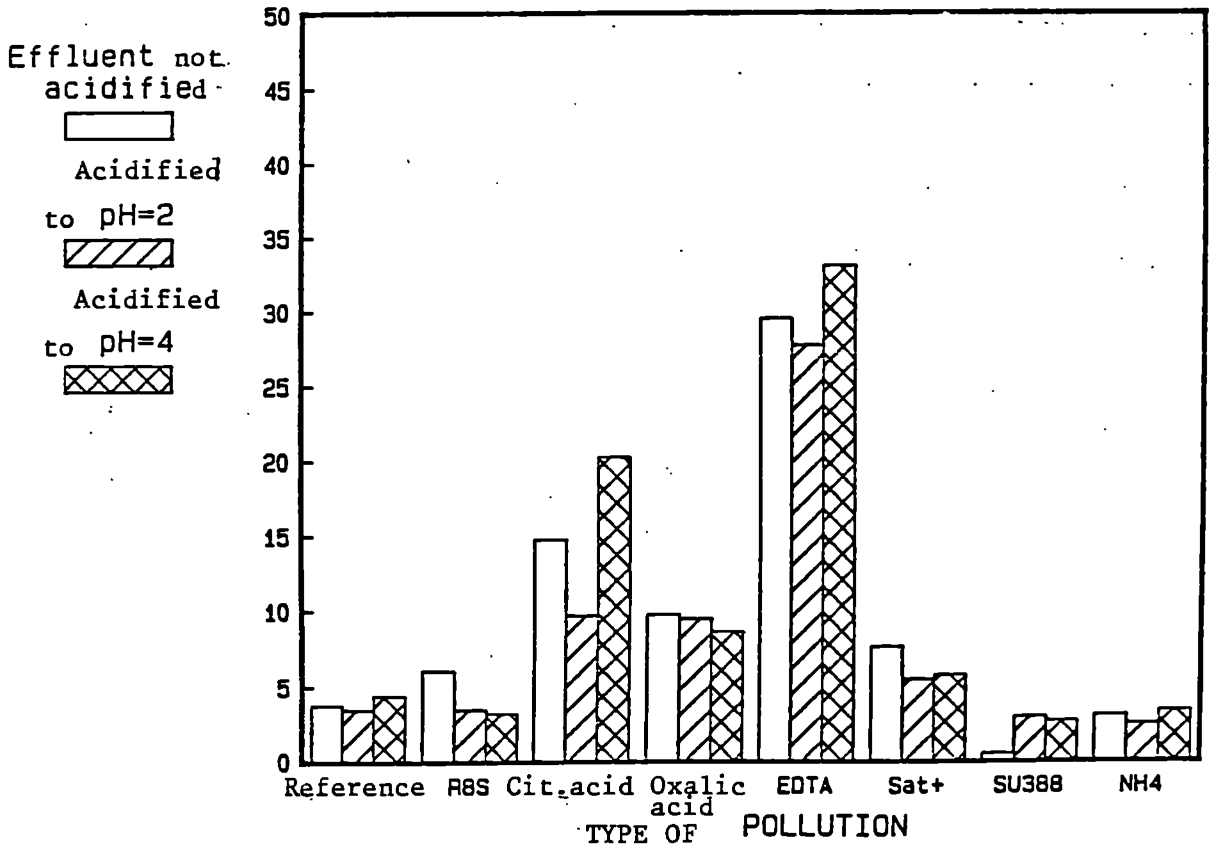


Figure 2

INFLUENCE of 50 ppm of POLLUTION - TOT. GAMMA ACT.



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

Contractor: ECN, Petten, The Netherlands
Contract No.: FI1W/0008
Duration of contract: June 1986-July 1988
Period covered: January 1987 - December 1987
Project Leader: A. van Dalen

A. Objectives and Scope

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

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

B. WORK PROGRAMME

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

B.1. Radiation resistance

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

B.3. Porosity regarding tritiated water.

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

C. Progress of work and obtained results

State of advancement

The main body of data on modified sulfur cement preparations containing low level waste were collected during this year of laboratory investigations. Due to the low permeability of the matrix material the time needed for an evaluation of this type of waste form exceeds the period described in the ANS publication on the short-term test-procedure (100 days of leaching).

After about 200 days the samples containing the simulated borate waste showed small cracks,probably due to the formation of hydrated borate crystals. This effect was not reflected by a change in leaching behaviour.

In most preparations an additional filler has been used in order to get "dilutions" of the waste materials in the matrix and to provide strength in case of preparations for tritiated water diffusion.

The choise of these fillers was made according to the experiences in the USA regarding the mechanical strength of the products.

Diffusion measurements with HTO indicate that asbestos is conducting water better compared to chalk probably due to the fibrous structure of asbestos.

SEM inspections of leached samples showed a depletion of Ca.

Use of the KEMA incinerator ash as a filler resulted in the lowest diffusion coefficients for HTO. Analysis of the main components in the ash indicated that Al_2O_3 may be the cause of this behaviour. Accordingly preparations of modified sulfur cement with only Al_2O_3 as filler were made. During the preparation it was observed that the melt degassed spontaneously, so presence of small airbubbles in preparations can be avoided. As a result a higher compressive strength was measured.

If the specific volume of water inside the micropores of the modified sulfur cement preparations is equal to the normal value of 1 cm^3 per g then the extrapolation of the weight increase by water uptake leads to a porosity of about 10 %. The diffusion coefficient of HTO indicates a very low permeability. A tentative explanation of this difference may be the presence of a relative large amount of not interconnecting micropores.

The leaching of radionuclides from the sulfur cement waste form is best represented by the diffusivity because the matrix material does not dissolve. The effective diffusion coefficients measured by the flux of radioisotopes from the solid material into solution is in good agreement with the values obtained from the measurement of the thickness of the depleted layer.

Progress and results

B.1 Radiation resistance

A few samples of the series to be used for compressive strength measurements after gamma irradiation have been tested also for compressive strength after 9 months storage. These unirradiated samples showed a higher compressive strength compared with the initial, unirradiated, samples. The effect of irradiation up to 16 MGy may be an accelerated ageing.

Gamma irradiation up to 2 MGy of samples in aluminum cans to retain gaseous radiolytic products did not result in measurable concentrations by gas analysis. Higher doses are under investigation.

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

The results obtained for compressive strength measurements and leachability of samples containing PbI_2, KEMA incinerator ash with ^{134}Cs, ^{90}Sr, $^{152,154}Eu$ and ^{60}Co, simulated borate waste with ^{137}Cs, ^{90}Sr and ^{60}Co and ECN pond sludge with mixed beta-gamma emitters are presented in the table.
At first sight the solubility of the compounds incorporated in the modified sulfur cement seems to be the main parameter for leaching. One batch of ion-exchangers treated with sulfur for dehydrogenation prior to incorporation in modified sulfur cement showed that the ion-exchange material does not show swelling anymore. Cylindric samples after 300 days contact with humid air or water showed practically no sign of attack.

B.3 Porosity regarding tritiated water.

The diffusion coefficients of HTO through a 3 mm disk of modified sulfur cement filled with several substances, e.g. asbestos, chalk, incinerator ash have been measured. The results are also included in the table.

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

For the study of metal corrosion by modified sulfur strips of the following metals and alloys were covered with modified sulfur cement with chalk as filler: lead, stainless steel, mild steel, aluminum, copper and brass. The inspection of the metal surfaces will take place after about a half year of storage.

Modified Sulfur Cement Preparations:

Compressive strength and effective diffusion coefficients

composition filler + "waste"		compr. strength MPa	diffusing species	D_{eff} m^2s^{-1}
chalk		32	HTO	4.10^{-15}
chalk + PbI_2	22%	43	I	3.10^{-15}
	30%	56	I	5.10^{-16}
	40%	46	I	2.10^{-16}
	51%	46	I	1.10^{-15}
			HTO	8.10^{-16}
chalk + KEMA ash	10%	66	^{134}Cs	8.10^{-14}
	15%	66	^{90}Sr	2.10^{-16}
	20%	69	$^{152,154}Eu$	2.10^{-17}
			^{60}Co	$\sim 10^{-20}$
chalk + borate	5%	9	^{137}Cs	2.10^{-14}
	10%	16	^{90}Sr	1.10^{-14}
	15%	23	^{60}Co	$\sim 10^{-20}$
Al_2O_3	25%	64		
	43%	78		
	43%	68		
chalk-asbestos			HTO	5.10^{-14}

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

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

Contract No : FI-1-W/0009

Working period : 01.01. - 31.12.1987

Project leader: : B. Ganser

A. OBJECTIVES AND SCOPE

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

B. WORK PROGRAMME

1. Qualification of process and product control

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

3. Additional investigations

4. Comparison of data and establishment

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Because of some licensing problems concerning our company area NUKEM-A, to which is belonging our technical lab for cementation, and technical problems at the construction work of ROBE 2, we have a delay in our practical work of more then 6 month. Actually we have completed the work concerning B.1 and B2.1. The other parts of our work programme are actually going on.

Progress and results

1. Qualification of processes and product control

According to the waste acceptance criteria for the disposal in the KONRAD mine we defined for the plants ROBE, MOWA and the continuous mixer the following process parameters resp. instrumentations:

- ROBE (fig 1): Vaccum facility (300 - 70 mbar), temperature sensor (evaporator), temperature difference measuring (cooling water), heating energy, stirring energy (evaporator), balance of evaporator, level sensor (distillate sampling container), drop sensor (distillate); automatic function

- MOWA (fig. 2): level sensor (liquid concentrate tanks), torque measuring/ hydraulic drive, balance for cement; automatic function

- Continuous mixer (fig. 3): Density measurement/flowmeter for liquid waste, dosing balance for cement, torque of stirrer (mixer), balance for container, automatic regulation of waste/cement feed.

2. Treatment of radioactive wastes

As the inactive test operation for the continuous mixer we performed conditioning experiments of reprocessing concentrate directly in a final disposal container type II (KONRAD). For this we determined the accuracy of the product relevant instrumentation and tested the system for a long time test (8 h). The dosing balance for cement worked with a very good accuracy within its gravimetric function (bandwidth $\pm$ 1 %); during the filling of the feed container (volumetric function) the accuracy was determined to $\pm$ 5 %. The liquid feed pump, controlled by a flowmeter (magnetic inductive) had the same constant rate like the dosing balance ($\pm$ 1 %). In total the feed bandwidths of cement and liquid waste are $\pm$ 5,1 %, that means a W/C-ratio variation in case of the reprocessing recipe (W/C = 0.4) of max. 0.38 - 0.42. Within these limits, the product properties can be seen as constant.

3. Additional investigations

Beside radiometrical properties and mechanical parameters (homogeneity, mass) the water content of ROBE-products is the only factor, for which the typical ROBE-product (waste class II, waste product group 06) has to be characterized. Directly concerned is the softening point of the products, which has to be higher than the final disposal temperature of 50 °C. During the standard operation the salt suspension is flowing out at 70 °C - 90 °C and becomes solid during cooling.

For waste simulates, covering the given composition bandwidths of evaporator concentrates from Biblis and Gundremmingen, lab experiments were performed in order to get the product values to fulfill the softing point criteria.

To reach this property, the salt concentrates must have a water content of max. 22 %: This is corresponding to a defined distillation temperature for a regulated pressure for a given concentrate and can be performed easily by the automatic process.

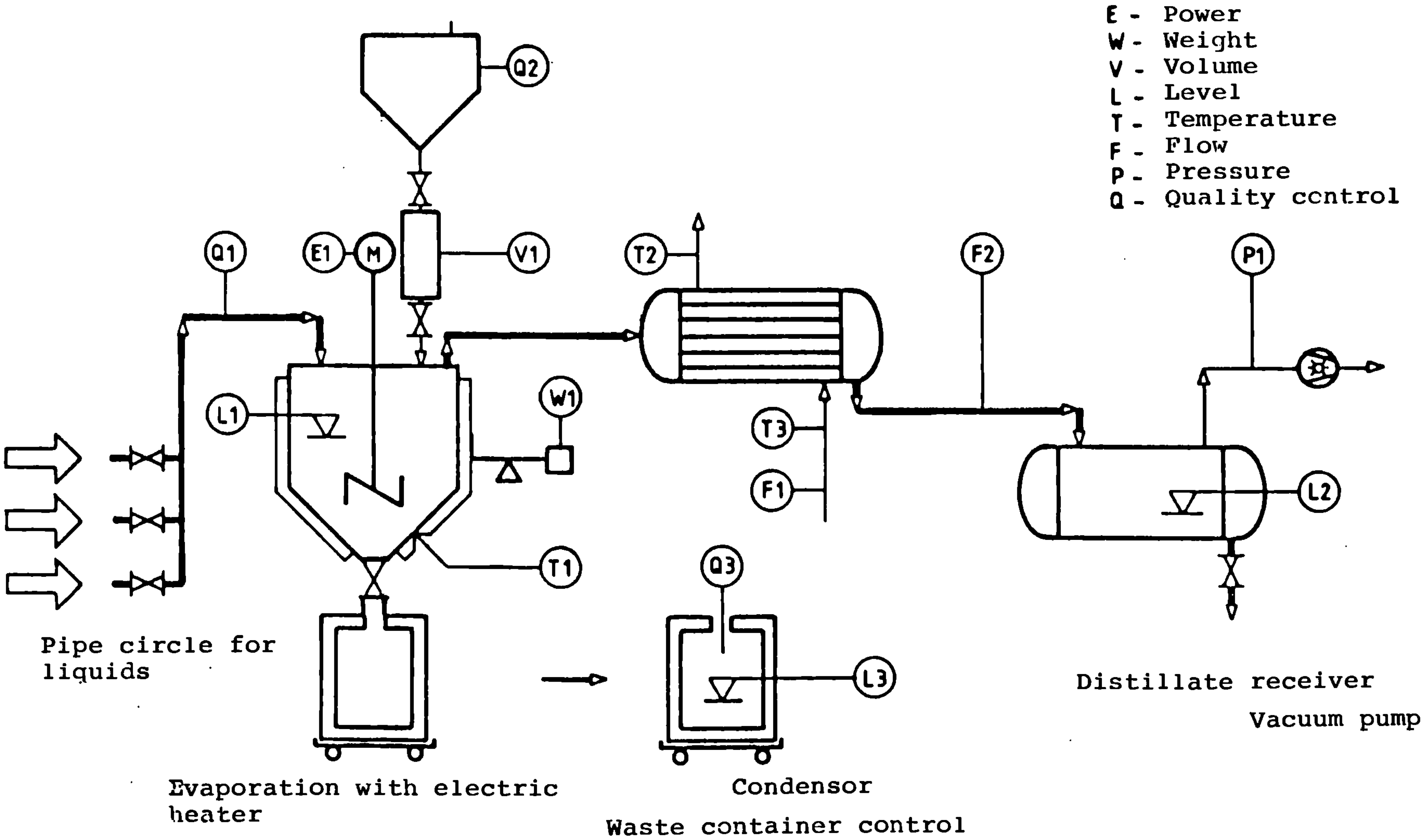
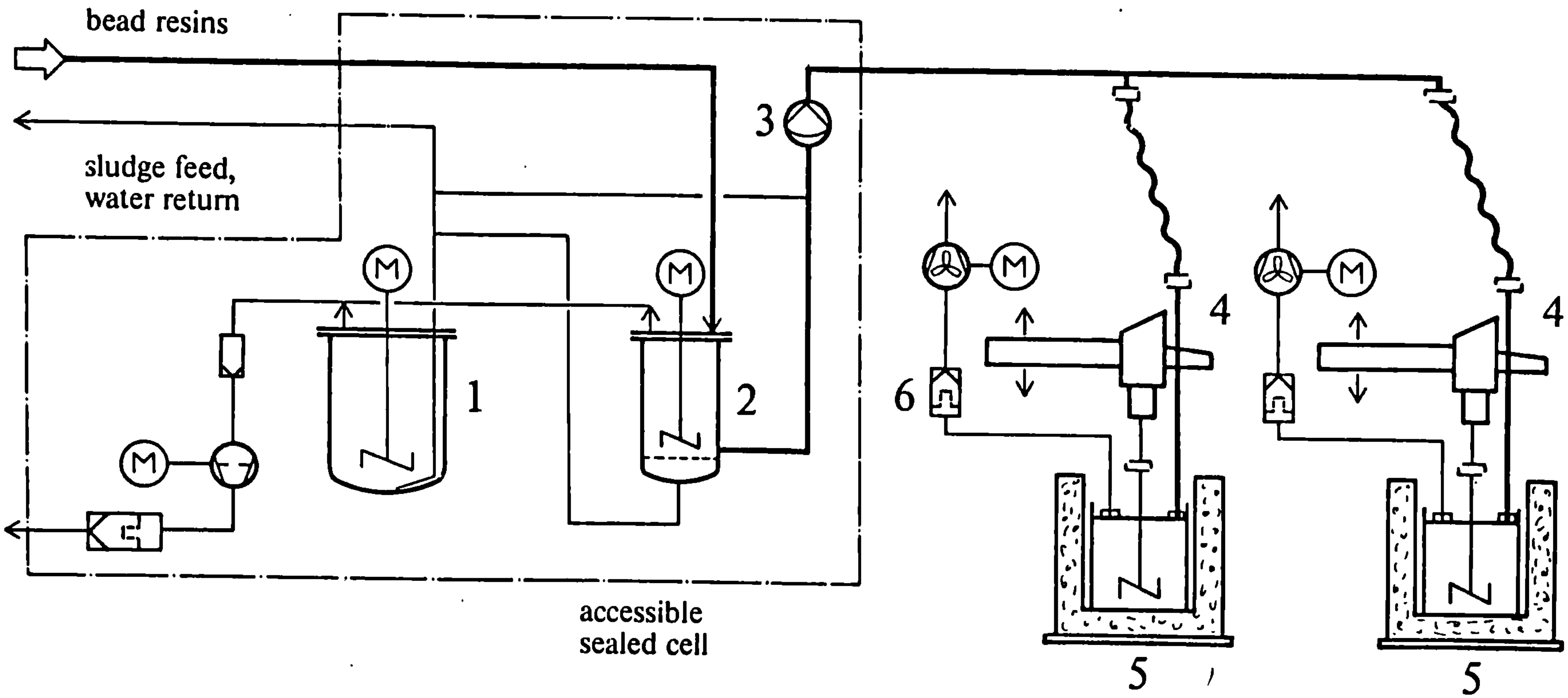


Fig. 1: Flowsheet ROBE
product relevant process instrumentation



1 Sludge metering tank (incl. level sensor)
2 Granular resin metering tank
3 Membrane pump
4 Filling head
5 Filling station
6 HEPA-filter
7 Vacuum pump

Fig. 2: Simplified diagram of MOWA

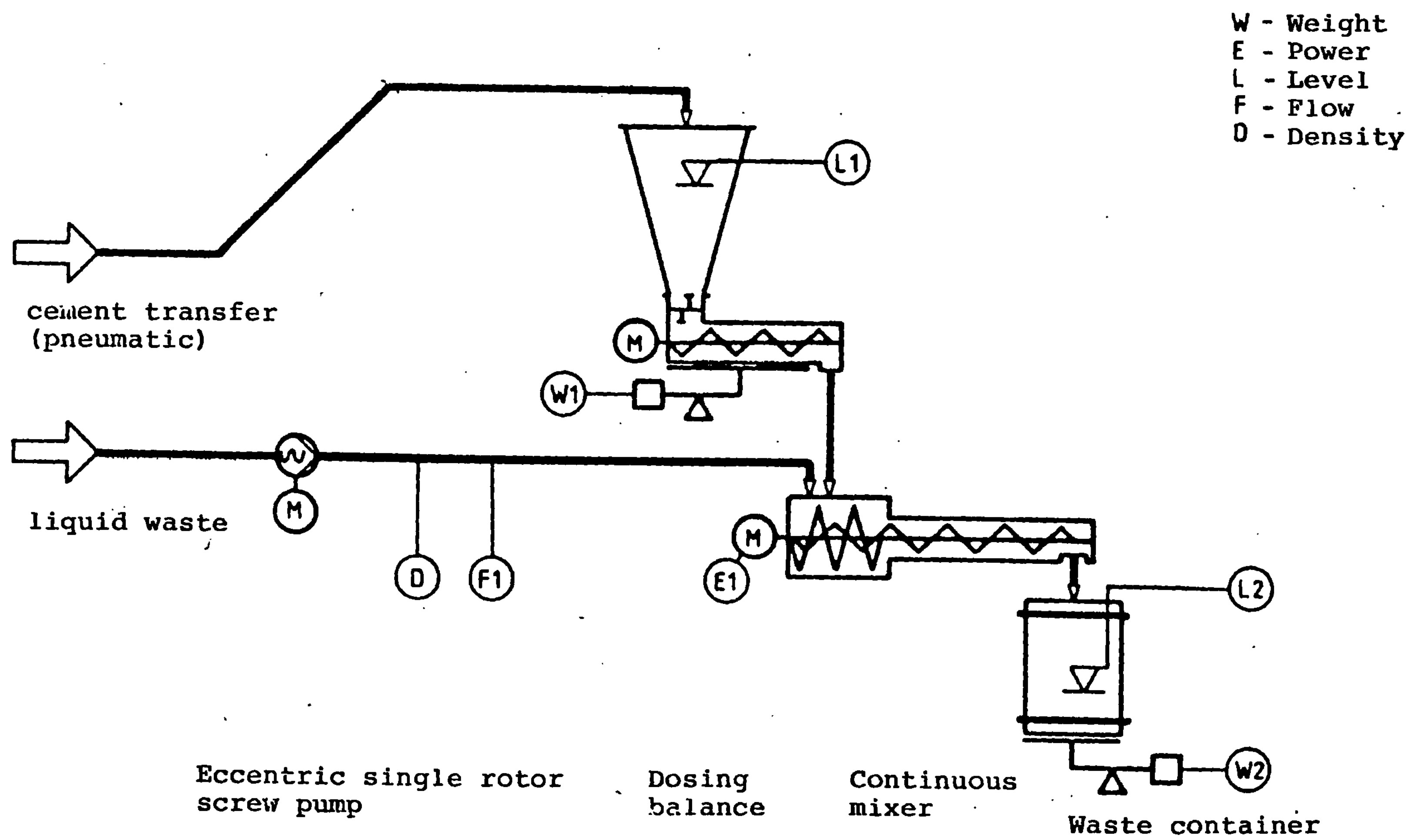


Fig. 3: Flowsheet continuous mixer
Process instrumentation

Conditioning of ashes from combustion plants in special melting furnaces

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

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

Working Period : 01.01.-31.12.1987

Project leader : B. Ganser

A. Objectives and Scope

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

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

B. Work programme

1. Aquisition of basis data

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

2. Construction of a pilot plant

3. Laboratory experiments

- Testing of process parameters
- Characterisation of final products

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

During the reported period we performed and concluded our laboratory melting experiments with different ash simulates and different additives. The products were characterized by the achieved volume reduction, the leaching behaviour and mechanical strengths. To construct a pilot plant, we defined the criteria for a technical equipment and contacted corresponding manufacturerers.

Progress and results

1. Aquisition of basis data

We completed this part of our contract with cost estimations of the expected melted products and melting process compared with other possible ash conditioning methods (cementation, high force compaction).

Concerning 1 m^3 of raw ash the following factors have been determined:

- Volume reduction
- Costs for final disposal (KONRAD)
- Investment
- Consumption, material (energy, additives, container)
- Costs of service companies (TRANSNUKLEAR, KWU)

The resulted estimated costs are:

- Melting: 5500 DM/m^3 (Depending strongly on investment)
- High force compaction: 5000 DM/m^3
- Cementation: 6100 DM/m^3 (Depending on volume reduction)

2. Construction of a pilot plant

Based on the literature data and the results of the laboratory experiments (described below) we contacted furnace manufacturers. The random criteria for the pilot plant are (see also fig. 1):

- 50 kg ash per day
- 50 %/30 % addition of Na-tetraborate (1000 °C/1300 °C)
- In can melting
- Heating by current resistance
- Melting can accessible for e.g. manipulators
- Off gas treatment by incinerator

During the first half of the next year the pilot plant will be installed.

3. Laboratory experiments

3.1 Melting experiments

According to the literature data we continued the melting experiments with 6 selected ash simulates. The total mass of simulate used for each experiment was 50 g. The melting devise was a muffle furnace. Additives used for melting point reduction were Na-Tetraborate, Boron Trioxyde, Na-Carbonate, Na-Phosphate and glass frit. Temperatures were 1000 - 1300 °C.

Na-Tetraborate was the most successful additive, followed by Boron Trioxyde and glass frit. At 1000 °C the addition of 50 % Na-Tetraborate was enough to melt all simulates (1300 °C: only 30 %). The average volume reduction factor achieved at 1000 °C was 2.9 (1300 °C: 3.6) at densities between 1.9 - 2.9 g/cm^3.

3.2 Product characterization

At all samples produced with 1000 °C/Na-Tetraborate we performed leach tests according to ISO 6961. Analysis was done for the structure element Boron and the doting elements Cs, Eu, Mn and Co. The release is determined by diffusion. The diffusion coefficient (D_e = 1 E-17 m^2/s) and the leach rates (R_N = 5 E-5 g/cm^2d for Cs) are significantly better than from cemented ashes (see tab. 1).

At the cylindrical samples the compressive strength was measured. Because of the not standardized size the results can be seen only as orientation. The values were between 5 - 17 N/mm^2.

Table 1: Comparison of Cs leach rates (R_N) and Diffusion coefficients (D_e) of conditioned ashes

Conditioning process	R_n (g/cm^2d)	D_e (m^2/s)
Melting	5 E - 5	1 E - 17
Cementation	1 E - 3	2 E - 13
Bituminization*	1 E - 4	1 E - 14
Glass products*	1 E - 6	3 E - 19

* Average data from different products

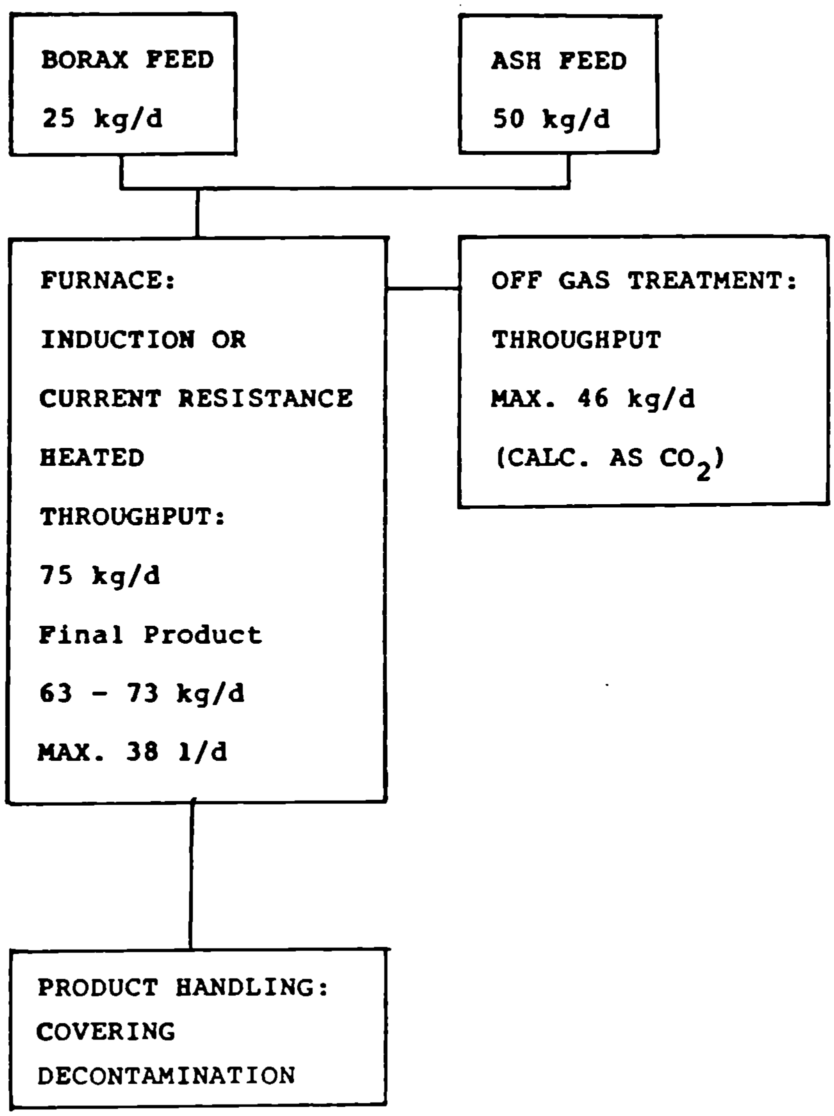


Fig. 1: Flow diagram of a melting process (1000 °C, 50 % Borax)

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

Contractor: CIEMAT, Madrid, Spain.

Contract Nº: FI1W/0142.

Duration of contract: From September 87 to December 89.

Period covered: September 87-December 87.

Project leader: S.J. Ortiz.

A. OBJETIVES AND SCOPE

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

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

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

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

B. WORK PROGRAMME

B.1. Bibliografic review.

B.2. Identification of Spanish spent IX resins.

B.3. Dewatering experiments.

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

B.5. Interaction between cement and IX materials.

B.6. Freeze/thaw stability.

B.7. Leaching tests.

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

B.9. Full-scale tests.

C. PROGRESS OF WORK AND OBTAINED RESULTS

According with the given information from the spanish nuclear power stations, three ion exchange resins(Amberlite IRN-150, mixed beads, Duolite ARC-9351, cationic beads and Duolite MB-200 mixed powder) have been selected taking into account more use and amount discharged.

Portland cements more produced in Spain are: ordinary (P-350 and P-450); modified (PA-350 and PA-450); high early strenght (P-450 ARI); puzzolanic (PUZ-350 and PUZ-450) and sulfate resistant (P-350 Y). Also, puzzolanic, high alumina and blast furnace slag cement are produced.

The following cements will be used on this R&D proyect:

- Portland PA-350 (Puzzolanic, blast furnace slag and fly ash content less 20%).
- Portland P-350 Y (sulfate resistant, $AC_3 \leq 5\%$ and $AC_3 + FAC_4 \leq 22\%$).
- Puzzolanic V-350 (fly ash content 65%).
- Blast furnace slag (slag content 65%).

The experimental activies realized until now have been the ion exchange resins swelling determination. Bead mixed resins have been saturated with boric acid-lithium hidroxide solutions and bead cationic resins with lithium hidroxide solutions.

The Image Analyzer technique (OPTAMAX V) has been used for the size determination of dried and wet bead resins. This technique gives the distribution and number of particles in function of size and volume within an area including the corresponding histograms.

At present, the obtained results are not too good therefore the image analyzer technique is being adapted to our needs.

2.B. Waste from reprocessing plants, plutonium fuel fabrication plants, and research centres

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

Contractor:	ENEA-CRE Casaccia, Rome, ITALY
Contract n°:	FI1W-0011
Duration of contract:	July 1986 - March 1988
Period covered:	January - December 1987
Project Leader:	L. Pietrelli

A. OBJECTIVE AND SCOPE

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

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

The direct vitrification of this waste would require a complex vitrification plant and result in a large amount of vitrified waste. Therefore our goal is to separate this liquid waste into two parts:

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

In Figure 1 is shown a conceptual flowsheet for the management of 85 m^3 of 1AW-MTR waste.

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

The low-level waste fraction must be suitable for cementation, and it should be reduced to the smallest practical volume.

Scope of research work under this CEC contract is to study and compare the proposed chemical processes by technical and economical criteria.

B. WORK PROGRAMME

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

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

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

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

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

B.6 General considerations and Final Report.

C. PROGRESS OF WORK AND OBTAINED RESULTS

B.1 Development of chemical flowsheets

In order to fulfil these research objectives, some chemical flowsheets for the waste treatment have been studied, at laboratory scale with simulated and traced solutions.

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

- the **acidic flowsheet** based on the Cesium separation by precipitation with Phosphotungstic Acid (PTA), and on the separation of Strontium and Actinides by Polyantimonic Acid (PAA), directly from the acidic 1AW-MTR solution;
- the **alkaline flowsheet,** based on the alkalinization with NaOH of the waste solution to pH>13 (in order to trasform the Aluminum in water soluble Sodium Aluminate); at this pH value, Strontium and Actinides are separated by co-precipitation on Ferric Hydroxide floccs. Cesium is then separated by selective precipitation by Sodium Tetraphenylborate (NaTPB) or by adsorption on zeolites.

Acidic flowsheet

A Cesium precipitation process using PTA was studied during the first step of the contract /2/.

Assuming the addition of one mole of PTA per mole of Cs in the acidic waste solution (without any pH adjustment), a Cs Decontamination Factors (DF) of 100 can be achievied at room temperature. Addition of 0.1-0.2 moles of KNO_3 to the initial feed should be provided because coprecipitation of Cs and K should improve the Cs recovery. High contact time (>15 hours) were required at 25°C to obtain high Cs DF values and to obtain a particle size suitable to perform an efficient solid-liquid separation.

About the separation of Sr and Actinides from Acidic waste by adsorption on Polyantimonic Acid (PAA) unfortunately the strong competition due to the high salt ions content in the 1AW-MTR drastically reduce the Pu removal from the solution (DF≈10 after 20 hours) /2,3/.Also the Sr adsorption capacity is reduced from ≈70 mg/g PAA /4/ to ≈1 mg/g PAA.

To increase the low Pu Decontamination Factor obtained with the acidic process some experiments have been performed using an Actinide specific reagent, normally used in the TRUEX solvent extraction process, called CMPO (Octyl(phenil)-NN- diisobutylcarbamoylmethylphosphine Oxide) /5/. Tests were performed using CMPO adsorbed on PAA, this product was then used to fill a column. The result, shown in Table II, were not satisfactory: in fact after only 26 columns bed volumes (≈5 hours working) the Pu DF decrease from $\approx 10^3$ to 3.3. It is probably due to low PAA specific surface (20.9 m^2/g) and then the limited impregned capacity.

The comparison of the results obtained with PAA and PAA+CMPO shows that although at the beginning very high Plutonium DF may be obtained with PAA+CMPO, after a relatively small amount of waste solution (if compared to the total amount of available CMPO) the significant decrease of Pu DF does not permit an appropriate decontamination. On the other hand, the use of a different inorganic support with higher surface (e.g. silica) could increase the efficiency of adsorption by CMPO but, in this case, an additional specific adsorbent for the Sr would be necessary, this increasing plant complexity and final vitrified waste volume.

Alkaline processes

Both processes are based on the alkalinization with NaOH of the 1AW-MTR solution to pH>13. The objective of this step is to neutralize the free acid and then to transform the Aluminum Nitrate into soluble Sodium Aluminate.

$$HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O \quad (\Delta H = -13.8\ kcal/mol)$$
$$Al(NO_3)_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaNO_3$$
$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

$$HNO_3 + Al(NO_3)_3 + 5NaOH \longrightarrow 4NaNO_3 + NaAlO_2 + 3H_2O$$

Fe, Pu, Sr, RE, Np and Am are quantitatively precipitated as hydroxides, while essentially Al, Na and Cs remain in the supernatant. Mercury is distributed both in the supernatant (about 50%) and the precipitate /2,3/.

A large volume of $NaNO_3$ waste will be generated from the addition of the NaOH but, on the other hand, to immobilize the LLW in solid form, this liquid waste must be neutralized anyway before the cementation process.

During the first half of the contract some aspects of the alkalinization have been studied. At pH>13 the iron present in the waste solution precipitates, and the Strontium and the Actinides are separated by coprecipitation with Ferric Hydroxide [2]. The removal of Actinides (Pu, Np, Am) and Strontium, at constant Iron concentrations, increases linearly with pH and the removal process takes place rapidly and no substantial differences have been observed increasing the digestion time from 30 minutes to 20 hours.

The Actinides and Sr DFs found in the tests carried out at laboratory scale using simulated and traced waste solutions, have been generally higher than 100 provided that an efficient solid-liquid separation is performed.

Special attention must be devoted to minimize the volume of precipitate, in fact by adding the acidic waste solution to the NaOH concentrated solution (10 M) and not *viceversa*, about 50 ml/l 1AW of wet precipitate was obtained instead of more than 200 ml/l 1AW when NaOH was added to the acidic solution.

Cs separation by Sodium Tethraphenylborate (NaTPB)

The attractive feature of the Cesium recovery by NaTPB is its ability to provide a high Cs DF (>10^3) from alkaline supernatant in a single batch precipitation /2/. A further advantage of this process is that alkalinizaztion and Cesium precipitation could be carried out in the same reactor tank.

Cesium recovery using NaTPB as reagent is dramatically improved when the mole ratio Na-TPB/(Cs+Rb+K) is greater than 1 /6,7/. This indicates that there is a strong competition between the cations in the precipitation reaction. Once the cation concentration is equivalent to the NaTPB concentration, the recovery of Cs is very efficient. Some problems during the precipitation, due to high Potassium concentration, coming mainly as an impurity of NaOH, could occour during the alkalinization: therefore it is very important to add a NaOH with low

Potassium content in order to avoid problems with Cs competition for NaTPB.

The recovery of Cs from the alkaline solution is indipendent of solution pH in the range of 10 to 13 and 30 minutes are sufficient to obtain an high Cs-DF /2/.

A potential disadvantage of this process is that it may be necessary to operate the decomposition of NaTPB before feeding it in the vitrification furnace, in order to avoid the production of some volatile and flammable organic compounds. However, using NaOH with low K content the NaTPB requirement for the total 85 m^3 of HLW will be minimized /3/.

From thermal decomposition (see Figure 2 and Table III) of NaTPB it results that just a small amount of benzene, a large amount of biphenyl and other organic compound derive from several combinations of phenyl rings are produced from NaTPB decomposition /3/. In addition, it has been found that most of the excess reagent remain solubilized into the surnatant. Therefore it does not seem to be necessary to operate a radioactive organic reactor to destroy TPB^- as used in other plants /8/.

Cs separation by zeolite

After the 1AW-MTR waste alkalinization to pH>13 by its addition to 10 M NaOH solution the centrifuged (or filtrated) solution is sent to the IE-96 zeolite columns to remove Cs with $DF \approx 10^3$ /2/. The columns tests performed at laboratory scale /3/ have confermed the high Cs and Sr loading capacity , from the breakthrough curve shown in Figure 3 the Cs exchange capacity is 1.34 mg/Cs/g IE-96.

After processing, the Cs-loaded zeolite ion-exchanger will be blended with the alkaline waste sludge and glass frit, then converted to a glass waste form.

When the zeolite will be used at pH>13 the slow exchanger dissolution is possible due to the aluminium present in the silica structure. These difficulties shold not be encountered when treating the 1AW-MTR waste because the exchanger will be loaded only once, then vitrified.

B.2 Sampling equipment to analyse the 1AW-MTR waste

At present the 1AW-MTR waste is stored in two stainless steel tanks that unfortunately have been designed without any sampling apparatus.

To make the sampling and then the analyses and the laboratory "hot tests" of the waste, ENEA has designed and realized a sampling equipment consisting of:

- a particular "cork plug" that penetrates into the tank to allow the suction of the solution previously homogenized by bubbling;
- an 8 litre capacity "cendrillon" 15 cm Pb shielding (it can shield untill 1200 Ci of Cs-137);
- a glove box where are located all the "hot" piping connections and the controls for the transfer of the radioactive solution from the tank to cendrillon and *viceversa,* and from the cendrillon to sample bottle and *viceversa;*
- a vacuum system to provide the transfer of the solution;
- a special sample container designed for bottles of variable capacity (from 10 to 1000 ml) that provides the solution transfer from the tank to the hot cell.

B.3 Hot cell fitting

To allow the realization of process tests on real samples a hot cell has been equipped with a mini pilot plant that mainly consists of:

- a glass reactor equipped with mechanical stirrer, temperature and pH control;
- a peristaltic pump with changeable head and flow-control;
- a centrifuge;
- a set of columns provided of a safe containment "tank" to avoid any unwanted discharge of radioactive waste;
- usual laboratory equipment (balance, magnetic stirrer, dryer, etc).

The mini pilot plant will be operated by remote controls and telemanipulators.

D. REFERENCES

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/3/ PIETRELLI,L., GROSSI,G., CEC Contract FI1W-0011-IS,2nd Progress Report (January-July 1987).

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/6/ BRAY,L.A., et al.,ANS Int. Meeting,Jackson Hole,Wyoming (USA),1982. Proceedings Vol 1, pp 345-356.

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Table I Estimated chemical and radiochemical composition of the 1AW-MTR solution (*)

Elem.	**Conc.**		**(Ci/1)**	**Elem.**	**conc.**		**(Ci/1)**
Al	27.01	g/l	-	Ru	13	mg/l	negl
Hg	1.34	"	-	Ba	12	"	0.56
Fe	0.56	"	-	Sr	7.8	"	0.6
Si	0.14	"	-	Sm	7.3	"	1.2E-2
Zr	35	mg/l	-	Y	5.0	"	0.6
Nd	35	"	-	Np	1.8	"	1.3E-6
Mo	27	"	-	Pu	2.5	"	1.4E-3
Ce	20	"	-	Pm	0.07	"	6.3E-2
Cs	17	"	0.6	Am	4 E-03	"	1.3E-5
H+	1.1	M		SO4--	0.006	M	

Total Activity = 2.44 Ci/l

(*) estimated by Origen Code and /or process analytical data.

Table II: Pu-DFs obtained by PAA+CMPO compared with PAA Pu-DFs (*). CBV=Column Bed Volume

	PAA+CMPO			PAA	
Time	PuDF	CBV	Time	PuDF	CBV
	$>10^2$	1.7		6.0	2.2
	"	3.0		4.1	3.6
	"	4.6		3.8	5.5
	"	6.0		3.9	7.0
	4.8	18		4.3	15.3
5 H	3.3	26	46 H	6.8	49.0

(*) the column dimensions and then the adsorbent content were different:
PAA+CMPO= 1.44 g, PAA=7.5 g

Table III: Comparison TG data with theoretical NaTPB organic composition

	% theor.	% found	
		Air	Nitrogen
C_6H_6 (or similar)	89.9	90.4	82.3
Na, B or other	9.8	9.6	17.7

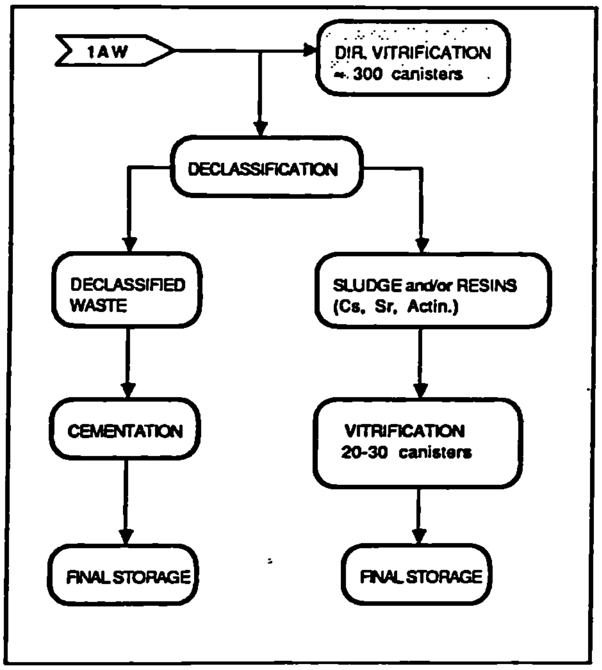


Fig. 1 Conceptual flow-sheet for the management of 1AW-MTR liquid waste

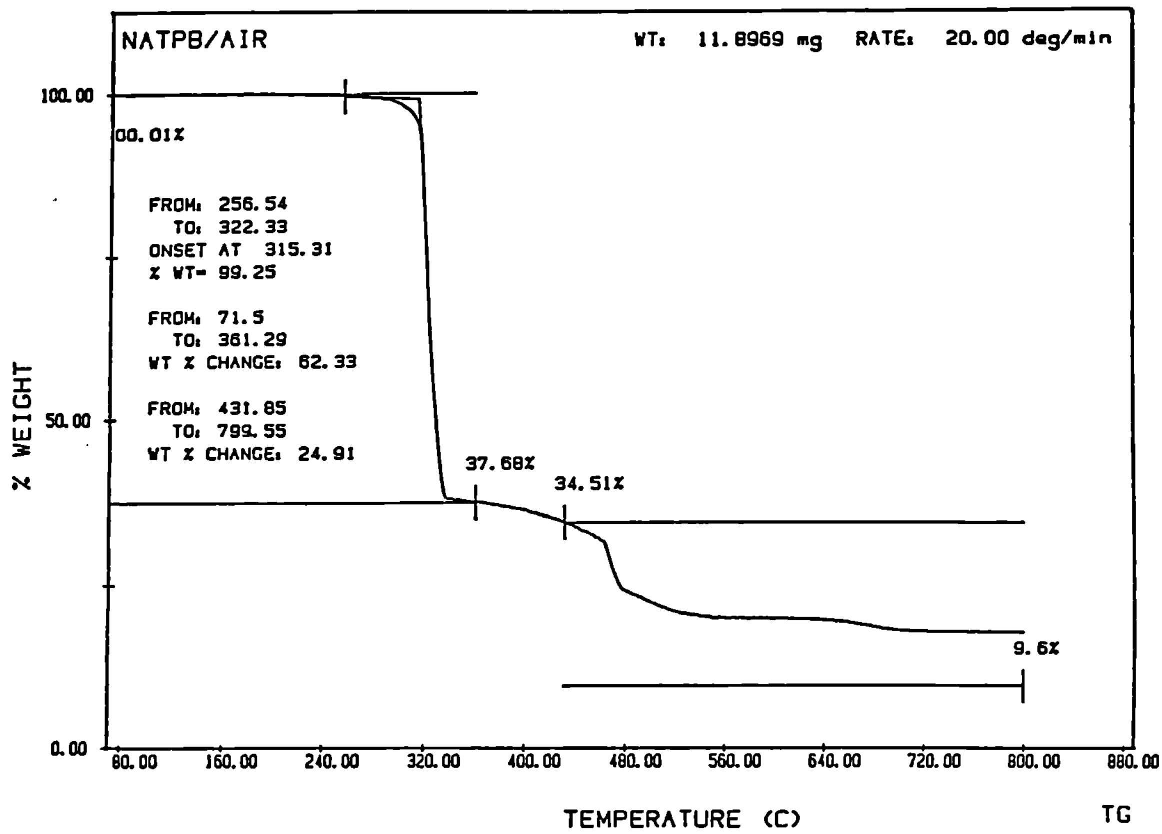


Fig.2 TG curve in air of NaTPB

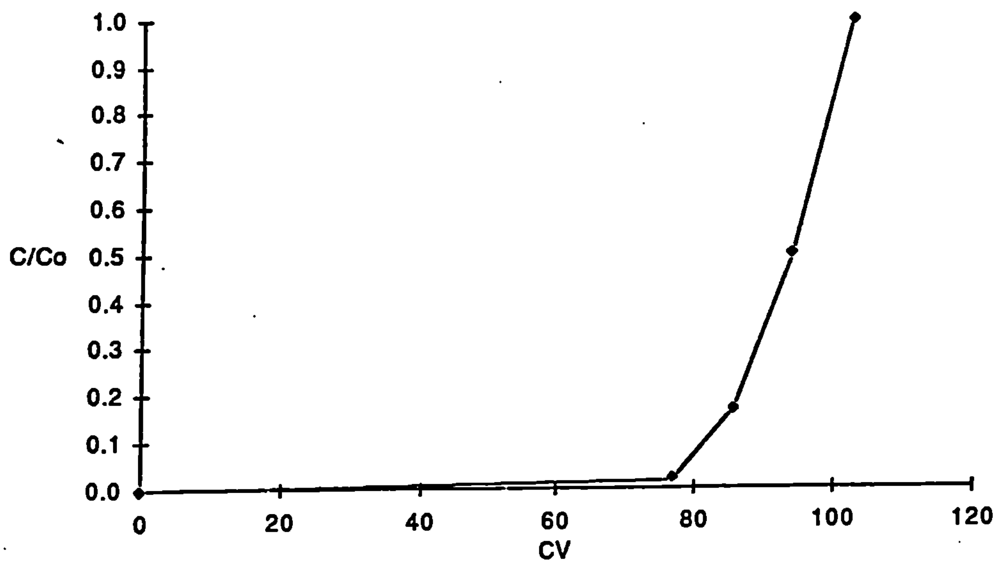


Fig.3 IE-96 Zeolite break-through curve

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

Contractor: CEA, Marcoule, France
Contract No: FI1W-0014
Working Period: October 1986 - March 1989
Project Leader: N. Jacquet-Francillon

A. Objectives and Scope

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

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

The objectives of this programme are:

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

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

B. Work Programme

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

C. Progress of Work and Obtained Results

State of Advancement

Development of the melting unit in the shielded cell required considerable testing, but has now been completed. The difficulties encountered were primarily due to the small size of the crucible (60 mm in diameter) and to the limited power rating and unsuitable frequency of our generator (75 kW, 10 kHz).

Process reference tests were conducted for final qualification of the equipment and operating procedures. The tests were carried out on inactive materials, but this time under actual cell operating conditions: the resulting reference ingots and slags will be characterized.

The programmes covering active ingot characterization and slag incorporation in R7T7 glass have been defined, and the actual investigation is about to begin.

The general work progress status is as follows:
- B.1 is completed
- B.2 is progressing normally
- B.3 and B.4 are pending regulatory approval for active work in the cell.

Progress and Results

1. Melting Unit Development Work (B.1)

Development work included the following steps:
- equipment modification to remote manipulation requirements in the cell,
- equipment calibration (hull feed device, ingot drawing system, washing column, etc.),
- determination of ingot production requirements by gradually bringing the facility to normal operating conditions (electrical parameters, startup tests, drawing tests, etc.),
- verification of equipment and process reliability by producing 11 metal ingots from inactive hulls close in size to the actual active clads.

The major ingot manufacturing parameters are indicated in Table I.

Hulls exceeding 45 mm in length may have been responsible for jamming the feed device. Oversize wastes (e.g. pin end-pieces) will have to be eliminated from the hull batches used to produce active ingots.

Melting is feasible provided the unit is started up with a massive metal load of between 600 and 700 g depending on the nature of the hulls. With zircaloy hulls part of this load is stainless steel to lower the initial bath temperature and avoid having to use the maximum generator power.

Slags are used in the form of cylindrical particles prepared in the laboratory (powder pressing followed by heat treatment). After melting the slag can be remelted with alkaline carbonates for dissolution in cold HNO_3 and analysis.

2. Inactive Reference Tests (B.2)

The four planned inactive tests were completed:
- two ingots were produced by melting Z2 CN 18/10 stainless steel hulls (tests IR04-IR05),
- two ingots were produced by melting zircaloy-4 hulls (tests ZR01-ZR02).

Two other inactive ingots were produced from a mixture of 84% zircaloy-4, 10% stainless steel and 6% inconel (tests ZIR1-ZIR2); this composition is representative of metallic wastes from reprocessed OBRIGHEIM reactor fuel.

The slag mass balances for these tests are indicated in Table II.

- Spontaneous descaling of stainless steel and zircaloy-stainless steel-inconel ingots together with light surface peening allowed recovery of about 98% of the initial slag mass. A smaller amount of slag (approx 86%) was recovered in the pure zircaloy tests since a fraction of the slag adhered strongly to the bottom of the ingot in the initial melting zone.
- The quantity of slag recovered from the off-gas treatment system never exceeded 1% after of melting stainless steel or zircaloy alloy batches. The much higher melting temperature of pure zircaloy seems to account for the slag volatility which was five to ten times higher in this case.

The cell will soon be equipped with an ingot slicing machine that can be entirely dismantled by remote manipulation, capable of cutting up massive metal ingots for characterization.

Table I: Principal Metal Ingot Fabrication Parameters

	Stainless Steel	Zircaloy-4
Hulls to be melted	approx 3 kg	approx 2.3 kg
Startup metallic load	Stainless steel cylinders	Zircaloy cylinders + stainless steel disks
	630 g	670 g + 30 g
Slag	CaF_2: 75% MgF_2: 25%	CaF_2: 50% BaF_2: 50%
	Pellets: 20 mm dia x 8 mm high	
	5.2 g/pellet	6.0 g/pellet
Power requirement	60 - 65 kW	70 - 75 kW
Hull feed rate	4 $kg \cdot hr^{-1}$	2 $kg \cdot hr^{-1}$
Slag feed rate	approx 20 g descaling	approx 100 g descaling
	1 pellet per cm of drawn ingot	
Ingot drawing rate	20 $cm \cdot hr^{-1}$	12 $cm \cdot hr^{-1}$
Melting time	approx 45 min	approx 70 min
Final ingot	approx 3.6 kg	approx 3.0 kg
	57 mm dia x 180 mm high	

Table II: Slag Mass Balance for Process Reference Tests

Hulls	Stainless Steel	84% Zircaloy-4 10% St steel 6% Inconel	Zircaloy-4
Slag Composition	CaF_2: 75% MgF_2: 25%	CaF_2: 50% BaF_2: 50%	CaF_2: 50% BaF_2: 50%
Slag % of Ingot Weight	approx 3%	approx 6%	approx 6%
Slag Recovered on Ingot	approx 98%	approx 98%	approx 86%
Slag Recovered in Dust Separator	approx 0.2%	approx 0.2%	approx 2%
Slag Recovered on Crucible Head	< 1%	< 1%	approx 3%
Unrecovered Slag	approx 1%	approx 1%	approx 9%*

* Most of the unrecovered slag remained attached to the ingot surface

Hot Isostatic Pressing of Pu-Containing Ashes

Contractor: CEA, Marcoule, France
Contract No: FI1W-0015F (CD)
Duration of Contract: October 1986 - September 1989
Project Leader: A. Jouan

A. OBJECTIVES AND SCOPE

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

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

This investigation covers both the process itself and the resulting material. It is being carried out jointly with industrial firms where isostatic presses are available. The final phase will compare the end products obtained by pressing with melted ash products.

B. WORK PROGRAM

B1 Production of actual inactive ashes obtained from batch furnaces or from continuous industrial pilot facilities for the final tests.

B2 Recuperation of industrial ash with similar compositions for technological feasibility tests.

B3 Determination of pressing parameters at laboratory scale on actual inactive ashes.

B4 Production of intermediate scale blocks from actual inactive ashes to determine the physical and mechanical properties of the resulting material.

B5 Production of a 30 cm diameter block using industrial ashes.

B6 Preliminary design work for an industrial unit to allow comparison with a melting facility.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

The optimum isostatic pressing conditions for actual ash material have now been determined. The decisive criterion was the solidity of the resulting material as affected by the container filling method and the pressing temperature, pressure and time. This investigation provides a basis for assessing the advantages of additives which could modify the physical state of the compressed material by incipient melting, although this would penalize the storage volume.

Results

Laboratory scale experiments in cylindrical mild steel containers 36 mm in diameter and 170 mm high were conducted to observe the influence of the major process parameters.

* Container Filling Method: The natural ash bulk density (0.3 $g \cdot cm^{-3}$) is too low: they must first be packed in the container at room temperature using a single-action piston to increase the density to about 1.6 $g \cdot cm^{-3}$. Pressed cakes with a few percent moisture content may be prepared and stacked in the container, or the ashes may be packed directly in the container if this is found to be advantageous.

* Pressing Temperature: The sintering quality depends on the process temperature. The ideal value is the incineration temperature (700-800°C) which ensures thermal and chemical stability. Tests at higher temperatures up to 1300°C showed that gas pockets formed in the seal welds and the material was pitted or cracked.

* Pressure: Tests were conducted under pressures ranging from 100 to 150 MPa at 700°C. The material obtained at 120 MPa or higher exhibited excellent cohesion and could be machined without crumbling.

* Pressing Time: The standard process times investigated ranged from 1 to 4 hours. Tests combining the three variables showed that the best results were obtained under the following conditions: 4 hours at 700°C at 150 MPa, or 2 hours at 800°C at 150 MPa. The second test produced the material with the highest density.

* Flux Additives: Various frit compositions were investigated in fission product vitrification studies; the one with the lowest melting point for which the formula can be reproduced using ash components was selected as a basis for comparison. When ashes were mixed in equal weight proportions with an additive containing silica, boron and phosphorus, the resulting product resembled the selected frit composition. Pressing tests are now in progress with this mixture.

The photo in Figure 1 shows a cross section through a test cylinder obtained by isostatic pressing for 2 hours at 700°C under a pressure of 120 MPa. The powdered stainless steel filler in the seal weld was also sintered, and adhered to the cylinder walls. The material was cut into a cube without crumbling.

The ongoing work will now investigate the potential of additives for enhancing the physical and mechanical properties of the material.

List of Publications

The work conducted to date was initially presented in Brussels on January 2, 1987, during the first Task 2 meeting. Additional results were presented in the first semiannual report (October 1987) and at the second meeting in Frankfurt (December 13-16, 1987).

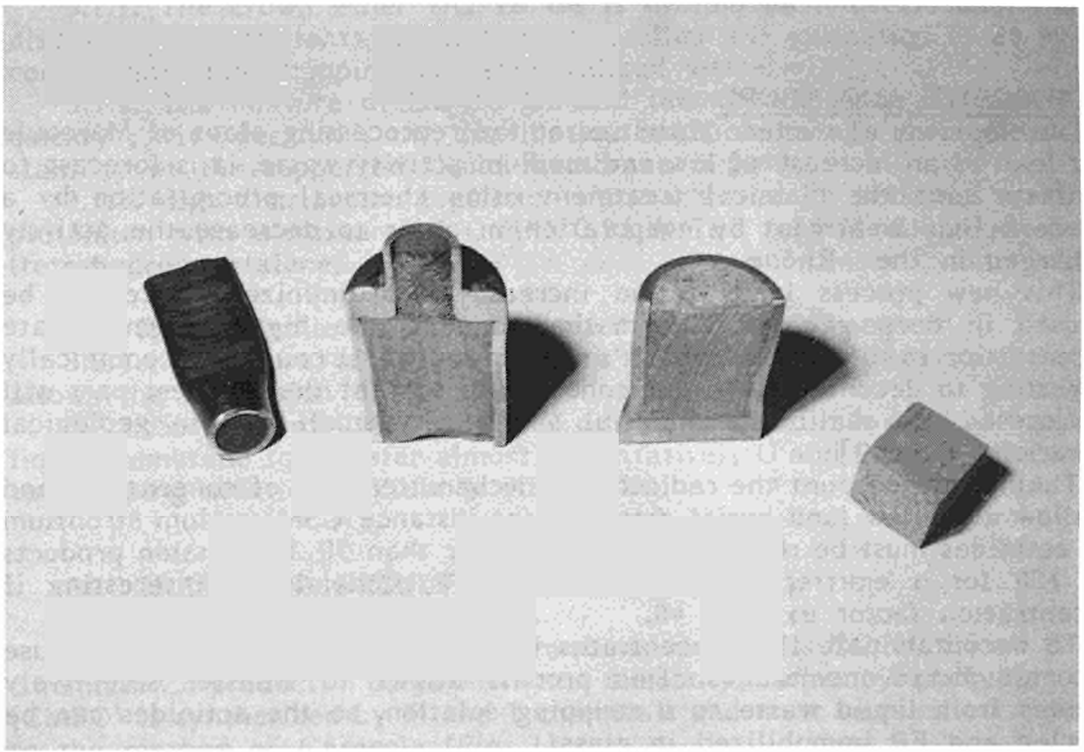


Figure 1 - Cross Section of Finished Product

Utilisation of liquid membranes for the treatment of reprocessing concentrate

Contractor : CEA, CEN Cadarache, France
Contract n° F II W /0016
Duration of contract : January 1987 - December 1989
Period covered : January 1987 - December 1987
Project leader : J.F. DOZOL

A. OBJECTIVE AND SCOPE

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

This new process leads to an increase of bituminized wastes to be disposed in deep geological formation, due to the high sodium nitrate concentration in the concentrate. It's the reason why it could be economically interesting to decontaminate this concentrate so that the greatest part will be disposed in shallow land burial and a very small part in geological formation [Table 1].

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

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

B. WORK PROGRAMME

2.1. Choice of extractants diluents and stripping solutions :

2.1.1. The highest distribution coefficients for strontium from concentrate are obtained with DB 18 C6 diluted in C2 H2 Cl4. Demineralized water is used as stripping solution.

2.1.2. The extractant used for recovery of actinides in evaporation concentrate is a mixture of CMPO (0,25 M) and TBP (0,75 M) diluted in decalin and stripping solution is a solution of sodium citrate.

2.2. Supported liquid membrane process for treatment of concentrate :

2.2.1. The life-time of DB 18 C6/C2 H2 Cl4 membrane is very short, the leaching of extractant being important. The life time of the supported liquid membrane is strongly increased by using decanol as diluent instead of tetrachloroethane.

2.2.2. For removal of actinides, the mixture CMPO (0,25 M) TBP (0,75 M) in decalin is choosed, the stripping solutions being sodium citrate. The stability of supported liquid membane is good and allows the removal of actinides in concentrate.

C. PROGRESS OF WORK AND OBTAINED RESULTS
ETAT D'AVANCEMENT

3.1. Choice of the components of the aqueous phase

3.1.1. The crown ether DC 18 C6 is diluted in tetrachloroethane. The distribution coefficients are sufficient to allow the extraction of 85 Sr from concentrate and stripping in demineralized waste.

3.1.2. The mixture of DC 18 C6 and tetrachloroethane is leached very quickly ; with decanol , the distribution coefficients are lowered but the stability of the supported liquid membrane is good.

3.1.3. High distribution coefficients are achieved for actinides mainly for plutonium with a mixture of CMPO 0,25 M/TBP 0,75 M diluted in decalin (tetrahydronaphtalene).

3.2. Results achieved with supported liquid membrane

3.2.1. A mixture of DC 18 C6 and decanol immobilized on membrane allows the extraction of about 70 % of Sr.

3.2.2. Solution of CMPO and TBP diluted in decalin is used as supported liquid membrane to transfer almost quantitatively U and Pu from concentrate to stripping solution (Yield $\geqslant$ 95 %).

PROGRESS AND RESULTS

4.1. The extractant used for strontium removal is DC 18 C6 an Aldrich Chemical Co product. n octyl phenyl nn diisobutyl carbamoyl phosphine oxide (CMPO) is syntherized by M and T chemicals and must be purified according to the method of Casaccia (Fig. 1).

Celgard 2500 and 2502 are used as solid support for the liquid membrane. The thickness of flat membrane is respectively 25 and 50 µm, the normal porosity is 45 %. The supported liquid membrane is prepared by soaking the sheet in the mixture of extractant and diluent. All the experiments are performed using cell at 30±1°C under a constant stirring rate of 200 or 250 rpm (Fig. 2).

4.2. The tetrachloroethane allows to obtain high distribution coefficients but can't be used as supported liquid membrane because of the high leaching rate. Using decanol as diluent, the distribution coefficient are smaller, but the stability of supported liquid membrane is strongly improved. It is possible to transfer about 70 % of strontium from concentrate to demineralised water used as stripping solution. At the beginning of experiment, the rate of transfer of strontium is enough high, but decreases drastically with time. Many reasons can explain this phenomenon. :

- Decrease of acidity of the concentrate, because HNO3 in transfered by crown ether /decanol ; the acidity increases in the stripping cell leading to an increase of distribution coefficients of strontium in organic phase and a decrease of the efficiency of the stripping solution.

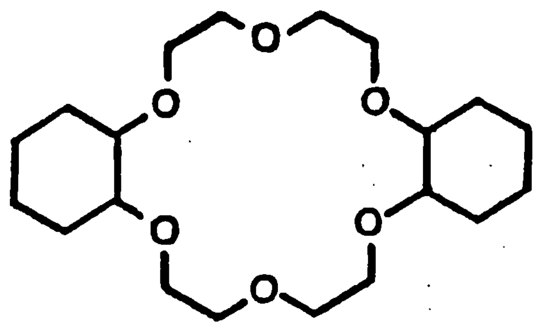
- Precipitation of some slightly soluble salts ($CaSO_4$ ...) of the concentrate on the membrane.

4.3. For the removal of actinides from concentrate with CMPO and TBP, as in the case of strontium extraction, a transfert of acidity is observed from concentrate to the stripping solution but the actinides are almost quantitatively removed from concentrate to the stripping solution of sodium citrate.

Table I

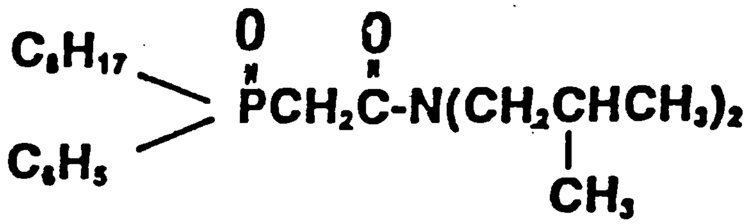
Evaporator concentrate composition

Component	Mass of component per liter of feed ($g.l^{-1}$)
$Ca(NO_3)_2$ 4 H_2O	7,11
$Mg(NO_3)_2$ 6 H_2O	2,00
$Fe(NO_3)_2$ 9 H_2O	5,23
Na_2SO_4 10 H_2O	26,24
Na_3PO_4 12 H_2O	23,27
NaF	3,19
NaCl	0,19
$UO_2(NO_3)_2$ 6 H_2O	4,70
Na_2SiO_2 5 H_2O	4,80
$NaNO_3$	323,04
Total	399,77
HNO_3	63



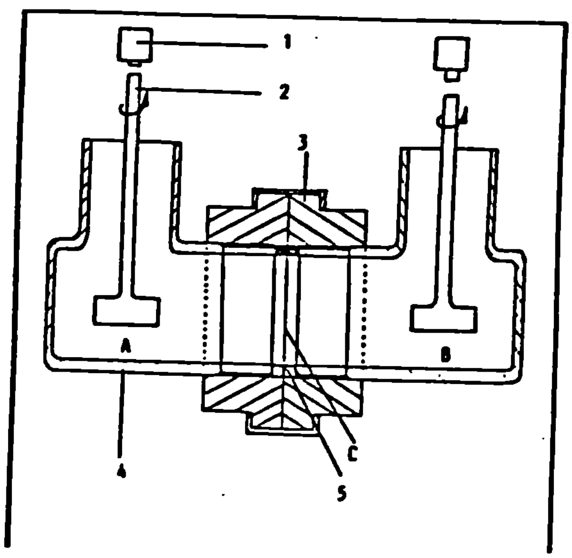
DC 18C6

Dicyclo 18 couronne 6



Octyl phenyl NN diisobutyl carbamoyl methyl phosphine oxide

Fig. 1 : EXTRACTANTS USED



1. Electric motor
2. Stirer
3. Clamp
4. Cell
5. Membrane

A. Evaporator concentrate
B. Stripping solution
C. Membrane impregnated with solvent

Fig. 2 : SUPPORTED LIQUID MEMBRANE CELL.

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

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

A. OBJECTIVES AND SCOPE

The overall objective of this programme is to improve the design and operation of membrane plant for radioactive waste treatment by the incorporation of new process developments into an existing active ultrafiltration pilot plant facility. The plant performance is to be evaluated for improvements in plant throughput and decontamination factor when processing a real radwaste.

B. WORK PROGRAMME

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

C. PROGRESS OF WORK AND OBTAINED RESULTS

STATE OF ADVANCEMENT

Two new types of membrane module have been installed in the pilot plant facility and used to process Harwell site low level radioactive waste.

One of these new modules contained ceramic microfiltration membranes; the other module contained novel stainless steel filters. Since two new membranes were tested in 1986, sufficient information has been acquired in order to select the most promising for further, more detailed, testing.

The performance of new precipitation agents has been examined at both laboratory scale and in the pilot plant facility. Copper ferrocyanide, whose potential as a Cs^{137} and Co^{60} absorber was examined at the laboratory scale last year, has now been tested at the pilot plant scale and significant advance in understanding the mechanism of nuclide absorption have been made. In addition a range of new promising ion exchange materials, that could be used for $\beta\gamma$-activity absorption prior to ultrafiltration, has been identified and subjected to preliminary tests. Of these materials, zirconium phosphate and titanium phosphate appear to be the most promising, and titanium phosphate has now been produced in a form suitable for use in the pilot plant facility in the coming year.

The potential for reducing membrane fouling and maintaining higher flux by the electrical pulse method of direct membrane cleaning (DMC) has been demonstrated in tests using both stainless steel microfiltration and zirconia/carbon composite ultrafiltration membranes. Design of a crossflow module incorporating DMC has now been completed. A prototype unit is being constructed and should be available for testing in the pilot plant facility during the coming year.

PROGRESS AND RESULTS

2.2 New Precipitation Agents

The potential of some new precipitation agents to enhance $\beta\gamma$ removal has been tested using both simulated wastes and real Harwell low level waste (LLW). The materials assessed were commercially available powdered forms of titanium phosphate (TiP), zirconium phosphate (ZrP), manganese dioxide (MnO_2), polyantimonic acid (SbA) and ammonium molybdophosphate (AMP). TiP, ZrP and SbA all showed better β removal than that achieved by copper ferrocyanide alone. In contrast the γ removal achieved using copper ferrocyanide was better than for TiP, ZrP or SbA. This result suggests that Sr^{90} (as β emitter) may have been removed from the waste by these three ion exchangers. AMP proved to give a poorer performance than copper ferrocyanide as a Cs^{137} absorber and did not appear to improve the absorption of any other nuclide from LLW. MnO_2 performed well as a Sr absorber at pH8 but its efficiency as a Sr absorber was low at pH4.5. As a result of these tests TiP or ZrP and SbA were selected as the absorbers with greatest potential for Sr removal from LLW at pH4.5.

Initial tests also showed that TiP and copper ferrocyanide could be used together in the treatment of LLW. However, the combined addition of SbA and copper ferrocyanide to LLW gave a reduced Cs^{137} removal compared with the use of copper ferrocyanide on its own. It was also found that appreciable levels of antimony (~ $0.5 mg/\ell^{-1}$) were present in the permeate. Future work will therefore concentrate on the use of TiP or possibly ZrP. TiP has been manufactured with a typical size range of 0.02-0.04mm in contrast with the commercial powder which had a size range of 0.5-1mm. This freshly prepared TiP appears to give a better β absorption than the powdered form

Additional work has been carried out on the absorption of Cs^{137} and Co^{60} from Harwell site waste (LLW) by copper ferrocyanide. These experiments at both laboratory and pilot scale indicated that at $4mg/\ell^{-1}(Fe(CN)_6)$ Cs^{137} was removed very effectively. The Cs^{137} absorption kinetics have also been shown to be dependent on the concentration of copper ferrocyanide in the circuit. The absorption of Co^{60} from LLW appeared to require a minimum level of addition of copper ferrocyanide to the LLW. Figure 1 shows how the threshold level of addition was about $10mg/\ell^{-1}$ $Fe(CN)_6$.

A series of small scale ultrafiltration tests has been carried out on a second type of radwaste [Harwell medium level waste (MLW)] to determine the effect of pH on the suspended solids concentration and the achievable decontamination factor (DF). For two batches of MLW the ultrafilterable solids loading was found to increase with pH from $125mg/\ell^{-1}$ at pH4 to 400mg/ℓ at pH9. The α D.F. in both cases also increased from ~ 4 at pH5 to ~ 100 at pH9.

2.3 Tests with alternative membranes

Two further crossflow filters have been tested using the pilot plant. These were a Ceraver alumina membrane and a prototype Variable Spring Filter (VSP). The Ceraver module contained alumina membrane tubes with a nominal pore size of 0.2µm. The tests indicated that this membrane reduced the permeate α activity to less than 1.5×10^{-3}Bq $m\ell^{-1}$ whilst giving a flux of 3m d^{-1}.

The VSP filter consisted of six helically wound stainless steel elements with a total filtration area of $0.06m^2$. This unit was supplied by Parkman Group. The springs were operated with a filtration gap of approximately 6µm. The application of filter aid was necessary to prevent rapid fouling of the filter. A flux of approximately $3m.d^{-1}$ was achieved with an α content in the filtrate of less than 1.5×10^{-3} Bq/ml^{-1}.

2.4 Tests with electrically assisted process

A microprocessor controlled test rig has been commissioned and used to examine the dewatering of $Fe(OH)_3$ slurries up to 5wt% solids at a 5µm sintered stainless steel powder filter under crossflow conditions. Periodic electrical cleaning (DMC) increased the permeation rate at a reduced crossflow velocity. With the modified Pall filter, the efficiency of the cleaning pulses for 3wt% $Fe(OH)_3$ at 1m s^{-1} increased up to 5s duration and current densities up to 180mA cm^{-2}. No further benefit was achieved for repetitions more frequent than 3.5 minutes. Typical improvements of 60% were observed in performance, although further advances may be expected for purpose designed equipment optimised for both crossflow and electrical cleaning. DMC has also been successfully used to maintain the permeate flux during the washing of a 5wt% $Fe(OH)_3$ floc to reduce its salt content. Studies of weight loss from stainless steel filter materials indicate that negligible degradation is expected under operating conditions of pH10, 100-200mA cm^{-2}.

DMC has also been further examined at a Carbosep M4 membrane on LLW pre-concentrated by conventional UF. In comparison to conventional UF, up to 100% increases in permeability (to 1m d^{-1} bar^{-1}) were observed at low crossflow (1m s^{-1}) without any degradation in DF under optimised cleaning conditions of 1s pulses at 50-100mA cm^{-2} every 20 minutes.

Detailed fabrication drawings for scaled-up three tube DMC filter units have been completed for both Carbosep M4 and sintered stainless steel fibre (3μm) tubes. Manufacture of the Carbosep unit is now being undertaken.

2.5 Tests with ancillary equipment items

No new pieces of equipment have been introduced to the pilot plant during the year. The magnetically coupled pump (manufactured by Klaus Union) which recirculates the concentrate around the UF loop has now operated for more than 6000 hours without any operational problems.

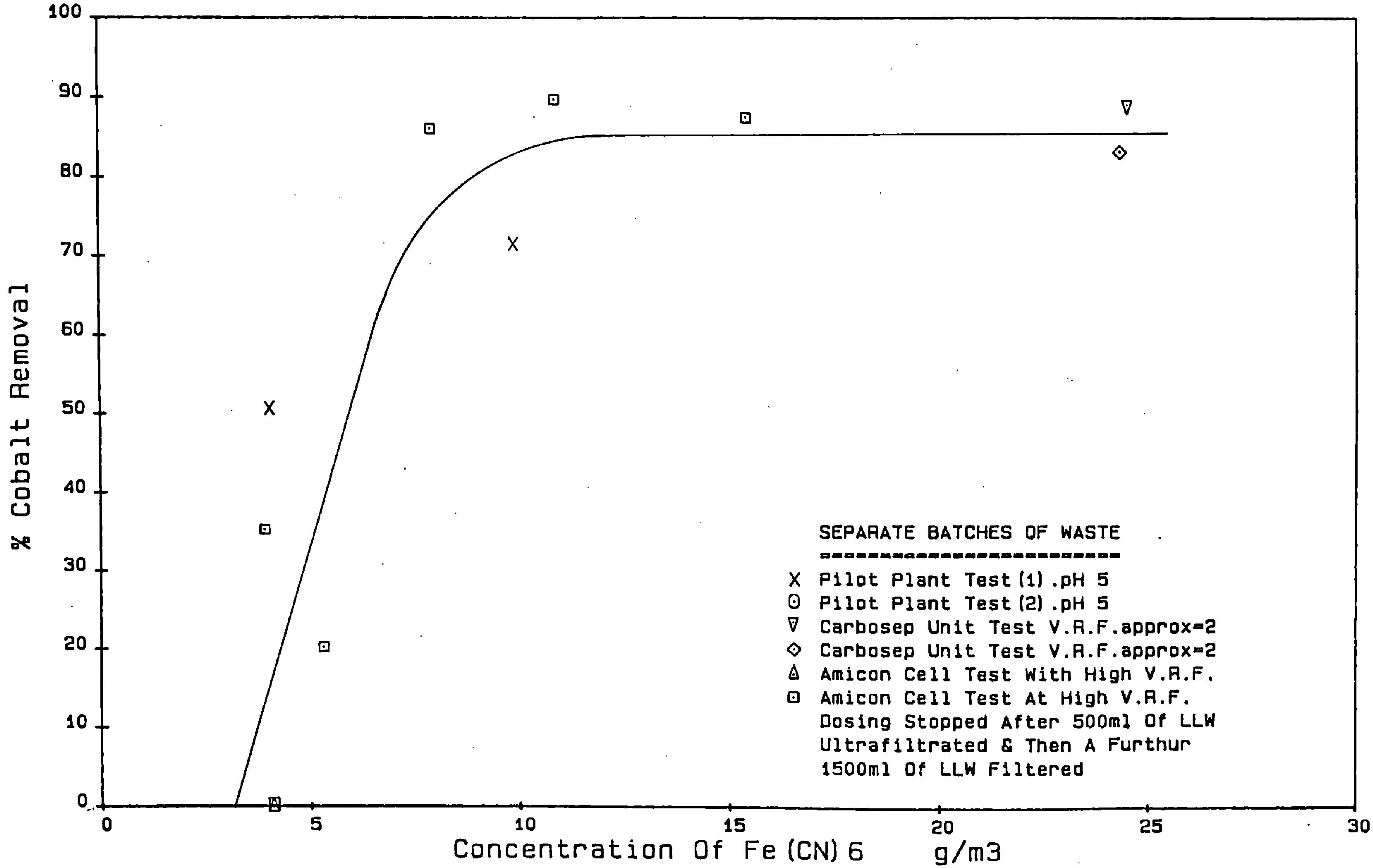


Figure 1 Cobalt Removal As A Function Of Ferrocyanide Concentration

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

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

A. Objectives and Scope

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

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

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

B. Work Programme

2.2 The design, construction and commissioning of a 0.1 m^3/h EIX module and its ancillary pumps, tanks and control gear for the treatment of waste solutions.

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

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

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

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

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

C. Progress of Work and Obtained Results

Summary

0.2 x 1 m electrodes for the 0.1 m^3/h electrochemical ion-exchange (EIX) plant have been successfully fabricated by a mould route. Inactive commissioning experiments were conducted with a mixed Amberlite CG50/IRC84 electrode identified during small scale tests to have optimal properties of absorption kinetics, completeness of absorption and cell resistance. At half the design throughput DFs of 20,000 were observed, falling to 2000 at 75% and 200 at 100%. This decline over an extended 38 h test may have partly been caused by electrode deformation. A minor design change will prevent this occurring in future.

Small scale tests on Zirconium Phosphate (ZrP) have shown it to have excellent EIX properties, although hydrolysis is observed at pH > 12. While this restricts its use for complete cation removal in a flow cell due to high current densities at the entrance of the cell, under the polarity reversal conditions used for enhancing selectivity, hydrolysis becomes negligible. A fully active 0.1m^3/h plant has now been built in the Harwell effluent treatment centre to test 0.4 m^2 ZrP electrodes for the treatment of active waste streams including site waste.

A high capacity EIX system for actinide removal, suitable for scale-up, has still to be identified. Preliminary experiments with polyantimonic acid and sodium titanate gave a DF of only 1.3 for Pu removal from 1M HNO_3. In 0.1M NH_4NO_3 at pH 1.5, ZrP gave a DF of 2 from a 0.1 MBq/ℓ solution. Some desorption was observed on polarity reversal. Extended surface area Ti mesh electrodes have given a DF of 1.6 in 1 h from a 0.1 kBq/mℓ Pu solution at pH 3 - corresponding to an absorbed capacity of 2.7 kBq/cm^3 of electrode. 100% desorption was observed in 1M HNO_3 at -0.45 V(SCE). Improved performance for a flow cell is anticipated from more alkaline pH and pre-anodized titanium.

Progress and Results

2.2 Design, construction of a 0.1 m^3/h EIX module for the treatment of $\beta\gamma$ waste solutions

The prototype inactive plant constructed during 1986 has been commissioned during 1987. Due to the paucity of information on inorganic ion-exchanger performance under electrical control at that early stage of the programme, organic resin electrodes were used for this demonstration. From small scale batch experiments, Amberlite CG50 was shown to have a relatively high resistance, though good absorption kinetics and able to reduce cation levels to < 0.1 ppm. Amberlite IRC84, on the other hand, had a lower resistance but had poorer kinetic and absorption limits. However, electrodes containing a mixture of Amberlite CG50 + IRC84 displayed optimum properties of low electrode resistance, good kinetics and a low effluent cation level. Scaled-up electrodes (0.4 m^2) based on this composition were successfully fabricated using a newly developed mould route. Using a 200 ppm Cs (Cs_2CO_3) feed, concentration reductions of 20,000 and 2000 were achieved respectively for throughputs of 50 ℓ/h and 75 ℓ/h. At 100 ℓ/h, DFs of 200-40 were measured over a further 38 hours; though the decline in performance may have been partly caused by inadequate electrode restraint. A change in design will eliminate this problem in future cells.

In parallel with this scale-up work, inorganic EIX systems have been examined. Small scale tests showed that they did not suffer from shape change during operation, were thinner by a factor of 3 than organic electrodes, and have the promise of superior selectivity. Zirconium phosphate (ZrP) has been shown to have excellent performance for the removal of Cs and Sr, although hydrolysis at pH >12 leads to a reduction in EIX performance. While this can occur in a flow cell in the desalting mode, where relatively high current densities and hence pHs are experienced at the leading edge of the electrode, under the current reversal conditions used for selectivity enhancement, this is not a problem, as the current density distribution is more uniform. In addition, a new source of ZrP has been found to be ten times less susceptible to phosphate leaching. 0.4 m^2 electrodes have been made with this material and shown not to deform in the 0.1 m^3/h flow cell.

2.3 Treatment of genuine βγ wastes in 0.1 m^3/h plant
Having demonstrated EIX inactively at the 0.1 m^3/h scale, a new plant has had to be built in the Harwell effluent treatment area for tests on active wastes (Figures 1 and 2). This also incorporates a pH control to adjust effluent pH during desorption in order to prevent ZrP hydrolysis. The plant also differs in that two opposed ZrP electrodes are being used to enhance selective removal by polarity reversal. The 10-20 Amp cell current can be switched at intervals of 1-50 seconds. After a few final inactive tests, active trials are expected to commence shortly.

2.5, 2.6 Electrosorptive treatment of α wastes
As early work had shown that Pu could be removed from quite acidic solution (1-5M HNO_3) onto electrode materials at potentials where stable oxide film growth occurred (in particular at Ti and C), further work has been carried out to identify electrodes with a higher absorption capacity. Two types of system are being examined: EIX electrodes, where a thick layer of absorbing material is incorporated in the structure; and high surface area electrically conductive electrodes.

EIX electrodes fabricated from polyantimonic acid and sodium titanate were disappointing as only 20% of the Pu in a 0.01 g/ℓ stream of 1M HNO_3 was removed. However, as these are unproved EIX absorbers, further experiments are being conducted on materials known to be effective under electrical control (including ZrP, oxidized carbon and IRC718).

Experiments on ZrP have demonstrated a DF of 2 from a 10 μg Pu/ℓ in 0.1M NH_4NO_3 at pH 1.5 under passive absorption. Due to the low pH, further electrically enhanced removal at -1 $mAcm^{-2}$ was negligible, although some desorption was observed on polarity reversal. Improved performance is expected at pH > 4. 40% of the Pu in a pH 3 10 μg/ℓ Pu 0.1M NH_4NO_3 waste was removed in an hour at a 146 cm^2 Ti electrode fabricated from mesh spot-welded into a 7 cm^3 volume. This corresponded to 128 Bq/cm^2, or 2.7 kBq/cm^3 of electrode - a volume reduction factor of 23. The optimum potential is between 0.5 and 2 V(SCE). 100% Pu desorption was observed in 1M HNO_3 at -0.45 V(SCE). Improved performance is expected at higher pH and at pre-anodized Ti. Even from these pessimistic figures, the 10 ℓ/h flow cell is estimated to be only 30 x 8 x 4 cm.

List of Publications

/1/ BRIDGER, N.J., TURNER, A.D., Electrochemical Ion-exchange for medium active liquid waste treatment. Annual Progress Report June-December 1986, AERE-R12507.

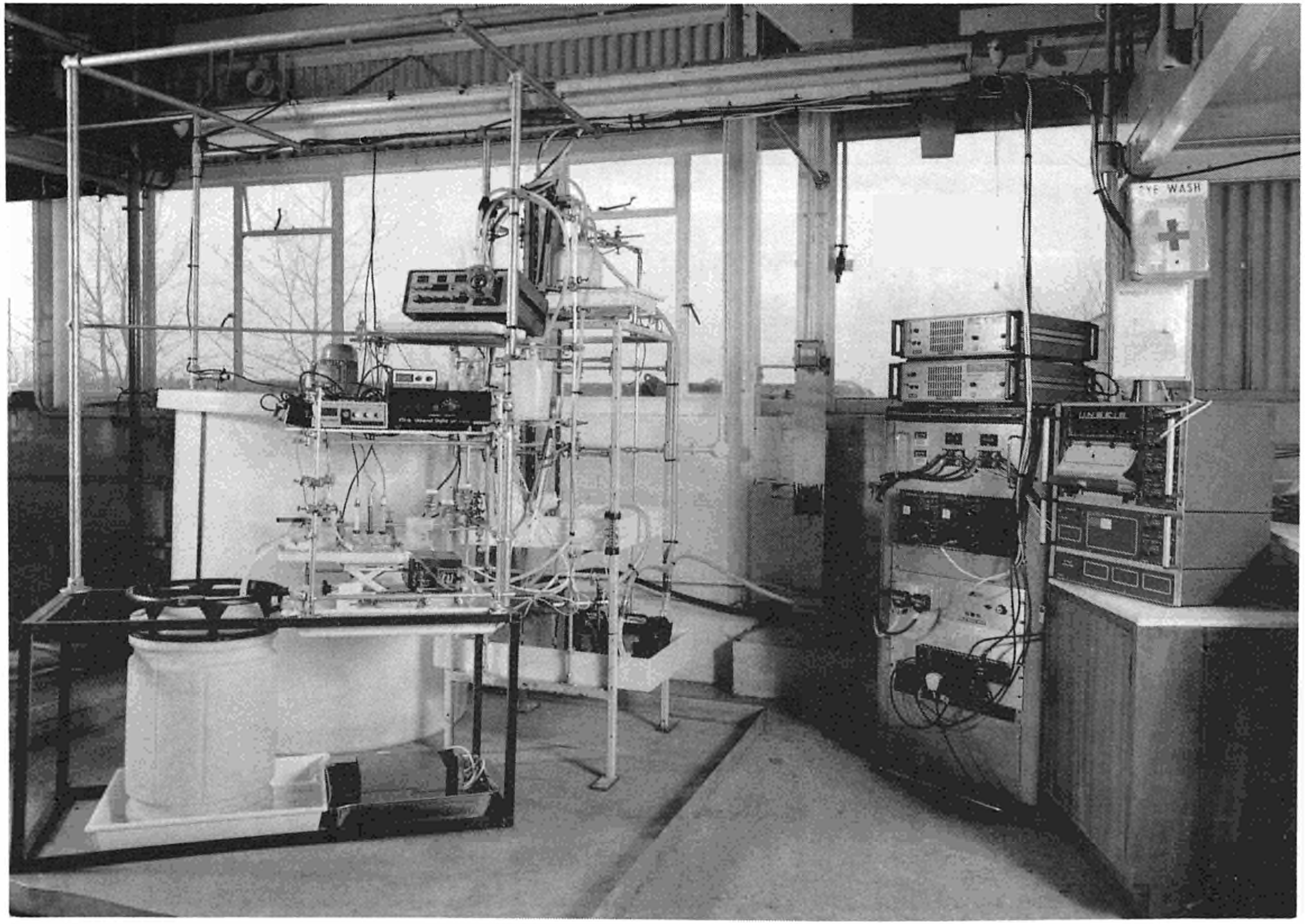


Figure 1 General view of active 0.1 m^3/h EIX plant.

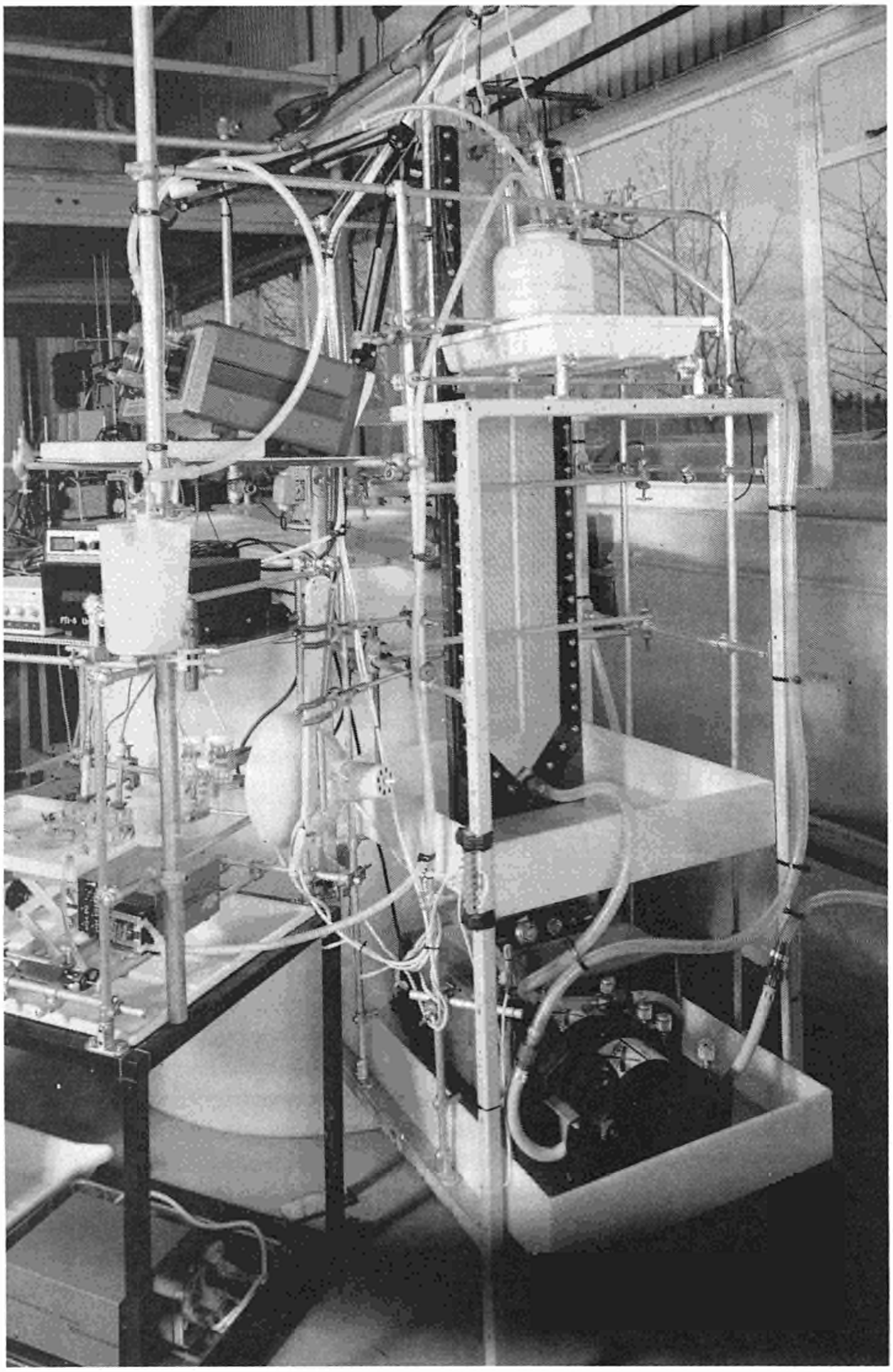


Figure 2   0.1 m^3/h EIX treatment cell.

CONDITIONING OF FUEL HULLS AND STRUCTURAL MATERIALS BY HIGH PRESSURE COMPACTION

Contractor: KfK, Karlsruhe, Federal Republic of Germany
Contract No.: FI 1W-0020-D (B)
Duration of contract: July 1986 - December 1989
Period covered: January 1987 - December 1987
Project leaders: G. Boehme, H. Frotscher, S. Nazaré

A. OBJECTIVES AND SCOPE

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

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

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

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

B. WORK PROGRAMME

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

C. PROGRESS OF WORK AND OBTAINED RESULTS STATE OF ADVANCEMENT

The volume reduction of Zircalloy hull and structural materials by cold pressing has been investigated on a lab scale. The results of these studies will provide the basis for the compaction of these materials on a technical scale.

For the experimental work Zircalloy hulls with a length of 5 mm and 25 mm were used. As received as well as partly oxidized material was used in the experiments. The compaction was carried out in cylindrical dies in which a steel container with an internal diameter of 48 mm or 100 mm could be fitted.

For the investigations on a technical scale Zircalloy hulls and Carbon steel hulls with a diameter of 10 mm and a length of 50 mm and realistic H + S material were used. Experimental material were filled into thin-walled cans with a diameter of 285 mm. The press used has a press-force of 30 MN. The filled tins were placed into the pressing die and compacted with a maximum pressure of 400 MPa. The speed of the ram and the height of the tins were varied. The force VS. distance diagrams were recorded and the product density determined as function of the pressure.

For the planned transport of active hulls a transport concept was worked out and a safety study performed.

Progress and results

2.3.1 Inactive investigations of the behaviour of hulls under high pressure on a laboratory scale

A density of about 70% T.D. is attained with a pressure of about 250 MPa. Considerably higher pressures are required to obtain a significant additional increase in density.

A higher densification is obtained when partially oxidized hulls are used due to their embrittlement.

Hull segments with a larger length: diameter ratio are oriented with their axis perpendicular to the pressing direction. As a result the compaction behaviour is improved.

The use of lubricants does not lead to a significant improvement in the densification.

The results of the void volume analysis reveal that no major density gradients occur neither in the radial nor in the axial direction.

2.3.2 Inactive investigations of the behaviour of hulls under high pressure on a technical scale

- All force versus distance diagrams recorded during hull compression are characterized by the small rise in force up to 85% working stroke. Only during the last 15% of the working stroke the compression force undergoes a steep rise.

- A second feature is the bent characteristic curve associated with the reduction in force. This course is the result of resiliance of elastically deformed machine parts and of the compacted waste form.

- The maximum compression force which can be applied is limited by the pressing die. Of all pressing parts mechanically loaded, the pressing die suffers from the highest specific load. The compression force should not exceed 30 MN for 400 mm die diameter and 650 mm die length.

- In case of application of a compression system of large dimensional stability and with least resiliant waste forms a rise in density from 14.4 to 75% T.D. is expected. This corresponds to a reduction in waste volume by the factor 5.2.

- When lubricants were used, hull boxes of different heights were involved and the die velocities were variable during compression, no significant impact on final compaction was observed in comparisons.

2.3.3 Determination of the surface of inactive compacts as a function of the compacting pressure

Quantitative image analysis is being performed on sections of the samples compacted on a technical scale in order to determine the porosity and porosity gradient in the samples. Initial results reveal that for the height of the samples no significant porosity gradients occur in the samples.

2.3.7 Transport of active hulls and active densified product

- The concept of the planned hull transport from WAK to SCK includes the specification of the hull packaging, the shielding cask, and the loading and unloading techniques.

The safety evaluation performed shows that self-ignition of the canned, not immobilized heap of hull debris due to decay heat and reaction heat is improbable.

List of publications

S. Nazaré, Semi-annual report I. 1987
KfK-No. 04.02.06P12C, July 1987

H. Frotscher, S. Nazaré,
Semi-annual report II. 1987 is being prepared.

SOLIDIFICATION OF TRU-WASTE BY EMBEDDING IN A CERAMIC MATRIX

Contractor : Kernforschungszentrum Karlsruhe GmbH / FRG
Institut für Nukleare Entsorgungstechnik (INE)
Contract N° : FI1W/0021-D (B)
Duration of contract: July 01, 1986 - December 31, 1988
Period covered : January 1987 - December 1987
Project Leader : A. Loida

A. OBJECTIVES AND SCOPE

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

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

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

B. WORK PROGRAMME

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

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

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

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

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

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

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

Main items during the year 1987 were the preparation, respectively the characterizations of very high TRU-waste loaded alumosilicate-based ceramics containing original dissolver residues from the FBR-reprocessing and these ceramics containing original ashes from the dry incineration of burnable TRU-wastes. X-ray-powder diffractometry, optical light microscopy and scanning electron microscopy were the mostly applied investigation methods.

Progress and results

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

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

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

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

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

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

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

By means of X-ray-powder diffractometry the phase composition of these specimens has been determined as an assemblage of

- corundum (Al_2O_3)
- mullite ($Al_6Si_2O_{13}$)
- $(Pu,U)O_2$
- RuO_2.

Leach-tests after the ISO-draft yielded a Plutonium leachrate in the range between 10^{-7} and 10^{-8} g/cm²d.

2. Determination of the maximum waste loading for the ceramic matrix, characterization of the final products.

Original TRU-ashes from the dry incineration of burnable TRU-wastes, received from EUROCHEMIC/Mol (EUR 1/1), have been immobilized in the ceramic matrix KAB 78. The waste loading ranged beetween 20, 30, 40, 50 and 60 wt.-%. Main chemical components of this TRU-ash were SiO_2, C, Al_2O_3, CaO, Fe_2O_3 and Na_2O. Its content of TRU-oxides was about 9 wt.-%. The basic chemical composition of the sintered ceramic products is listed in Table II.

Table II: Basic chemical composition of alumosilicate-based ceramics, loaded with 20,30,40,50 and 60 wt.-% of original TRU-ashes (EUR 1/1) in wt.-%

waste loading degree / Component	20	30	40	50	60
Matrix					
- Al_2O_3, SiO_2	83.60	75.10	65.95	56.43	46.30
Ashes					
- TRU-oxides	1.90	2.80	3.85	4.85	6.02
- SiO_2, Al_2O_3, CaO, Fe_2O_3, Na_2O,...	14.50	22.10	30.20	38.71	47.70

The specific α-activity of these TRU-ashes containing ceramics increased from 1.24 E 8 Bq/g (3.4 mCi/g) to 3.77 E 8 Bq/g (10.2 mCi/g) by increasing the waste content from 20 to 60 wt.-%. In function of the waste loading the densities of the ceramics decreased from 2.63 to 2.03 g/cm³, their compressive strength decreased from 365 to 69 N/mm² and their open porosity increased from 1.7 to 12 vol%. By means of X-rax-powderdiffratometry the phase composition has been determined as listed in Table III.

Table III: Phase composition of the alumosilicate-based ceramics, loaded with original TRU-ashes from the dry incinceration (EUR 1/1) in function of the waste content (wt.-%)

Phase / waste loading	20	30	40	50	60
Corundum Al_2O_3	++	+	+	(+)	-
Plagioclase $(Ca,Na)\ Al_{2-x}Si_{2+x}O_8$ $0<x<1$	+	+	+	+	++
Spinel AB_2O_4 $A = Mg,Mn,Zn,Ni$ $B = Al,Fe^{3+},Cr^{3+}$	(+)	(+)	+	+	++
Hematite Fe_2O_3	-	(+)	(+)	(+)	(+)
$(Pu,U)O_2$	++	++	++	++	+++

- phase not recognizable
(+) phase shows weak reflections
\+ phase shows significant, strong ++, very strong +++ reflections.

A series of leaching tests after the ISO-draft using Q-brine as solvent has been performed. They have been running for six months and have just been coming to an end.

DECONTAMINATION OF REPROCESSING CONCENTRATE BY MEANS OF INORGANIC ION EXCHANGE AND EXTRACTION CHROMATOGRAPHY

Contractor:	KfK, Karlsruhe, Federal Republic of Germany
Contract No.:	FI1W-0022 D (B)
Duration of contract:	July 1986 - December 1989
Period covered:	January 1987 - December 1987
Project leader:	W. Faubel

A. OBJECTIVES AND SCOPE

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

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

Therefore the main objective of this contract is to assess the performances of these alternative treatment processes for decontamination of reprocessing concentrate. The contract deals with the demonstration and feasibility for decontaminating medium level reprocessing concentrate through successive treatment involving experiments in 1, 20 and up to 100 liter of genuine waste.

B. WORK PROGRAMME

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

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

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

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

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

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

B.1.6. Complementary lab-scale tests for improving Ru decontamination.

B.2. Installation of the equipment required for decontamination tests at the 20 - 100 l scale.

B.2.1. Inactive testing.

B.2.2. Active testing using genuine medium level reprocessing concentrate.

B.3. The experimental programme will be completed with a thorough data evaluation.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The technical feasibility of the partitioning of genuine concentrated nitric acid intermediate level waste (ILW) solutions from PUREX process into a small high and a large low active waste volume by employing chromatographic methods has been demonstrated for a 1 liter scale. ^{134}Cs, ^{137}Cs were selectively separated with a decontamination factor (DF) greater than $1 \cdot 10^5$ in a newly developed "suspended bed" column filled with the microporous inorganic exchanger ammonium molybdatophosphate. ^{125}Sb and the actinides/lanthanides with the valence state 3 + are retained with DF's between 40 and 1000 on metal oxides of Sb or Mn and on an extraction chromatographic column containing N-Octyl(phenyl) N,N-diisobutyl carbamoyl methyl phosphine oxide on an organic or inorganic support, respectively. ^{106}Ru and ^{60}Co were removed on a column loaded with dimethyl glyoxime on an organic matrix with DF's greater 20.

The general work progress status is as follows:
B.1., B.1.1., B.1.2., B.1.3., B.1.4., B.1.5., B.1.6. are completed.

B. 2., B. 2.1., B.2.2., B.3 are processing normally.

Progress and results

Experiments in 1 l scale (B.1., B.3.)

The gross decontamination of 1 liter concentrated aqueous, nitric acid intermediate level waste after passing the filter, the Bio Beads SM 7 and all 4 columns (fig. 1) reaches a value of total activity, that permits to consider the effluent as low level waste (LLW). The activities for each isotope before and after the chromatographic treatment in Bq/l are shown in table I /1/.

Table I: Activity of ILW before and after treatment and decontamination factor (DF)

Nuclide	Activity of ILW in Bq/l		DF
	before	after	
Am-241	1.3×10^8	$< 1.0 \times 10^4$	$> 1.3 \times 10^4$
Ce-144	1.1×10^8	$< 1.0 \times 10^4$	$> 1.1 \times 10^4$
Co-60	6.6×10^7	3.2×10^6	2.1×10^1
Cs-134	1.3×10^8	$< 1.9 \times 10^4$	$> 6.8 \times 10^3$
Cs-137	1.3×10^9	$< 1.1 \times 10^4$	$> 1.2 \times 10^5$
Eu-154	1.9×10^7	$< 1.0 \times 10^4$	$> 1.9 \times 10^3$
Eu-155	1.5×10^7	$< 1.0 \times 10^4$	$> 1.5 \times 10^3$
Ru-106	5.2×10^8	2.7×10^7	1.9×10^1
Sb-125	1.4×10^8	3.5×10^6	4.0×10^1

< under detection limit

The actinides/lanthanides with 3+ valence state and cesium are separated with decontamination factors (DF's) between 10^3 and 10^5, for Eu and Cs, respectively. DF's of around 20 to 40 have been reached for Co, Ru and Sb; also sufficient to accomplish the requirements of regulations limiting the dosis of a transported containement to 100 micro Sv/h in 1 meter distance from the surface. For the values, obtained in this work (table IV) calculations with the program PROMAX for filling the low level waste effluent into 400 liter drums into cement by 10 % loading, lead to a value far below the required 100 micro Sv/h in 1 meter distance from the surface /2/.

After solving the partitioning problem of ILW into a large volume of low level waste (LLW) and a relatively small volume of high level waste (HLW), the question comes up, how to minimize the "secondary HLW" consisting mainly of the materials in the columns used for the separation of the different elements?

Beginning with the filter (fig. 1), it has been revealed, that the precipitate consists - concerning the relevant gamma emitters responsible for the radiation dosis - mainly of ^{106}Rh/Ru, whereas the organic contaminates are almost free of any gamma activities. In the "suspended bed" column cesium, contributing to about 80 % to the total gamma dosis of the genuine ILW, is retained selectively on ammonium molybdato phosphate /3/, which can be easily taken out of the column by dissolving the exhausted AMP-1 in a very small amount of alkaline medium, which can be added to the vitrification process of the HLW. All following column materials will be foreseen for cement of bitumen products, also the glass wool filter. The Bio Beads SM 7 can be treated as low level waste.

A very important parameter in this content is represented by the loading capacities of the various sorbing materials, which can determined for all relevant elements in small column experiments adding to a simulated ILW or 1 M HNO_3 solution the adequate amounts of tracers and carriers of the specific nuclides and elements, respectively; except for antimony and ruthenium for chemical reasons, namely, the nearly insolubility of antimony and the tremendous variety of ruthenium complexes in nitric acid solutions, not permitting suitable simulation of Ru-species /4/. For cesium, the loading capacity of about 60 g_{Cs}/kg_{AMP-1} in different nitric acid concentrations has been already published /3/. In order to determine loading capacity of the 3+ valent actinides and lanthanides breakthrough curves for europium have been measured, as mentioned above, using ^{152}Eu tracer and a $1 \cdot 10^{-3}$ M Eu-carrier in 1 M HNO_3 with and without a high salt loading of 300 g $NaNO_3$, the maximum occurring in the ILW. The increase of the breakthrough, defind as the first point of measureable activity above the detection limit of the Ge-detector, by a factor of 2 from 11 to 22 g $_{Eu}$/kg $_{resin}$ can be explained by the so called "salting out" effect. Furthermore experiments to elute the europium from the CMPO resin employing a weak alkaline medium (pH 8) revealed a significant influence on the temperature, diminishing the elution volume from 60 to 15 ml by increase of the temperature from 25 to 75°C; opening the possibility of a reuse of this relatively costly CMPO resin.

Data evalution (B.3.)

Taking into account on one hand the capacities of each column material and on the other the existant quantity of elements in the ILW, the needed amount of resins for a 350 tons/year reprocessing plant can be extrapolated. In the case of unknown the breakthrough curves of relevant elements, the numbers of necessary column materials is estimated from the 1 liter experiments. The results, depicted in table II, show that a total amount of about 300 kg per year secondary waste are to be expected on column materials.

Table II: Secondary wastes arising from column materials by reprocessing of 350 tons
* Estimated values taking as a basis the 1 l experiments

Names of materials	elements name	elements amount [g/350 t]	Amount of material [kg]
glaswool	-	-	70*
SM 7	organics	-	50*
AMP-1	CS	105	2
Sb_2O_5/MnO_2	Sb, Mo	1155	70*
CMPO	R, E + Lh	552	30
DMG/carbon	Co + Ru	5600	70*
		total	292

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/1/ Faubel, W., Menzler, P.-M., Sameh A. Ali, RECOD 87, Paris, Aug. 23 - 27 (1987).

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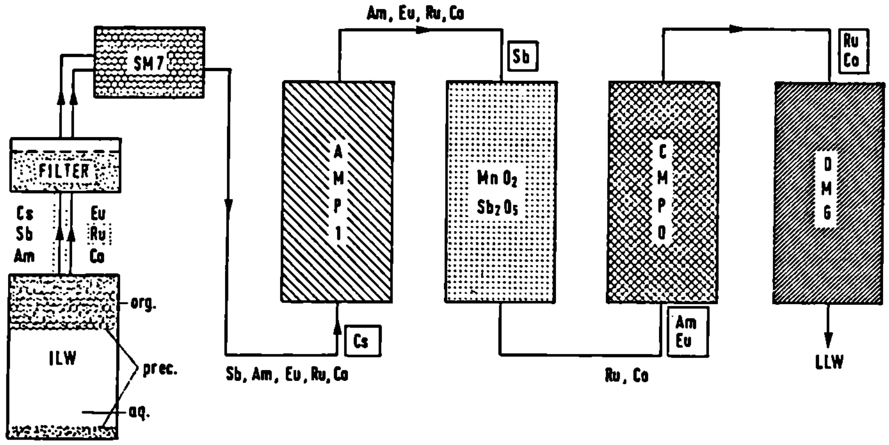

Fig. 1: Flowsheet of the chromatographic decontamination of ILW solutions.

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

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

A. OBJECTIVES AND SCOPE

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

These are the goals of the project:

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

B. WORK PROGRAMME

2.2 The different streams of tritiated waste waters which are expected to arise from the operation of the Wackersdorf reprocessing plant were identified as well as their chemical and radiochemical composition.

2.3.1 Before the enrichment of tritium by catalytic-chemical exchange and electrolysis can be carried out, remaining contaminations in the waste water must be removed by means of a pretreatment step, i.e. ion exchange or distillation. The decontamination factors achieved hereby will be reported.

2.3.2 Using an electrolyser operating with a Solid Polymer Electrode (SPE), experiments concerning the lifetime and performance modifications of the SPE by contaminations were started.

C. PROGRESS OF WORK AND OBTAINED RESULTS

2.2 INCIDENCE AND DISTRIBUTION OF TRITIUM IN THE REPROCESSING OF LWR NUCLEAR FUELS

The major fraction of the fuel element tritium inventory goes into solution during fuel dissolution, partly in the form of tritiated water, while a further fraction remains bound as a hydride in the zircaloy cladding.

In the PUREX-process, in order to keep the quantity of tritiated water as small as possible an additional tritium scrubbing column, TS, is connected in series. In this column the organic product flow from the HS column is washed by tritium-free nitric acid TSS and the tritium is thus practically completely reextracted /1/. Less than 1 % of the initial TS inventory then still remains in the organic product flow, that is < 0,02 % of the fuel element tritium content. In contrast to the tritium-free TSS solution, the other scrubbing solutions of the highly active extraction fraction such as HAS and HSS, as well as the nitric acid used for fuel dissolution and HAF adjustment, are produced using recycled water from the high active cycle and are thus tritiated. It is thus possible to restrict the tritium in a small volume of water to the high active sector of the reprocessing plant and to withdraw the excess water from the acid recovery facility.

The quantity of excess water at a reprocessing plant of 350 tonnes of uranium per year, as planned for the Wackersdorf site, amounts approx. 700 m^3/a, with a tritium content of about 2,6 PBq (70 000 Ci), corresponding to approx. 32 % of the initial tritium inventory.

This tritiated waste water still contains slight metallic impurities as well as fission product and actinide contaminations. The DWK (German Company for the Reprocessing of Nuclear Fuels) assumes the following values for a burn-up of 40 GWd/t and a cooling down period of 7 years:

Tritium	$3,7 \times 10^{12}$ Bq/m^3	(100 Ci/m^3)
fission products	$2,1 \times 10^{7}$ Bq/m^3	(10^{-3} Ci/m^3)
actinides	7×10^{5} Bq/m^3	(10^{-5} Ci/m^3)

"Table I" gives details of nuclide specifications. The table is based on data compiled by the DBE (German Company for the Construction an Operation of Final Repositories) on the basis of DWK information and their own research /2/, as yet no data are actually available from the Wackersdorf reprocessing plant.

2.3.1 PRETREATMENT OF THE TRITIATED EXCESS WATER FOR ELECTROLYSIS

Tritium must be removed from excess waste water, i.e. it would have to be enriched and electrolysed to form gaseous HT for the fixation in form of zirconium hydride.

The excess water still contains impurities and radioactive contaminations which may impair the devices in the combinded electrolysis exchange process (CECE). This excess water must therefore be subjected to pretreatment since for instance electrolysers may only be operated with water of an electrical conductivity of < 2 µS.

For the experiments on a pretreatment of the excess water (crude waste) by distillation, a simulated crude waste solution was prepared with the composition given in "Table II". The solution had a pH-value: 2.3; conductance: 29,8 µS.

Distillation without previous neutralization led to a insufficient decontamination of only 13.1 % (DF = 8). When the initial solution was neutralized and the distillation was performed via a 30 cm long rectification column, only 1 % of the initial radioactivity was present in the distillate (DF = 100; pH-value: 7; conductance: 0.147 µS).

A relativly large measuring error resulted due to the low count rates in the measuring speciems of the distillates. In the following experiments 100 times the quantity of the radionuclides Ru+Rh-106, Ce+Pr-144, I-131, Cs-137, relative to the reference solution was added.

The results of the overall radioactivity measurements and individual nuclide determinations by gamma-spectrometry are summarized in "Table III".

2.3.2 ELECTROLYSIS EXPERIMENTS

The first electrolysis experiments were carried out with a hydrogen generator model 7525 operated together with a solid polymer electrode (SPE) supplied by the PACKARD Instrument Company. This device requires a good water quality of < 5×10^{5} Ohm/cm, i.e. < 2 µS. It electrolyzes 245 ccm/day of water and generates 13.5 l of hydrogen gas per hour.

In order to test the ion loading capacity and thus the lifetime of an SPE cell in an initial quick-motion experiment, a solution with 3.5×10^{-7} g/l of potassium iodine, corresponding to 8.2×10^{-8} g/l K and 2.7×10^{-7} g/l I, was applied as simulate. After electrolysing 5 liters of this solution (ion supply = 4.1×10^{-7} g K and 1.34×10^{-6} g I) the operating voltage of the SPE has risen from originally 5.2 V to 7.3 V and the electrolyser could no longer be operated.

These experiments, in particular those about the behaviour of I-131 and Cs-137 contaminants remaining in the distillates, will be continued.

REFERENCES

/1/ BAUMGÄRTNER, F., Thiemig Taschenbücher, Volume 66, Part II pp 1-33, München (1978)
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TABLE I: IMPURITIES AND NUCLIDE SPECIFICATIONS IN THE EXCESS WATER (CRUDE WASTE) FROM REPROCESSING

IMPURITIES: Fe: 0,2 mg/l Cr: 0,1 mg/l
Mn: 0,1 mg/l Ce: 0,3 mg/l
HNO_3: 0,006 Mole/l

Nuclide	spec. activity Bq/m³ HTO	Nuclide	spec. activity Bq/m³ HTO
H-3	$3,7 \times 10^{12}$	Pu-238	
Sr-90	$3,61 \times 10^{6}$	Pu-239	
Y-90	$3,16 \times 10^{6}$	Pu-240	$9,1 \times 10^{2}$ (Pu-238, Pu-239, Pu-240, Pu-242, Pu-244)
Ru-106	$1,79 \times 10^{5}$	Pu-242	
Rh-106	$1,79 \times 10^{5}$	Pu-244	
Cs-134	$1,64 \times 10^{6}$	Pu-241	$1,74 \times 10^{4}$
Cs-137	$5,59 \times 10^{6}$	Am-241	$1,1 \times 10^{5}$
Ba-137m	$5,32 \times 10^{6}$	Cm-244	$5,9 \times 10^{5}$
Ce-144	$1,37 \times 10^{5}$		
Pr-144	$1,37 \times 10^{5}$		
I-129	$4,13 \times 10^{5}$		

TABLE II: SIMULATED "CRUDE WASTE"-SOLUTION

Nuclide	Bq/l	g/l
Ru+Rh-106	1.79×10^{2}	1.3×10^{-12}
Ce+Pr-144	1.37×10^{2}	1.16×10^{-12}
Cs-137	5.59×10^{3}	1.7×10^{-9}
I-129	4.13×10^{2}	6.3×10^{-5} x)
Fe	- -	2×10^{-4}
Mn	- -	1×10^{-4}
Cr	- -	1×10^{-4}
Ce	- -	3×10^{-4}

x) I-131 was used instead of I-129

TABLE III: RADIOACTIVITY AND INDIVIDUAL NUCLIDES IN THE DISTILLATES

	experiment 4			experiment 5			experiment 6		
	batch (Bq)	distillate (Bq)	%	batch (Bq)	distillate (Bq)	%	batch (Bq)	distillate (Bq)	%
-activity well-type-crystall	$6{,}92 \times 10^5$	$3{,}8 \times 10^3$	0,55	$4{,}09 \times 10^5$	$1{,}65 \times 10^3$	0,4	$7{,}53 \times 10^5$	$2{,}61 \times 10^3$	0,35
-activity -spectro-metry	$2{,}46 \times 10^6$	$8{,}5 \times 10^3$	0,35	$2{,}98 \times 10^6$	1×10^4	0,34	$3{,}78 \times 10^6$	$1{,}35 \times 10^4$	0,36
^{137}Cs	$1{,}55 \times 10^6$	+	+	$2{,}5 \times 10^6$	1×10^4	0,4	$2{,}65 \times 10^6$	$7{,}5 \times 10^3$	0,28
^{131}I	$9{,}1 \times 10^5$	$8{,}5 \times 10^3$	0,9	$2{,}4 \times 10^5$	+	+	$1{,}75 \times 10^6$	$5{,}8 \times 10^3$	0,33
^{144}Ce-Pr	+	+	+	$4{,}9 \times 10^4$	+	+	$4{,}3 \times 10^4$	+	+
^{106}Ru-Rh	+	+	+	$9{,}3 \times 10^4$	+	+	$5{,}57 \times 10^4$	+	+

+) = too low count rates, not evaluable

DECONTAMINATION OF PU CONTAINING INCINERATOR ASHES

Contractor: Kernforschungszentrum Karlsruhe GmbH / FRG
Institut für Nukleare Entsorgungstechnik (INE)
Contract N°: FI1W/0140-0(B)
Duration of contract: September 1987 - December 1989
Period covered: September 1987 - December 1987
Project Leader: H. Wieczorek

A. Objectives and scope

Amongst the different treatment options for solid Pu containing waste (PCW), incineration appears as one of the most promising one because of the high volume reduction factor achieved. Accordingly, the high Pu content in the resulting incinerator ashes could cause problems in view of the disposal criteria set up by safety authorities. Likewise, it may be valuable to recover Pu from these ashes for recycling in LWRs.

Since some of Pu is present in the ashes as refractory PuO_2, its dissolution in an aqueous medium requires the use of strongly corrosive media such as mixtures of HNO_3/HF which are difficult to recycle in the Purex process.

Therefore, the main aim of this R&D activity is to develop a new process for recovering Pu from incinerator ashes which is capable to meet three basic requirements: easiness of implementation, high Pu-recovery yields and no generation of major quantities of secondary wastes.

B. Work programme

2.3. Literature survey
2.4. Evaluation of the tests performed in the ALONA plant.
2.5.1. Characterization of the KfK and Marcoule incinerator ashes.
2.5.2. Pretreatment of ashes.
2.5.3. Pu-recovery from ashes.
2.5.4. Pu-purification.
2.5.5. Secondary waste.
2.6. Drawing-up of basic flow-sheets.
2.7. Cost evaluation.
2.8. Conclusions.

C. Progress of work and obtained results

State of advancement

The programme started in September 1987. Besides first results on the subjects indicated under 2.3.-2.5.1., the installations required have been ordered for execution of work under 2.5.2.-2.5.4.

Progress and results

2.3. The dissolving medium most frequently applied for refractory plutonium oxide is HNO_3/HF. If optimal conditions are maintained, 99 percent of plutonium can be dissolved within 3 hours. Process experience is available from processing 200 g plutonium per batch.

Since the process is applied only for recovery of weapon grade fissile material, the disadvantages of this process such as corrosion of the process installation and high quantity of secondary waste produced are rather considered to command less priority.

Dissolution of PuO_2 in incinerator ashes from wastes produced in the Mox-fuel fabrication will probably not require strong dissolution agents such as HNO_3/HF. However, other constituents of the ashes, especially chlorine and carbon, complicate the dissolution of plutonium oxide as experienced in electrochemical dissolution processes. Hot sulphuric acid readily dissolves PuO_2 contained in the ashes. But its use is limited by the saturation of ash constituents to 0.6 kg ashes per liter sulphuric acid.

2.4. In the ALONA plant 9.9 kg of incinerator ashes containing nearly 600 g of plutonium were treated in 1985 using hot sulphuric acid as dissolution agent for PuO_2. Within 15 hours 99 percent of plutonium was conconverted from oxide into sulphate which is only soluble in this agent up to 0.2 g Pu/l. The purification of plutonium by extraction with Primene-JMT 0.65 M in octanol/kerosene and subsequent precipitation as oxalate showed no differences with respect to processing plutonium from burnable solid waste.

2.5.1 The Marcoule incinerator ashes were produced by incineration of Eurochemics burnable Pu-containing waste. This waste was produced mainly in installations used for conversion of plutonium nitrate to oxide. Since the temperature in the first chamber of the incinerator did not exceed 800°C, the ashes adopted a dark grey colour due to the carbon residues (24 percent). The plutonium content amounts to 9.4 % (Am, U, 0.2 % each). The main non-radioactive constituents are: Si (16%), Al (10%), Ca (9%), Fe (6%), Na (3%), and Zn (2%). The content of chlorine amounts to 5%.

The ash is ground in a "heavy duty" coffee mill. The mean particle size after grinding was estimated at 0.05 mm. The ground material was homogenised in a cylindrical PVC-container equipped with longitudiual baffle blades; its free volume was more than 60%.

2.C. Optimization of waste management at source

OPTIMIZATION OF WASTE MANAGEMENT AT SOURCE

Contractor:	Associated Nuclear Services, Epsom, UK
Contract No.:	FI1W/0023
Duration of contract:	December 1987 - December 1988
Period covered:	December 1987 - December 1988
Project Leader:	M.W. Wakerley

A. OBJECTIVES AND SCOPE

Within the Community many countries have a large number of nuclear facilities producing radioactive waste. The largest volume of these wastes are in the low level category and disposal of low level waste (LLW) is practised in several countries. The study has concentrated on means of minimizing such wastes at their points of arising by either additional equipment and or administrative controls. The largest amounts of activity in wastes are associated with intermediate (ILW) and high level wastes (HLW) but arising of these waste are mainly set by the chosen process and the operator has less scope for optimizing the management of such wastes.

The goals of the project have been:

- collation and review of information on waste management practices at a number of different types of nuclear facilities, relating to the optimization of wastes at source;
- identification of the factors limiting efficient segregation of different waste types from each other.

The project has been predominantly funded by the UK Department of the Environment (DoE) and reflects a UK perspective.

B. WORK PROGRAMME

1. Review of international literature relating to the optimization of the management of LLW (and some ILW). Use was made of computer search facilities of large data basis in Europe containing information on European and American practices.

2. Visits to a range of nuclear facilities so as to establish current waste management practices and the constraints imposed upon the operators. The facility types were:

   (a) Fuel fabrication plant
   (b) Reactors (Magnox, Advanced Gas Cooled and Pressurised water)
   (c) Reprocessing plant
   (d) Research centre
   (e) Radio-isotope production unit
   (f) Hospital using radionuclides

3. Collation and analysis of the results of the literature survey and visits.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement:

- the literature review was undertaken;
- visits were made to:

  (a) Springfields Nuclear Fuel Fabrication Plant, in England, a large facility for natural and enriched uranium fuel production.

  (b) Doel, a four unit Pressurised Water Reactor site in Belgium. Hinkley Point, England, a site with both Magnox and Advanced Gas Cooled Reactors. Nuclear Waste Technology Branch of the Central Electricity Generating Board at Barnwood, England.

  (c) A brief visit to La Hague, France as part of RECOD 87 was made. Formal visits to the Sellafield, England and La Hague nuclear fuel reprocessing plants were not possible.

  (d) Dounreay Nuclear Power Development Establishment, Scotland, a centre for fast reactor reprocessing technololgy.

  (e) Amersham International's radio-isotope production plant at Amersham, England.

  (f) Royal Marsden Hospital, England which has a large radiotherapy unit.

- the results of the literature survey and visits were collated and analysed.

PROGRESS AND RESULTS

The programme of work has been completed and a draft report has been submitted in the CEC and DoE. The final report is being issued. The main conclusions are:

(a) Optimization of waste management by actions taken at source implies trade-offs between costs and impacts. However, waste minimization offers scope for reduced costs without increased impacts.

(b) Much of the ILW and HLW produced is a direct product of processes and almost the only optimization that can be performed for these wastes is the prevention of excessive dilution of the wastes. The main scope for optimization of waste lies with the minimization of the activity in and volumes of raw LLW.

(c) The major advantages of decreasing the activity and volume of waste appear to be threefold:

- reduced short-term costs of waste treatment, transport and disposal;

- conservation of existing storage and disposal sites and hence delaying new investment and/or shut-down of a facility and thereby reducing long-term costs;

- reduced operator dose, although shorter exposure to more concentrated waste might mean the reduction is slight unless self shielding is significant.

(d) The two main ways in which waste can be minimized by actions taken at source are facility and equipment design and administrative control.

(e) With regard to facilities and equipment, the aim of minimization of the generation of raw wastes is best accomplished by incorporation of features at the early design stage. A large number of examples have been given for the different types of nuclear facilities.

(f) With regard to administrative measures the aim of minimization of the generation of raw wastes can best be accomplished by having an organisational structure which ensures responsibilities for all aspects of waste management are defined. A number of examples of administrative measures have been given.

(g) It would appear that the best results with regard to waste minimization on a site are produced when the waste management group has specialist staff available to deal with all solid, liquid and gaseous wastes. There is a very considerable interplay between the management of the wastes in the different phases.

(h) The accountability of waste producers for the treatment of their wastes should be encouraged - Education is necessary to overcome the 'them' and 'us' attitude observed in some large organisations where operators regard waste handling as someone elses problem.

(i) Comprehensive education of operators appears essential. Starting with induction courses and followed by regular 'refreshers' attempts must be made to create operator awareness of the consequences of waste production.

(j) As a part of the training of stores and operational staff the fact must be emphasized that materials such as packaging which is excluded from the active areas cannot become 'suspect' contaminated waste, for which appropriate and costly treatment and disposal must be provided.

(k) There is often a conflict between working practices designed for ease of operation, safety and perceived cost with the wish to minimize wastes.

(l) Segregation is most frequently practised not at source but once wastes have been aggregated. There is a large body of evidence that suggests that a large percentagle of the volume of LLW is below the LLW limits.

(m) Segregation at source or once wastes are aggregated requires a high level of operator training and specialised instrumentation. As pressure rises due to disposal costs escalation more emphasis is likely to be placed on the provision of instrumentation to allow greater segregation.

(n) A vast array of techniques are available for processing wastes once they have been minimized at source, segregated and aggregated. These been described.

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

Contractor	: BELGONUCLEAIRE N.V., Dessel, Belgium
Contract N°	: FI1W/0024
Duration of contract	: May 1986 - October 1988
Period covered	: January 1987 - December 1987
Project leader	: H. Pauwels

A. Objectives and Scope

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

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

B. Work Programme

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

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

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

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

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

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

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

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

C. Progress of work and obtained results

State of advancement

The work on the individual tasks is progressing as scheduled in the work programme, the only exception being the task B.2.4; the work on the latter task will be started in 1988.

The waste drum scanner has been calibrated in 3 Pu concentration ranges; the detection limit and the variability of the geometric efficiency in the very low concentration range have been determined.

As to the items B.2.1 and B.2.2, systems are installed to confine the Pu bearing powders as much as possible within tight equipment. At the spots where the tightness of the equipment cannot be realized a spread of the Pu bearing powder is avoided by creating an air stream barrier and sucking the dust laden air into a dust collecting and separating unit. The installation of these systems has resulted in a substantial reduction of both the volume and Pu content of the waste produced.

As to the item B.3, detailed statistics have been worked out with respect to the waste production during 1986, during 1987 and during a past reference period.

Progress and results

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

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

The geometric efficiency of the system, i.e. the response to a fission source placed at any position within the sample cavity has to be as constant as possible since in practice the position of the Pu in a waste can is not known. The extent of this effect in the very low concentration range has been determined by performing measurements on waste cans which contained very small amounts of Pu at different positions within a non-contaminated waste matrix. It was shown by these measurements that the effect of the geometric efficiency variability becomes fairly important in the very low concentration range; at the detection limit of the apparatus the standard deviation on the Pu-weight which is caused by this effect may be as high as 35 %.

The waste drum scanner has been calibrated in three Pu concentration ranges by performing measurements on a series of simulated waste cans filled with a non-contaminated combustible waste matrix which contained samples of a fully characterized PuO_2 powder. The procentual root-mean-square deviations in the low, the medium and the high Pu concentration range are 4.13 %, 2.29 % and 1.78 %, respectively.

The detection limit of a neutron coincidence counter in a given configuration is mainly governed by the variability of the background and the length of the counting period. In order to estimate the detection limit of the neutron coincidence counter in its practical conditions of use the variability of the background has been determined by performing long series of blank measurements on waste cans which were filled with a non-contaminated waste matrix. At the 3 σ level the detection limits associated with counting periods of 100, 300 and 1400 s are 36, 19 and 5 mg Pu, respectively.

2. Results from the application of techniques, concepts and systems for:
   - the confinement of Pu bearing powders within tight equipment (B.2.1)
   - the limitation of the contamination within the glove boxes (B.2.2)

Waste production statistics have shown that in a MOX fuel fabrication plant more than 70 % of the Pu-contaminated solid waste is generated either during operations which involve the handling and transfer of powders or during the grinding of the sintered fuel pellets. Another conclusion which can be drawn from the waste production statistics is that these dust generating operations cause about 90 % of the total irrecoverable Pu losses during the MOX fuel fabrication process. These considerations have led BELGONUCLEAIRE to the development and the installation of systems in which :

- the Pu bearing powders are confined as much as possible within tight equipment installed within tight glove boxes and kept at a negative pressure with respect to the internal glove box atmosphere ('fourth confinement barrier');
- at the spots where the tightness of the equipment cannot be realized a spread of the Pu bearing powder is avoided by creating an air stream barrier and sucking the dust laden air into a dust collecting and separating unit. This unit consists of the following components :
  . dust collection points where air is sucked into the confining equipment creating in this way an air screen in the gap between the powder supplying and receiving parts of the equipment
  . a high throughput cyclone
  . a high efficiency cyclone
  . an electrostatic precipitator (optional)
  . a high efficiency air filter
  . an exhaust fan

Up to now BELGONUCLEAIRE has installed 5 standard dust collecting and separating units in its MOX fuel fabrication line. Three of them are in active operation; the remaining ones will be commissioned during 1988. Dust collection points are installed at every spot where a spread of Pu-bearing dust may arise.

The main conclusions which can be drawn from the operating experience gained up to now are the following :

- the amount of powder which is sucked into the dust collecting and separating units may range from 0.08 % to 0.50 % of the total amount of powder being transferred; 95 to 99.5 % of this fraction is retained by the cyclones;
- the powder fractions which are collected in the two cyclones can be directly recycled into the MOX fuel fabrication process;
- the glove boxes in which dust collection points are installed remain remarkably clean as compared with the old situation;
- it is estimated that by the systematic application of the fourth confinement barrier concept and the installation of dust collecting and separating units the volume of Pu-contaminated waste is reduced by 10 to 15 %;
- the application of this concept and the installation of these units reduce the Pu content of the waste in a spectacular way; it is estimated that this reduction amounts to about 80 %.

3. The transfer of Pu bearing materials in reusable containers (B.2.3)

As it is the common concern of the different PuO_2 receiving companies to minimize the amount of waste constituted by non-reusable packaging components a reusable PuO_2 powder can of the type presently

used by BELGONUCLEAIRE has been proposed as a substitute for the primary can of the COGEMA PuO_2 packaging concept. Although the parties concerned showed interest in this solution, it has not been retained. In the short range an inter-plant reuse of contaminated PuO_2 packaging components seems not possible. On the contrary, the idea of a maximum internal reuse of such components gains more and more ground.
The powder can presently used by BELGONUCLEAIRE for internal storage and transfer purposes has a very simple design. The internal height and diameter of the can are 221 and 100 mm, respectively; its capacity is about 3.5 kg of MOX powder at a powder density of 2.5.

Several hundreds of these cans are in use within the BELGONUCLEAIRE MOX fuel fabrication plant. They contain all kinds of powder blends and scrap material.

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

The destructive method for the determination of the Pu content of the incoming PuO_2 powder has been replaced by a non-destructive check of the relative homogeneity of each of the PuO_2 powder lots received. The total neutron flux of each can belonging to a given powder lot is measured and plotted as a function of the Pu content of the can as reported by the PuO_2 supplier. By applying a linear regression method on these data it is possible to point out the cans the results of which are outlying.

Presently, most of the Pu and impurity determinations are carried out on a composite sample taken from a 750 kg inspection lot instead of sampling and analysing each individual powder blend (70 to 75 kg).
It is estimated that by this reduction of the number of Pu and impurity determinations the amount of Pu lost in the effluents from these analyses is reduced by a factor of 4.

5. Qualitative and quantitative characterization of the waste generated at a Pu fuel fabrication plant; identification of the waste producing fabrication steps (B.3)

Detailed statistics have been worked out with respect to the waste production during 1986, during 1987 and during a past reference period. The main results are summarized in table I.

Table I : Waste production at the BELGONUCLEAIRE MOX fuel fabrication plant

	Production during the past reference period	Production during 1986	Production during 1987	Estimated production figures relating to a 35 tHM plant
1. Solid Pu-suspected waste				
Amount produced	22.5 m^3	20.8 m^3	32.4 m^3	45 m^3
Volume per kg of Pu in the final product (fuel rods)	66.8 l/kg Pu	60.8 l/kg Pu	46.2 l/kg Pu	25 l/kg Pu
Split-up according to the nature :				
- combustible	67.7 % by vol.	74.2 % by vol.	80.0 % by vol.	80 % by vol.
- non-combustible, compactible (except filters)	12.4 % by vol.	4.4 % by vol.	4.5 % by vol.	4 % by vol.
- non-combustible, compactible filters	17.8 % by vol.	19.0 % by vol.	13.2 % by vol.	14 % by vol.
- non-combustible, non-compactible	2.1 % by vol.	2.4 % by vol.	2.3 % by vol.	2 % by vol.
2. Solid Pu-contaminated waste				
Amount produced	17.1 m^3	14.3 m^3	21.5 m^3	36 m^3
Volume per kg of Pu in the final product	50.8 l/kg Pu	41.8 l/kg Pu	30.7 l/kg Pu	20 l/kg Pu
Split-up according to the nature :				
- combustible	48.6 % by vol.	64.8 % by vol.	60.3 % by vol.	$\sim$65 % by vol.
- non-combustible, compactible	43.5 % by vol.	31.5 % by vol.	32.7 % by vol.	$\sim$35 % by vol.
- non-combustible, non-compactible	7.9 % by vol.	3.7 % by vol.	7.0 % by vol.	$<$ 2 % by vol.
Split-up according to the Pu-content :				
0 to 0.4 g Pu per unit volume of 25 l	41.5 % by vol.	58.2 % by vol.	63.6 % by vol.	$\sim$65 % by vol.
0.4 to 2 g Pu per unit volume of 25 l	25.3 % by vol.	36.2 % by vol.	29.7 % by vol.	$\sim$30 % by vol.
2 to 5 g Pu per unit volume of 25 l	12.8 % by vol.	3.5 % by vol.	4.9 % by vol.	$\sim$ 5 % by vol.
5 to 10 g Pu per unit volume of 25 l	7.4 % by vol.	1.9 % by vol.	1.2 % by vol.	$<$ 1 % by vol.
10 to 15 g Pu per unit volume of 25 l	5.7 % by vol.	0.2 % by vol.	0.2 % by vol.	$<$0.2 % by vol.
15 to 30 g Pu per unit volume of 25 l	3.4 % by vol.	0 % by vol.	0.2 % by vol.	$<$0.2 % by vol.
30 to 50 g Pu per unit volume of 25 l	2.5 % by vol.	0 % by vol.	0.2 % by vol.	$<$0.2 % by vol.
50 g Pu per unit volume of 25 l	1.4 % by vol.	0 % by vol.	0 % by vol.	$<$0.1 % by vol.

Table I (cont'd)

Split-up according to the waste producing operations :				
. normal operations :				
- first blending and micronization of the UO_2 and PuO_2 powders	-	37.6 % by vol.	30.5 % by vol.	35 to 45% by vol.
- second blending of the powders }				10 to 15% by vol.
- pellet fabrication	-	35.1 % by vol.	36.7 % by vol.	15 to 20% by vol.
- filling and closing of fuel rods	-	11.2 % by vol.	15.6 % by vol.	15 to 20% by vol.
- destructive testing	-	16.1 % by vol.	8.9 % by vol.	5 to 10% by vol.
. exceptional operations :				
- major adaptations of the MOX fuel fabrication line	-	0 % by vol.	1.0 % by vol.	$<$ 1 % by volume
- major repairs of equipment	-	0 % by vol.	7.3 % by vol.	$<$ 1 % by volume
Total Pu content of the solid waste	3.29 kg Pu	0.41 kg Pu	0.68 kg Pu	$\sim$1 kg Pu
Amount of Pu lost under the form of solid waste (expressed as a percentage of the total Pu-throughput of the MOX fuel fabrication line)	0.98 %	0.12 %	0.10 %	$\sim$0.06 %
3. <u>Liquid Pu-contaminated waste</u>				
Amount of liquid Pu-contaminated waste produced	2.35 m^3	0.75 m^3	0.60 m^3	$\sim$1 m^3
Total Pu-content	105 g Pu	14.3 g Pu	3 g Pu	$\sim$15 g Pu
Amount of Pu lost under the form of liquid waste (expressed as a percentage of the total Pu-throughput of the MOX fuel fabrication line)	0.031 %	0.004 %	0.001 %	$<$0.001 %

CHAPTER 3

TASK No 3

Evaluation of conditioned waste and qualification of engineered barriers

CHAPTER 3

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

A. Objectives

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

Establishment of quality assurance in radioactive waste management

Integration of European research effort in the above fields.

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

Characterization of medium-activity waste forms :

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

Characterization of solidified high-activity waste forms :

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

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

Work on engineered barriers :

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

- Selection and characterization of suitable buffer materials.

C. 1985-1989 programme

a) Research on medium-active waste form characterization

- Long-term leaching behaviour :

  - Modelling of nuclide release phenomena in various repository environments

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

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

b) Research on high-active waste form characterization

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

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

c) Other engineered barriers

- The following subjects will be investigated :

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

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

  - Long-term effects of irradiation on barriers.

d) Development of standard test methods

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

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

D. Programme implementation

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

3.A. Medium-active waste from characterization

Medium Active Waste Form Characterisation:
The Performance of Cement-Based Systems

Contractor: University of Aberdeen, Old Aberdeen, UK.
Contract No. F1 1W 0025 UK (H).
Duration of Contract: 1st May '86 to 31 Dec. 1989.
Project Leader: F.P. Glasser.

A. Objectives and Scope

The project identifies the important features of cements and of blended cement pastes which will enable their long-term suitability as host matrices for radioactive waste to be defined. The modelling of cement degradation based on solubilities of calcium silicate hydrate gels is pursued and extended to incorporate other chemical components, e.g. alkalis. The importance of blending agents to system properties is assessed and the effects of inorganic and organic additives are reviewed. Solid-phase development in hydrating pastes is under investigation for application to a constitutional model and radiation effects, as well as interactions between the matrix and specific radwaste components, are being studied.

B. Work Programme

B.1. Solubility properties of several cement hydration products have been determined and applied to predictive models. Sorption experiments have been carried out using these products and electrochemical measurements have been conducted on extruded pore fluids.

B.2. Cements have been blended with slag and property measurements, as in B.1, have been executed along with phase characterisation studies.

B.3. The effects of organics on cement hydration have been reviewed and specific radwaste(U,I)-cement interactions have been investigated as in B.1.

B.4. Radiation effects on gas evolution and systen E_h are being assessed for Portland cement and its blends with pulverised fly ash (PFA).

C. The basic property measurements have led to the development of an equilibrium phase distribution model for cements blended with slag. The solution properties are predicted for the long-term based on this and earlier models for C-S-H /1,2/. Electrochemical measurements in slag cement pore waters have improved in reproducibility due to modified technique and the methods employed for chemical analyses of pore fluids are now capable of determining different aqueous sulphur species with a view to identifying potentially relevant electrochemical couples. Specific interations between U and cements has led to the identification of a calcium uranium hydrate which has favourable properties for the immobilisation of U in cements. I species are found to be sorbed by calcium aluminate sulphate hydrates. The effects of organics on cement hydration have been reviewed and an extensive list of substances has been categorised into their appropriate effects on cement set, e.g. retarders, accelerators etc. Specific organics such as TBP are currently being equilibrated with calcium silicates and calcium aluminates. The irradiation of cements and PFA-cements at dose rates of 2.8 $kGy.hr^{-1}$ lead to a drop in E_h although the PFA cement, under continued irradiation, shows a slow drift to more oxidising potentials.

Progress and Results

1. Development of the Phase Distribution Model

Phase characterisation studies on slag-cements coupled with literature evidence has led to the identification of potential long-term products of hydration for this system. These products are arranged into the assemblages illustrated in Figure 1 which are consistent with short-term expermental observations and thermodynamic limitations such that an equilibrium distribution of phases is predicted. Figure 2 shows the results for a range of slag:cement blends, the slag and cement having a typical chemical composition. The aqueous chemistry is predicted from solubility product data derived both from the literature /2,3,4/ and experiment. Two invariant points in the appropriate portion of the $CaO-Al_2O_3-SiO_2-H_2O$ system have been identified and Table I shows solution compositions at these points. Intermediate aqueous compositions have also been predicted.

Solubility Property Measurements

Solubility measurements on calcium silicate hydrate gels at 25°C have been extended to incorporate other components; gels have been prepared to contain Na_2O, K_2O and $CaSO_4.2H_2O$ and samples have been taken for analyses after ageing. Figure 3 shows typical aqueous composition data for Na^+-bearing gels; coexisting solid compositions are illustrated in Figure 4. Difficulties, caused by leaching of soluble alkalis during gel washing, have arisen and some account of this has been taken in interpretation of results.

Electrochemical Measurements

These have been obtained by a recently improved technique which reduces the risk of atmospheric oxidation of the sample. Results continue to substantiate the very reducing environment which occurs in high slag blends. These redox conditions are well poised with high aqueous concentrations of S^{2-} between 75 and 360ppm.

2. Aqueous Chemistry in Slag-Cements

An electrochemical titration technique /5/ has been employed to determine the relative amounts of aqueous sulphur species. S^{2-} is obtained directly and $[SO_3^{2-} + S_2O_3^{2-}]$ are obtained together, although it is not clear, as yet, whether the latter are oxidation products of S^{2-} caused by atmospheric contamination or if they were originally present in the pore fluid. A typical titration curve is shown in Figure 5. This titration can be extended to include determination of S° present in the polysulphide fraction, S_n^{2-} but further trials are required to assess the suitability of the procedure to slag-cements. Progress is currently being made with uv-visible spectrophotometry of slag cement pore fluids which produce spectra confirming the presence of S^{2-}. Additionally, a small absorption at λ ~ 350nm (see Figure 6) may be due to polysulphide. It is anticipated that quantitative data may be obtained by this method using the spectral information for sulphide species given in Table II /6,7,8/.

3. Specific Radwaste-Cement Interactions

Uranium

Uranium has been introduced to cement as $UO_2(NO_3)_2.6H_2O$ and UO_3. Analyses of extruded pore waters has shown the uranium concentration to be substantially reduced from the original hydrating concentration. The presence of slag enhances this retention of U by about one order of magnitude. Basic property measurements in the $CaO-UO_3-H_2O$ (Figure 7) system has led to the identification of a calcium uranium hydrate $Ca_2UO_5.1.3-1.7H_2O$ and a more crystalline phase $CaO.6UO_3.11H_2O$. In the presence of excess $Ca(OH)_2$ the former, more amorphous, phase is stable and therefore may immobilise U from solution. Solubility data for both calcium uranium hydrates are given in Table III.

Iodine

Concentrations are also found to be considerably reduced when aqueous iodine solutions are used to hydrate cements and slag cements, and the I^- and IO_3^- are assumed to be sorbed into the calcium aluminate sulphate hydrates AF_m and AF_t. Figure 8 illustrates the sorptive effect where OPC is found to be a better sorber than slag-cement. The dilution effect of the slag is thought to be the cause since a smaller volume of hydrates is produced in the short term. The redox properties of I are important. Figure 9 shows the relevant speciation. IO_3^- added to slag-cements is quickly reduced to I^-.

4. Radiation Effects

Cements and blended cements have been exposed to γ irradiation after crushing and slurrying with distilled water. All samples were made to water/solid ratios of 0.34 and were cured for 8 days at 55°C prior to irradiation. The variation in E_h was obtained using a Pt electrode. Figure 10 shows the results for OPC. The negative shift of E_h with time suggests a predominance of reduced species in the pore fluid. Previous studies had shown OPC to evolve H_2 during irradiation and absorb O_2 /9/ and this is consistent with the observed variation in E_h. Similar behaviour is observed for 3:1 PFA cement although the initially reducing effect is reversed on continued radiolysis. It appears that reduced species are not as long-lived as in the case of OPC, but O_2 is still absorbed.

List of Publications

1. Atkins, M., Beckly, A.N. and Glasser, F.P., "Influence of Cement on the Near Field Environment and its Specific Interactions with Uranium and Iodine". Presented at "Migration '87" in Munich due to be published in Radiochimica Acta.
2. Glasser, F.P., Macphee, D.E. and Lachowski, E.E., "Modelling Approach to the Prediction of Equilibrium Phase Distribution in Slag-cement Blends and their Solubility Properties". Presented at Materials Research Society Meeting in Boston due to be published in "Scientific Basis for Nuclear Waste Management XI".
3. Macphee, D.E., Luke, K., Glasser, F.P. and Lachowski, E.E. "Solubility and Ageing Studies of Calcium Silicate Hydrogels in Alkalis at 25°C". To be presented at the American Ceramic Society Meeting (March '88) and to be submitted to J. Am. Ceram. Soc.

References

/1/ Glasser, F.P., Lachowski, E.E. and Macphee, D.E., J. Am. Ceram. Soc., 70, (7) 481-485, (1987).
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/3/ D'Ans, J. and Eick, H., Zement Kalk Gips, 6, 197-210, (1953).
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/5/ Boulegue, J., Ciabrini, J.P., Fouillac, C., Michard, G. and Ouzounian, G., Chem. Geol., 25, 19-29, (1979).
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/8/ Avrahami, M. and Golding, R.M., J. Chem. Soc. (A), 647-651, (1968).
/9/ McHugh, G., Sambell, R.A.J., Spindler, W.E. and Mattingley, N.J., AERE-R12298.

Table I: Aqueous Compositions at Invariant Points in the Simulated BFS-OPC System

Species	Point 1	Point 2
$[Ca^{2+}]_{free}$	10.21×10^{-3}M	13.81×10^{-3}M
$[CaOH^{+}]$	4.73×10^{-3}M	8.66×10^{-3}M
$[Al(OH)_4^{-}]$	2.42×10^{-4}M	3.47×10^{-5}M
$[H_2SiO_4^{2-}]$	6.09×10^{-7}M	1.57×10^{-7}M
$[H_3SiO_4^{-}]$	1.93×10^{-7}M	0.37×10^{-7}M
$[OH^{-}]$	20.42×10^{-3}M	27.62×10^{-3}M
pH	12.31	12.44

Point 1: Aqueous composition above three solids, gehlenite hydrate + C-S-H (Ca/Si=0.9) + $Ca_4Al_2(OH)_{14}.6H_2O$.
Point 2: Aqueous composition above thres solids, calcium hydroxide + C-S-H (Ca/Si=1.8) + $Ca_4Al_2(OH)_{14}.6H_2O$.

Table II: Spectral Information Relevant to Quantitive Determination of Aqueous sulphide species

Species	λ_{max} (nm)	ϵ
S^{2-}	245	9100
HS^{-}	230	7200
$S_2O_3^{2-}$	217	3900
SO_3^{2-}	~227	similar to $S_2O_3^{2-}$
polysulphides		
S_2^{2-}	360	850
S_3^{2-}	420	95
S_4^{2-}	370	320
	300	1140
S_5^{2-}	380	640
	300	2000

Data from references /6/, /7/ and /8/.

Table III: Solubility Data for calcium uranium hydrate phases, aged 7 days.

Medium	Becquerelite $CaO.6UO_3.11H_2O$		$Ca_2UO_5.1.3-1.7H_2O$	
	$[Ca]x10^{-3}(M)$	$[U]x10^{-3}(M)$	$[Ca]x10^{-3}(M)$	$[U]x10^{-3}(M)$
Water	0.18	0.008	2.87	0.0006
$Ca(OH)_2$(pH~9.5)	0.33	0.08	0.042	0.001
$Ca(OH)_2$(pH~12.5)	18.84	0.006	19.58	0.004
simulated pore fluid	0.17	0.004	0.62	0.002

Simulated pore fluid corresponds to equal quantities of 0.2M KOH + 0.67M NaOH.

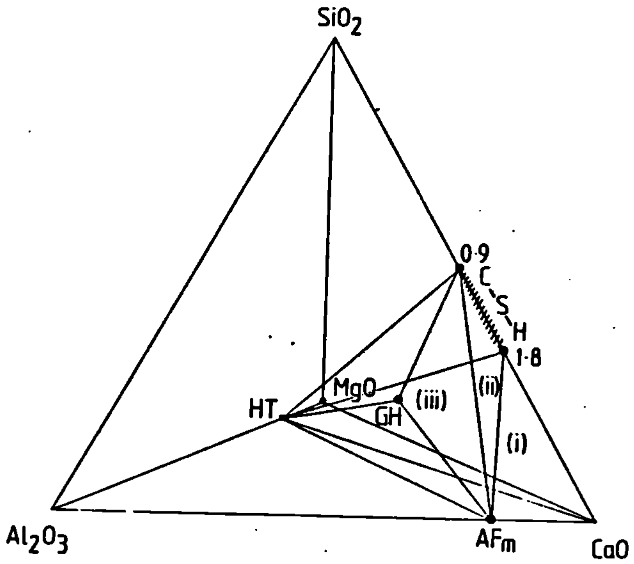


Fig. 1.

Phase relations in the water saturated $CaO-Al_2O_3-SiO_2-MgO$ system

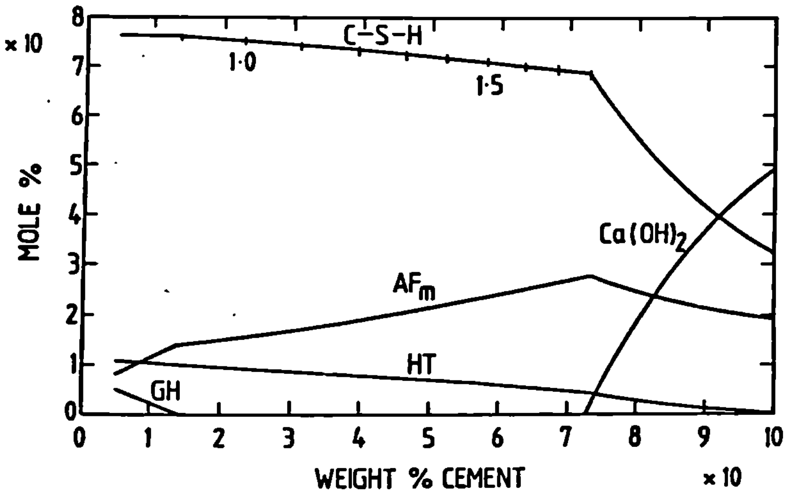


Fig. 2. Phase distribution in slag-cements

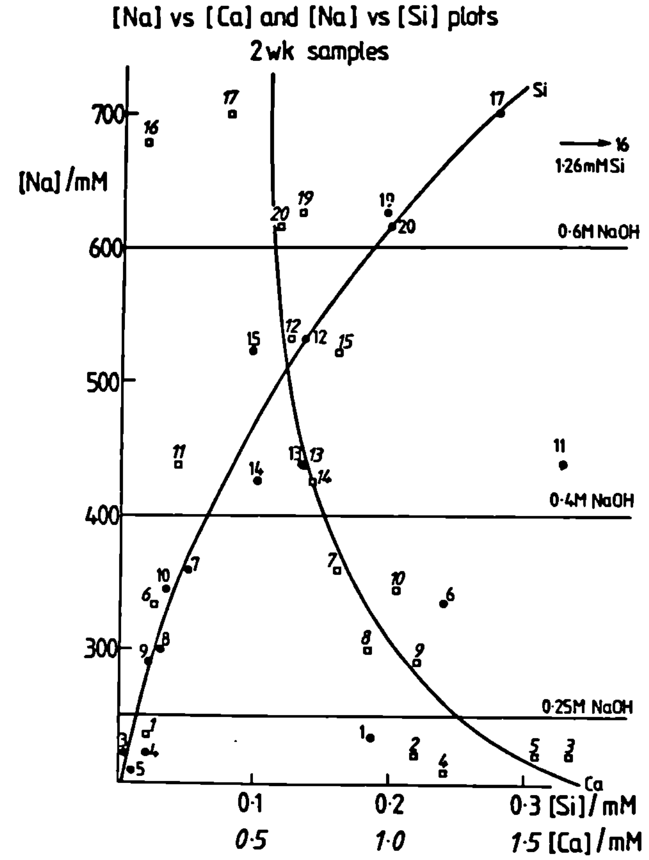


Fig. 3. Aqueous phase compositions above Na_2O-CaO-SiO_2-H_2O gels aged 14 days.

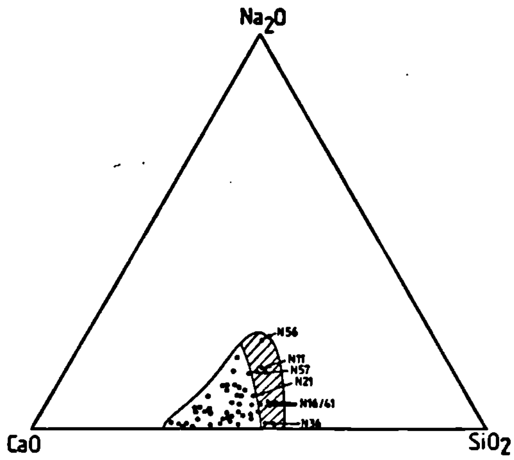
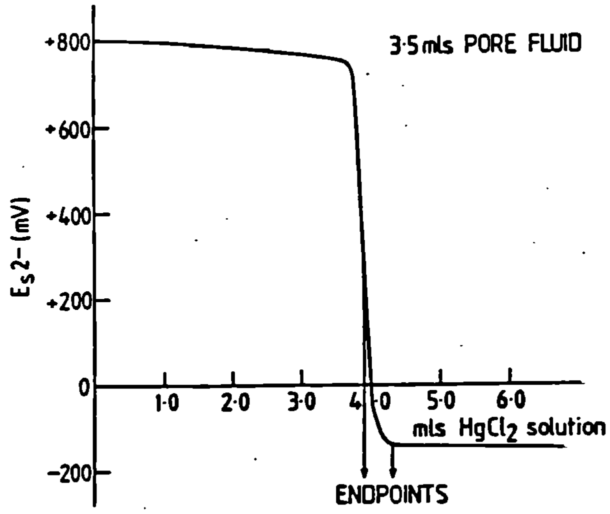


Fig. 4. Anhydrous compositions of representative Na_2O-CaO-SiO_2-H_2O gels aged up to 182 days.



: Titration of 80d. old 85% BFS-15%OPC pore fluid with 10^{-2}M $HgCl_2$.

$$[\text{Tot } S^{2-}] = \frac{3.9 \text{ mls}}{3.5 \text{ mls}} \times 0.01\text{M}$$
$$= 1.11 \times 10^{-2}\text{M, or 360 ppm.}$$
$$[SO_3^{2-} + S_2O_3^{2-}] = \frac{0.4 \text{ mls}}{3.5\text{mls}} \times 0.01\text{M} \times 2$$
$$= 2.29 \times 10^{-3}\text{M.}$$

Fig. 5. Typical titration curve for aqueous sulphide determination.

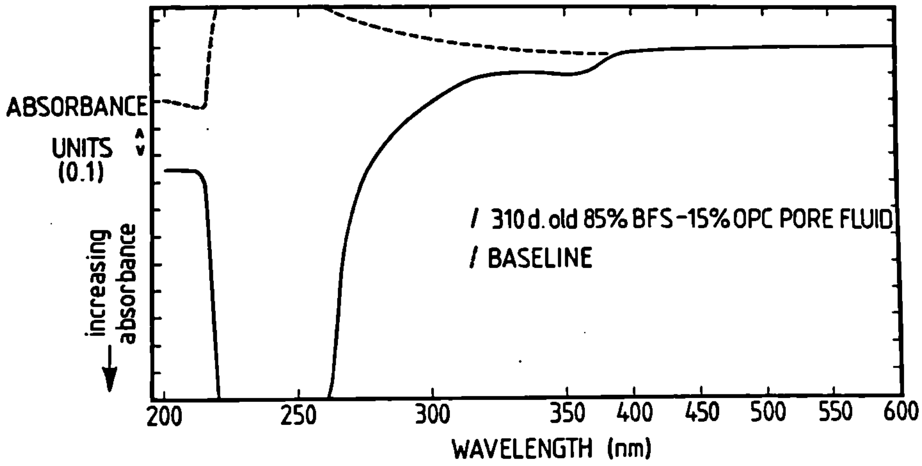


Fig. 6

UV-vis spectrum showing S^{2-} and polysulphide absorptions.

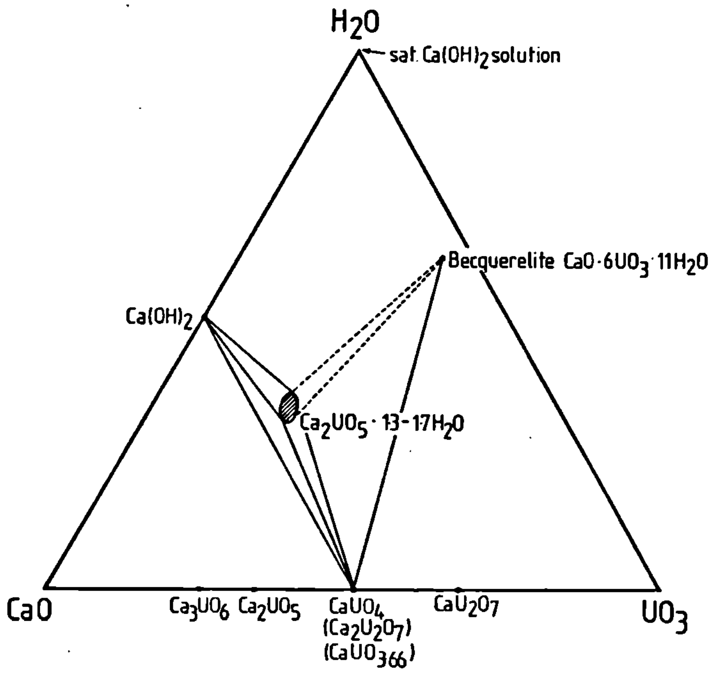


Fig. 7.

Phases observed in the $CaO-UO_3-H_2O$ system.

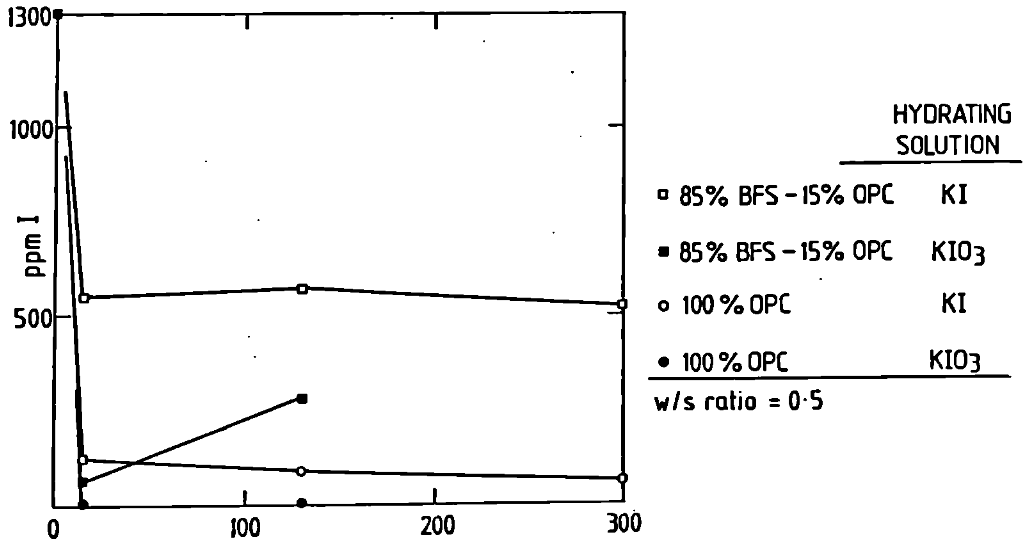


Fig. 8. Sorption of I^- and IO_3^- in cement and slag-cement pastes.

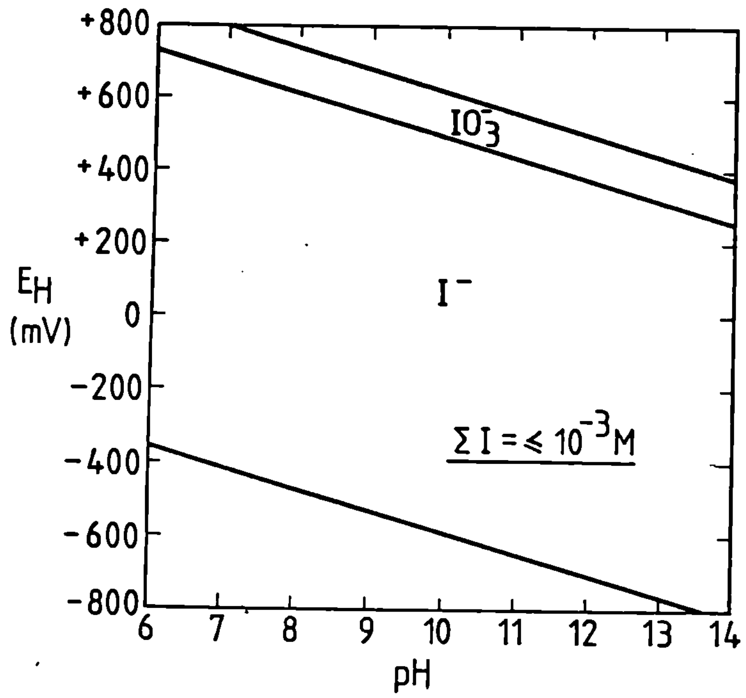


Fig. 9

Pourbaix diagram for iodine.

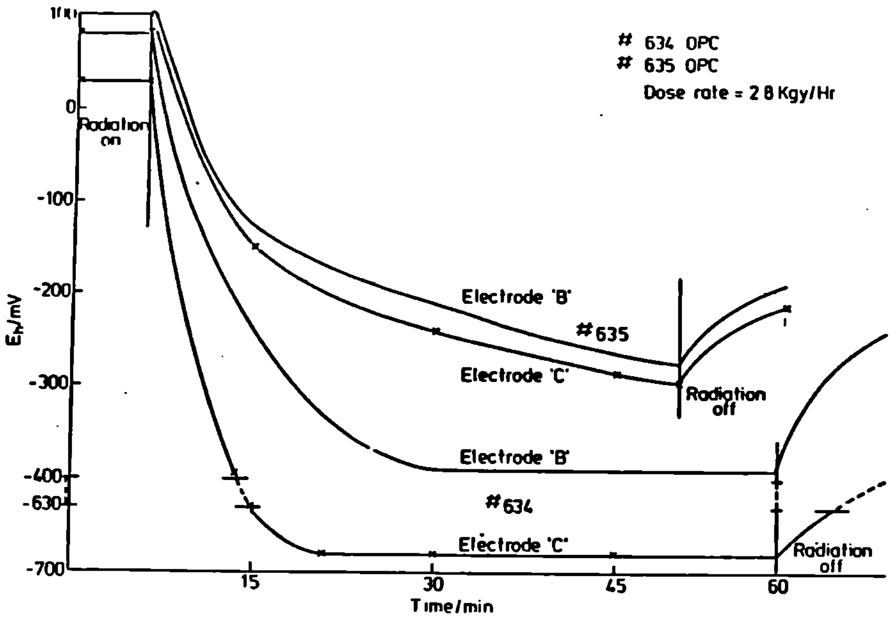


Fig. 10. E_h variations with irradiation does for OPC pastes.

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

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

A. OBJECTIVES AND SCOPE

The factors and mechanisms which govern the elution of certain ions from solidified low and medium level radioactive wastes in contact with water require further elucidation. Here, we study experimentally the kinetics of (i) leaching of Cs^+ and Sr^{++} from solids simulating concentrates embedded in cement, and (ii) leaching from model systems consisting of a polymer (cellulose acetate or an epoxy resin)and a soluble or insoluble salt. The development of theoretical modelling of the kinetics of ion release is also envisaged.

The main ultimate objective of this project is to provide the fundamental knowledge necessary for the sound evaluation of the hazard of long-term environmental radioactive pollution (via natural waters) from waste disposal sites.

B. WORK PROGRAM

B.1 Cement

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

B.2 Polymer

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

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

The study of leaching kinetics of inactive Cs^+ embedded in cement in the form of Cs_2SO_4, as well as the determination of the distribution of Cs in the relevant samples at various stages of the elution process and comparison with theoretical Fickian concentration profiles, were continued. Similar elution studies with specimens containing Cs-137, minor quantities of $CsNO_3$ as carrier and $NaNO_3$ were begun. In order to study the effect of atmospheric CO_2 on the elution of Sr^{++} in relation to the Sr content four series of specimens were prepared.

The elution of $CaSO_4$ and $SrSO_4$ embedded in polymer produced by hydrolysis of cellulose acetate was studied and preliminary experiments for the study of leaching of NaCl and $SrSO_4$ embedded in epoxy resin were begun.

The leaching behavior predicted by the theoretical model previously developed to describe the elution of soluble salts from a hydrophobic polymer, was studied by means of model calculations.

The WORK PROGRAM is progressing normally except item B.1(v) which started with some delay.

Progress and Results

1. Studies with cemented specimens (B.1)

The leaching experiments at 30° and 70°C of the three series of cylindrical cement specimens previously prepared /1/ of height $\ell \simeq 4$ cm (Series A at 30° and B at 70°C) or $\ell \simeq 1.2$ cm (Series C at 30°C) and diameter ∿4 cm containing inactive Cs_2SO_4 ∿3.4% by wt were continued. A new series of samples of the same form and size as in series A and B containing Cs-137 (∿10 µCi/sample), $CsNO_3$ (0.017% by wt) and $NaNO_3$ (∿8% by wt) was prepared and subjected to leaching at 30°C by stagnant distilled water /2/. The study of the distribution of non-eluted Cs in cement was continued, by slicing (into seven slices) of duplicate specimens of series A, B or D, at appropriate times in the course of leaching, and determining the concentration of Cs in each slice.

Elution curves typical of series A, B, C and D are presented in Fig.1, where the fractional amounts eluted ($\Sigma\alpha_n/A_o$) are plotted on a $\sqrt{t}$ basis. The plots for thick specimens (Series A,D) remain linear. The plots for thinner samples (Series C) curve downwards in keeping with the fact that $\Sigma\alpha_n/A_o > 50\%$ for these specimens /3,4/. At 70°C (Series B), some concave upward curvature can be discerned in the $\Sigma\alpha_n/A_o$ vs $\sqrt{t}$ plots, implying some acceleration of the elution process, perhaps due to pore enlargement and/or early release of Cs located in "gel" regions. The Fickian diffusion coefficients (D) of series A, B and C specimens estimated from the linear parts of the $\sqrt{t}$ plots did not differ significantly from the values derived previously when the leaching tests were less advanced /1/. Series D(Cs-137) specimens yield $D=4.8\text{-}7.4\times10^{-9}$ cm^2s^{-1} i.e. ∿5 times lower than the corresponding values of Series A /2/.

The distribution profiles of non-eluted Cs at different stages of the leaching tests for series B (70°C) are presented in Fig. 2 (where C=measured concentration of Cs in a slice of the specimen located at distance x from the exposed surface and C_o=initial Cs concentration). The experimental results have been fitted by theoretical curves calculated from the appropriate Fick law solution (equations 3.13 and 4.17 of ref. /3/) with D and surface concentration C_1 as indicated. The degree of fit seems reasonable and values of D employed agree with those obtained from the $\sqrt{t}$ plots of amounts eluted provided that the latter are corrected for the value of C_1/C_0 in order to take into account the portion of non readily eluted Cs.

Four series of cement samples (diameter ≃4 cm and height ≃4 cm) each containing ∿20 μCi Sr-90 (as $Sr(NO_3)_2$) and 8% by wt of $NaNO_3$ (Series E,F) or ∿20 μCi of Sr-90 (as $Sr(NO_3)_2$), 0.15% by wt of $Sr(NO_3)_2$ and 8% by wt of $NaNO_3$ (Series G,H) were prepared under full (Series E,G) or minimum (Series F,H) exposure to atmospheric CO_2 and will be subjected to leaching at 30°C.

2. Salt-Polymer Systems (B.2(i),B.2(iii))

Cellulose films of thickness ∿300 μm and area 10 cm^2 containing ca. 10%, 25% or 40% by vol. of $CaSO_4$ or $SrSO_4$ were obtained by hydrolysing the corresponding salt-loaded cellulose acetate films /4/. Leaching tests were performed by agitating the sample in frequently renewed water at 25°C. The elution curves follow a $\sqrt{t}$ law in conformity with the Higuchi equations /4/, with diffusion coefficient or permeability much higher than that of the corresponding cellulose acetate films, in keeping with the higher amount of imbibed water in cellulose.

Elution tests of NaCl or $SrSO_4$ embedded in epoxy resin (Ciba-Geigy Araldite LY554 resin mixed with Hardener HY554 in the ratio 100:20 by weight cured at room temperature)have been started. The samples were in the form of discs of thickness ℓ≃0.7 cm and diameter ∿5 cm (with only one flat surface exposed to eluant), containing 12%, 25% or 40% of salt by volume, and were subjected to leaching by stagnant distilled water at 30°C. The relevant elution curves, presented in Fig. 3 are linear vs $\sqrt{t}$ as far as they go at present. The percentage amounts eluted are much lower, and depend on A_o more markedly, in the case of the sparingly soluble salt ($SrSO_4$). In all these respects, the elution behaviour observed here is generally similar to that exhibited by cellulose acetate and cellulose specimens /2,4/.

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

The effect of the most important parameters of the model previously developed /1/ was studied by means of model computations. In particular, we investigated the form of the elution curve as a function of (i) the relative water and salt diffusion rates, (ii) the maximum value of water content in the presence of salts and (iii) the salt load.

References

/1/ AMARANTOS, S.G., PAPADOKOSTAKI, K.G. and PETROPOULOS, J.H., Annual Report 1986, GREEK AEC-EEC Contract No. FI1W/0026/00 (February, 1987). Also EUR 11354EN Vol. 1.

/2/ AMARANTOS, S.G., PAPADOKOSTAKI, K.G. and PETROPOULOS, J.H., Intermediate Report: January-June 1987, GREEK AEC-EEC Contract No. FI1W/0026/00 (August, 1987).

/3/ CRANK, J., The Mathematics of Diffusion, Chap. 3 and 4, 2nd Ed., Clarendon Press, Oxford (1975).

/4/ POTTIER, P.E. and GLASSER, F.P., Editors, Final Report - 2nd CEC Program 1980-84, pp. 149-153, EUR 10579 EN (1986).

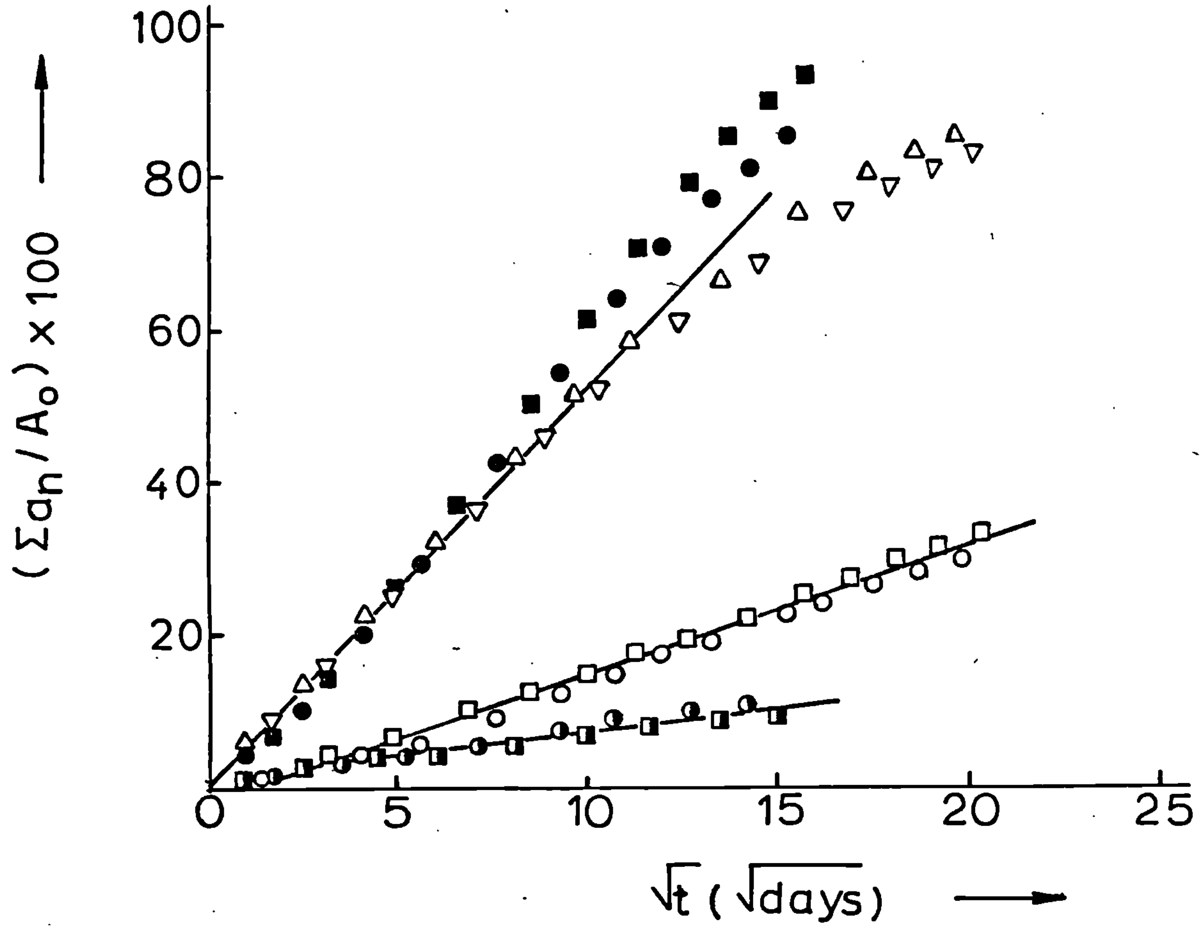


Figure 1. Elution curves of Cs from duplicate cemented specimens containing inactive Cs_2SO_4 (3.4% wt) at 70° (Series B; ●, ■) or 30°C (Series A,C; o, □ , ∇, Δ) or Cs-137 (10 μCi/sample), $CsNO_3$ (0.017% wt) and $NaNO_3$ (8% wt) at 30°C (Series D; ◐, ◧). Sample thicknesses: 1.2 cm (Series C; ∇,Δ) or 4.0 cm (Series A,B,D; o,□ , ●,■ , ◐,◧).

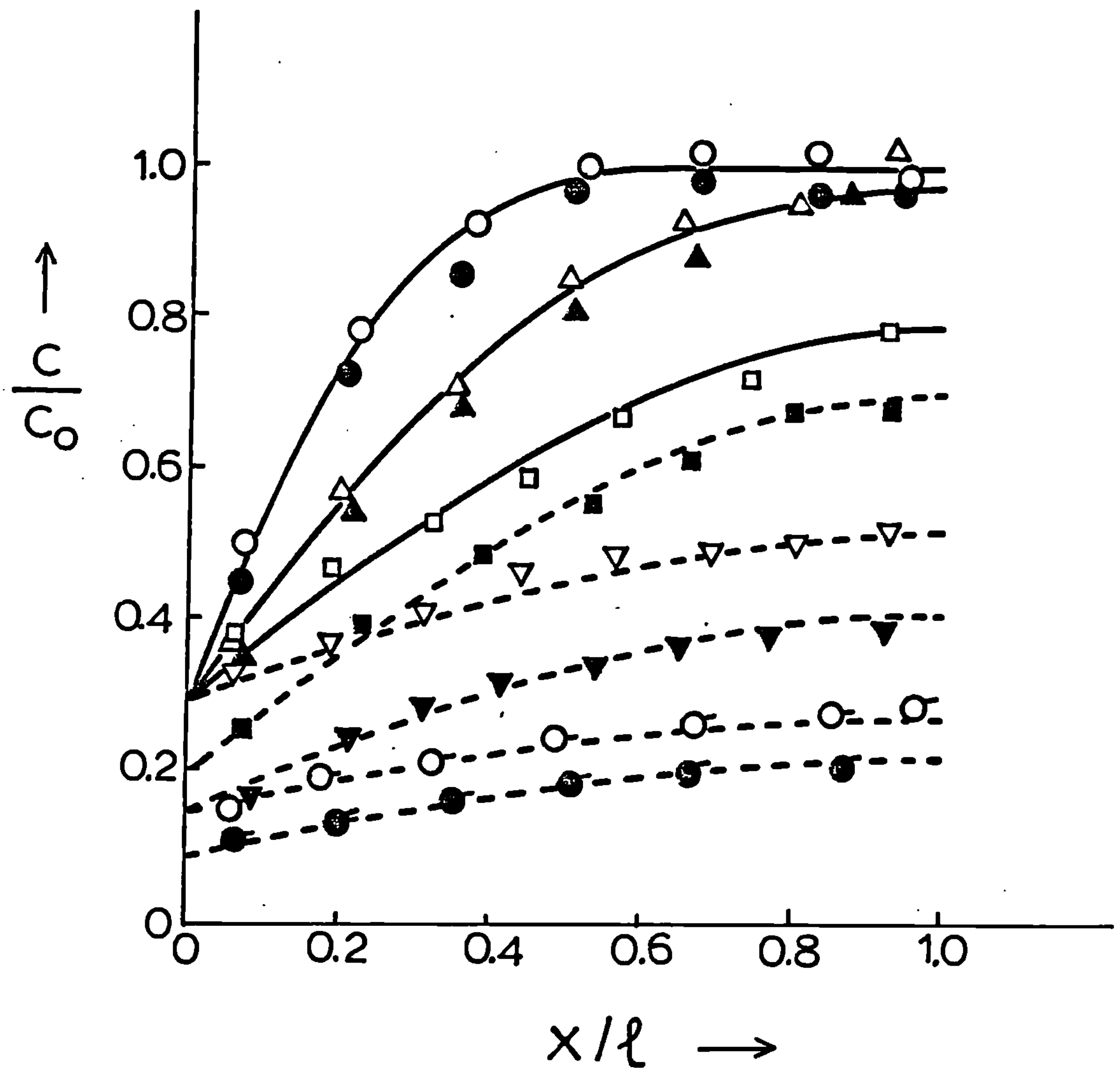


Figure 2. Distribution of Cs in cement samples after 6 (o,•), 21 (Δ,▲), 57 (□,■), 114 (∇,▼) or 174 (σ,●) days of elution at 70°C. Amounts eluted (%): 10.2 (o), 11.5 (•), 22.1 (Δ), 24.0 (▲), 37.1 (□), 45.0 (■), 54.5 (∇), 65.0 (▼), 76.0 (σ) or 82.0 (●). The theoretical concentration profiles correspond to $D=7.5\times10^{-7}$ cm^2s^{-1} (——) or 8.9×10^{-7} cm^2s^{-1} (---) and $C_1/C_0=0.30$ (o,•,Δ,▲,□,∇), 0.20 (■), 0.15 (▼,σ), 0.09 (●).

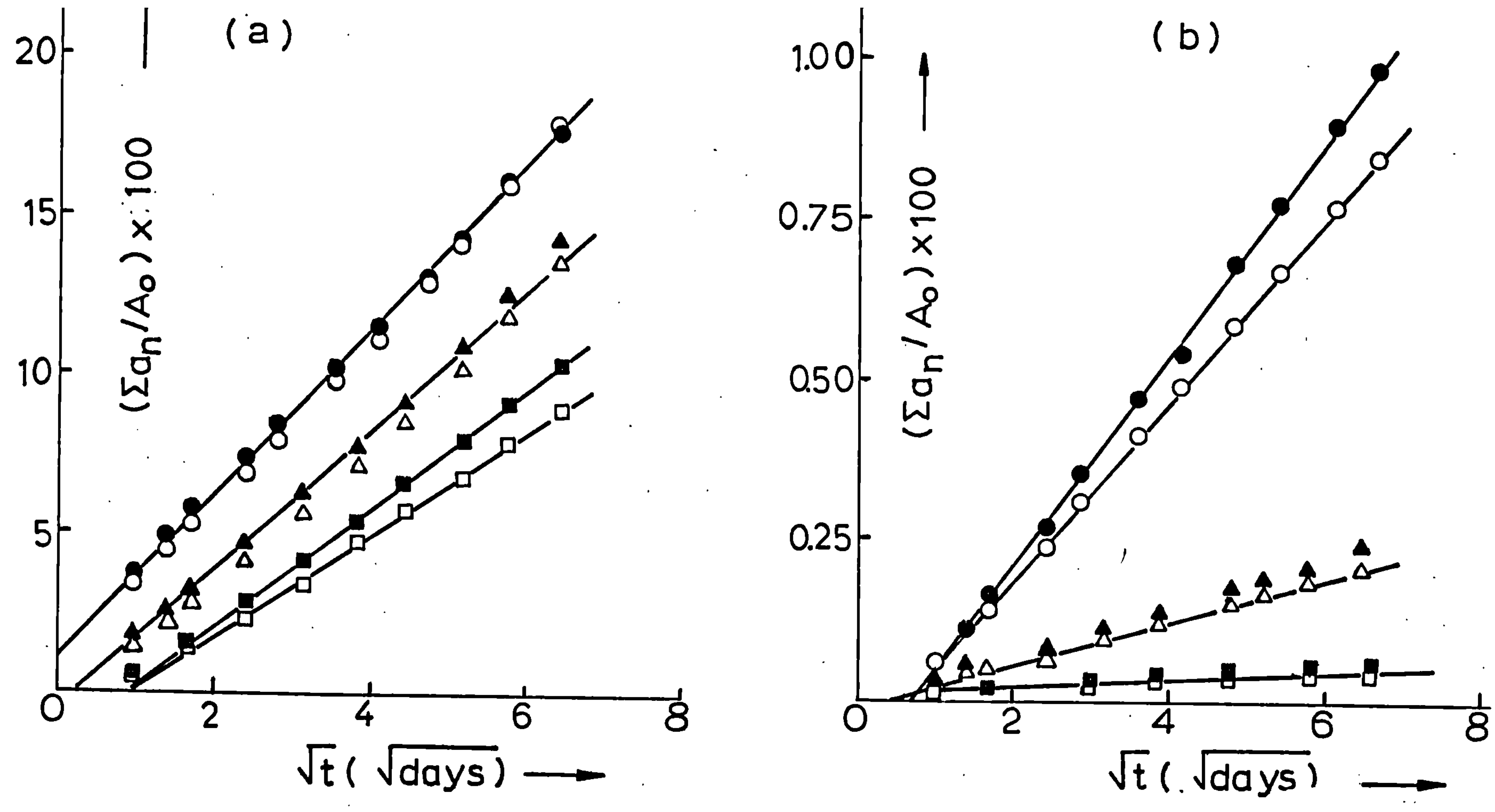


Figure 3. Elution curves at 30°C of (a) NaCl or (b) $SrSO_4$ from duplicate specimens (∿7 mm thick) of salt-loaded epoxy resin. Salt content (% vol): 12 (□, ■), 25 (Δ,▲), 40 (o,●).

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

Contractor: Risø National Laboratory, Denmark.
Contract No: FI 1W-0089-DK (B)
Working Period: July 1986 to December 1987 extended to December 1989.
Project Leader: K. Brodersen.

A. Objectives and Scope

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

One topic is the diffusive transport from waste through barriers of concrete or clay as influenced by internal or external conditions. The composition of water in equilibrium with various types of waste and concrete is influencing concrete corrosion and the possibility of crack-healing in concrete barriers. The influence of pore type distribution on diffusive transport through concrete is investigated. SANS-measurements are used in an attempt to follow the structure of degrading concrete. Consultations with Harwell have been held in this connection.

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

B. Work Program

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

C. Progress of work and obtained results

State of advancement

The work during the 2. and 3. half-year of the contract has covered most of the topics originally proposed. However, repeated or new experiments are needed i some areas to reach final conclusions. This will be done under the extension of the contract.

Progress and Results

1. Diffusive transport in porous barriers (B.1.)

The release of ^{134}Cs and ^{85}Sr from samples of cemented sodium nitrate (simulated RMA8) through low-quality barriers of concrete or kaolin were followed for 16 systems representing various conditions. It was found that Cs-release was enhanced by increased Na^+ and K^+ concentrations, by the presence of complexing agents and, somewhat surprising, by reducing conditions. The tendency to Sr-release is lower than for Cs and is strongly decreased in carbonate-containing water. The presence of slowly corroding iron has no immediate effect on the releases. Simulation of the experiments using the COLUMN code is delayed. A suplementary investigation of equilibrium extraction of small pieces of the material indicates that only about 20 % of the ^{85}Sr can be easily extracted.

2. Leaching compared with diffusion through slabs (B.2.)

The transport of ^{134}Cs and tritiated water in leaching of samles of 5 different types of concrete have been compared with the transport through slabs of the same materials mounted in diffusion cells.

It was found that the effective diffusion coefficients describing the leaching results increased with increasing water/cement ratio in the concrete. The same is the case for the permeability coefficient obtained from the flux through the slabs, while the diffusion coefficients obtained from the time-lags were of the same order of magnitude and probably determined by a few micro-defects in the slabs. The permeability was especially low for the sample containing silica-fume. The results are in general argeement with the theory based on pore structures formulated in /1/.

3. Deposition and degradation reactions in concrete.

A method for demonstrating the possibility of crack healing in samples of damaged concrete is under development, and decreasing hydraulic conductivities have been obtained as indication for crack healing. However, the results so far are mainly within the area of methodolody development.

A series of experiments has been conducted where two thin plates cast from (activated) cement paste of various types were equilibrated in contact with a small amount of water. Transport of Ca from plate to plate and deposition of new material was demonstrated. This is indirect evidence for crack healing mechanisms under suitable conditions and is also of interest in connection with leaching and degradation of concrete.

A method using small angle neutron scattering (SANS) to study the structure of thin plates of cement paste degraded by leaching, or in other ways, has been developed. The results on fresh samples are in agreement with Harwell studies on hardening cement paste /2/. Preliminary results on highly degraded cement paste indicate surprisingly high degrees of retention of the micro-structure even after removal of most of the calcium.

4. Cemented ion-exchange resins. (B.6.)

In absence of specifications for RMA3, samples of 8 different compositons of mixed-bed ion-exchange resin solidified in cement have been prepared. IX-contents from 10 to 12 % were included while the water/cement ratio (at 45% water in the resin beads) varied between 0.22 and 0.39.

The samples were tested for leaching of macro-components, water uptake and volume stability. The swelling was in general below 0.5 vol % after 200 days in water except for the sample with highest IX-content and w/c ratio, where the swelling reached 1.2 %. The samples appeared to be practicaly undamaged at the end of the water exposure, but after a period with air drying and renewed water immersion many of the samples failed completely. Ony two with silica-fume additive and two with low IX-content and low w/c ratio are still intact. The experience illustrates that cyclic testing is important for the evaluation of the volume stability.

5. Hygroscopic properties of cemented or bituminized waste (B.7.)

Water uptake in waste materials containing soluble salts, e.g. RMA8 or RMA9, occurs not only in contact with liquid water, but also from high humidity air. The phenomenon has been demonstrated for samples of cemented sodium nitrate as well as inactive Eurobitumen. The water uptake is associated with accumulation of strong salt solutions on the sample surface. The phenomenon may have safety implications under certain storage or disposal conditions.

6. Water diffusion in bitumen and swelling due to water uptake (B.8.,B.9.)

Diffusion of ^{134}Cs and tritiated water trough membranes made from bitumen containing precipitation sludges is under investigation. Thin membranes (~0.5 mm) are difficult to make without defects. Only preliminary results are available for thicker ones (~2 mm).

Unrestricted swelling and Na^+-leaching fra samples of inactive Eurobitumen exposed to water has been measured and was found to be considerably less than for active samples investigated at Mol /3/.

Swelling forces developing due to water uptake in a confined sample of the inactive Eurobitumen are followed and has after 170 days reached about 1 bar. The pressure is increasing slowly, but nearly linearily with time.

7. Microbial degradation. (B.10.)

An experiment with microbial degradation of ^{134}Cs containing nickel ferrocyanide precipitation sludge in presence of bitumen may indicate somewhat enhanced release of Cs. However, simultaneous contact with high pH water, eg. from equilibration with concrete, appears to be more important. Futher experiments are planned.

8. Ageing of bituminized materials (B.11.)

The flow properties of some 3.5 years old samles of bituminized ion exchange resin or sodium nitrate have been remeasured after undisturbed storage af 20°C. The viscosities appears to be increasing nearly proportionally with the square root of time. The viscocity i increased about a factor 4 in 3.5 years for all the materials..

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/1/ BRODERSEN, K. CEC report EUR 10821 EN (1986).

/2/ ALLEN, A.J. et al. Harwell report AERE R 12187 (1986).

/3/ POTTIER, P.E., GLASSER, F.P. ed: CEC Final report 2nd Program EUR 10579 EN (1986) pp 92-95.

Colloids Related to Low Level and Intermediate Level Waste

Contractor: UKAEA, Harwell, UK
Contract N°: F11W/0090-1
Working Period: January 1987 - December 1987
Project Leader: J.D.F. Ramsay

A. OBJECTIVES AND SCOPE

There is an increasing interest in the potential role of colloids in radionuclide migration processes /1,4/. The mechanisms of release of radionuclides from cement are of importance in predicting the long-term behaviour of low and intermediate level waste and here the near-field effects of colloids are very poorly understood.

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

This investigation is seen as providing basic information on cement leaching mechanisms and reference data for the transport modelling of colloids in the near-field environment. It is further anticipated that this contract will provide background for a second phase of experimental investigation of colloid migration and sorption behaviour which will have a direct application for transport modelling.

B. WORK PROGRAMME

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

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In our previous report /2/ preliminary experimental investigations of colloids and fine particulates in leachates from pure OPC cement were described using a combination of ultrafiltration and scanning electron microscopy together with light scattering techniques and it was concluded that a process of particle growth leading to the formation of colloidal aggregates occurred.

These investigations have been extended to include other OPC formulations containing BFS and PFA. Detailed examinations of filtered (nucleopore) particulates using SEM/EDAX techniques have been made. The effects of leaching temperature and prolonged contact time on the elemental composition and morphology of particulates have been established. The chemical composition of particulate and liquid phase components has been determined by inductively coupled plasma emission spectrometry (ICP-OES). Highly sensitive mass spectrometry (ICP-MS) has been used to determine the association of spiked tracers (Co, Ni, Ce, Eu, Th, U) with released particulates.

The effects of near-field chemical interactions on colloids which may arise in repository environments have also been investigated by photon correlation spectroscopy and electrophoretic mobility measurements. Measurements conducted with mica, montmorillonite, feldspar and silica colloids show that the high pH and Ca^{2+} concentration may have a dominant effect on colloid structure and stability.

Progress and results

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

1.1 SEM/EDAX investigations

The application of scanning electron microscopy combined with energy dispersive X-ray analysis to determine the elemental composition of particulates in leachates which were subsequently retained on ultrafilters having different nominal pore sizes was described in our previous report /2/. This technique has been applied further to obtain information on leachates derived from:

(a) pure OPC at 60°C
(b) OPC/BFS
(c) OPC/PFA mixtures at ambient temperature.

In (a) spherical particle clusters were a prominent feature, where the abundance of Si and Ca had a similar mole ratio. Although OPC/BFS yielded a greater heterogeneity both in particle morphology and elemental composition, Si was particularly abundant. In (c) irregular clusters were common; the elemental composition was more heterogeneous, Ca and Si being generally noted together with Fe and Al.

1.2 Chemical analysis of leachates by Inductively Coupled Plasma Emission Spectrometry (ICP-OES)

Over prolonged periods it has been observed that although undisturbed leachates remain clear to the unaided eye, finely divided particulate solids having a fluffy white appearance are formed, often as deposits adhering to the walls of the leaching vessel. The formation of such colloidal particulates is more marked at elevated leaching temperatures (60°C, 90°C). Procedures for separating the particulate solid fraction (>0.2 μm) in leachates from the liquid phase have been developed. An extensive survey of the elemental composition of both solid particulate and liquid fractions in a range of leachates has been carried out using ICP-OES analysis. This has included investigations of the effects of:

(a) leaching time
(b) leaching temperature
(c) cement composition (pure OPC; OPC/BFS; OPC/PFA).

A more detailed description and interpretation of our findings has already been reported /3/. However in general we note that on prolonged leaching and especially at higher temperatures there is a marked enhancement in the levels of Al, Si, S and Fe; concentrations of alkali and alkaline earth elements (Na, Mg, K, Sr, Ba) are far less influenced. This feature, which is illustrated for OPC leached at 60°C in Figure 1, can be ascribed to the formation of solid particulate phases by processes of nucleation and growth in solution. From more detailed interpretation of ICP-OES data, which is supported by X-ray diffraction analysis, it has been shown that a dominant component of the colloid particulate fraction is an amorphous calcium silicate hydrate phase. In leachates obtained from OPC mixtures other solid phases are present whose structure and composition is more complicated and as yet ill defined.

2. <u>Chemical analysis of leachates by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (B.3.)</u>

The release of spiked tracer elements simulating radionuclides (Co, Ni, Ce, Eu, Th, U) of potential importance in low and intermediate level waste has also been measured using the highly sensitive ICP-MS technique. Here nuclide levels down to $\sim 10^{-10}$ mol dm^{-3} have been determined in leachates subjected to different solid/liquid separation procedures. Total levels of Ce, Th, U and Eu leached from cement at higher temperature are markedly enhanced - by factors of 10^2 to 10^4. In contrast there is a much smaller effect on the release of Co and Ni (see Figure 2). This enhanced release occurs particularly with polyvalent elements which have a low limiting solubility and are readily hydrolysed in aqueous media to form colloids and hydroxide precipitates.

A clear correlation exists between the enhanced leachate levels of the spiked elements and those of certain elements which are contained in cement (Al, Si, S and Fe). This suggests that the polyvalent spiked elements may be released in association with particulate phases, particularly amorphous calcium silicate hydrate, formed in leachates /3,5/.

3. <u>Characterisation of colloids in repository environments (B.2)</u>

The effect of the near-field aqueous environment of cement on the behaviour of silica and clay colloids has been investigated by photon correlation spectroscopy and electrophoretic light scattering. These inorganic colloids have included silica (diameter ~100 nm), montmorillonite, kaolinite and feldspar and are typical of those likely to occur in natural ground waters or arise from bentonite backfill. The evolution of the near field has been simulated by progressively increasing the concentration of calcium hydroxide ($\sim 10^{-5}$ to $\sim 10^{-3}$ mol dm^{-3}). In general it is found that these inorganic colloids are destablished at Ca^{2+} concentrations exceeding 10^{-3} mol dm^{-3}. This effect can be ascribed to a progressive loss in negative surface charge resulting from sorption of Ca^{2+} ions from solution. This effect is confirmed by measurements of surface charge made with silica colloids in a Ca^{2+} concentration range from ~5 x 10^{-5} to > 2 x 10^{-4} mol dm^{-3}.

List of publications

/1/ RAMSAY, J.D.F., The role of colloids in the release of radionuclides from nuclear waste, AERE-R 11823 (1985)

/2/ RAMSAY, J.D.F. and AVERY, R.G., Colloids related to low level and intermediate level waste, AERE-R 12538 (1987)

/3/ RAMSAY, J.D.F., RUSSELL, P.J. and AVERY, R.G., Colloids related to low level and intermediate level waste - Progress Report 1st January - 30th June 1987, AERE-R 12763 (1987)

/4/ RAMSAY, J.D.F. The role of colloids in the migration of radionuclides from nuclear waste, Proc. of Conf. "Migration 87", Munich, 14-18 September 1987. To be published in Radiochimica Acta

/5/ RAMSAY, J.D.F., AVERY, R.G. and RUSSELL, P.J. Physical characteristics and sorption behaviour of colloids generated from cementitious systems, Proc. of Conf. "Migration '87", Munich, 14-18 September 1987. To be published in Radiochimica Acta

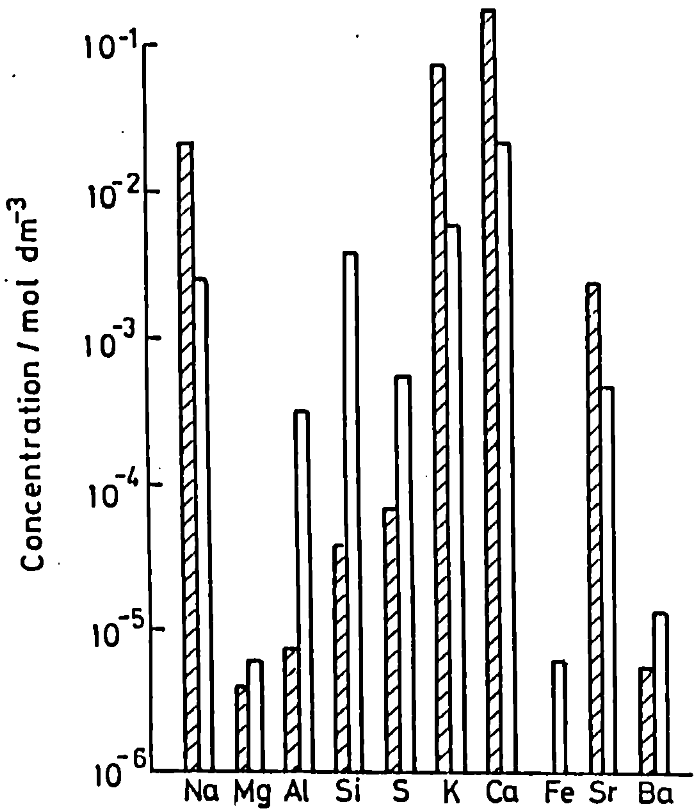

FIGURE 1. CONCENTRATIONS OF ELEMENTS LEACHED FROM OPC AT ~25°C AND 60°C AFTER ~38 DAYS AS DETERMINED BY ICP- OES

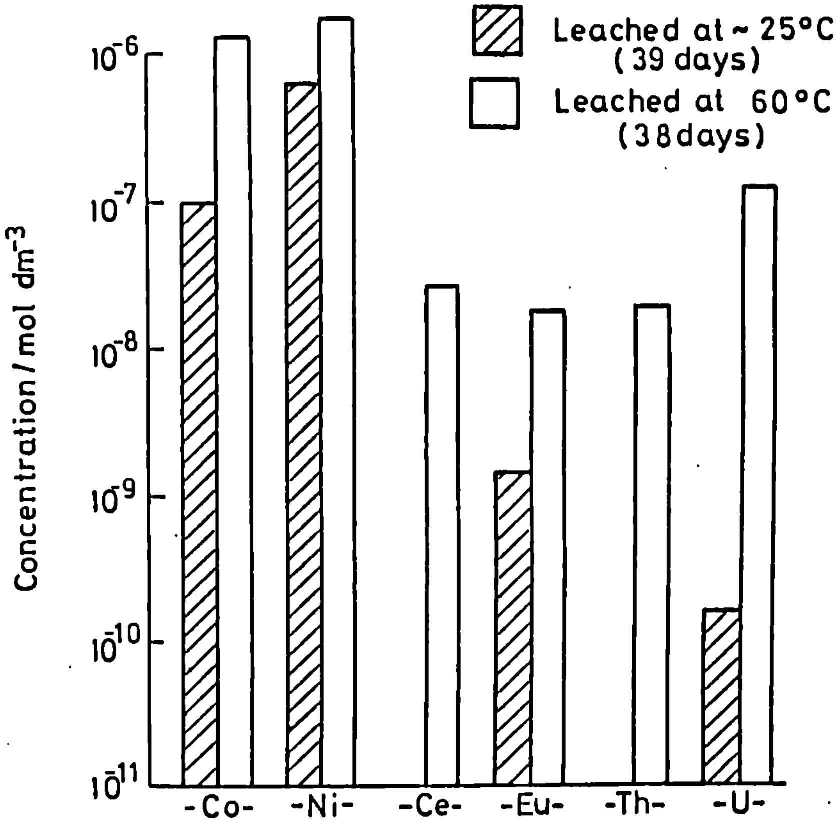

FIGURE 2. CONCENTRATIONS OF SPIKE ELEMENTS LEACHED FROM OPC AT ~25°C AND 60°C AFTER ~38 DAYS AS DETERMINED BY ICP-MS

Near-Field Modelling in Cement Environments

Contractor: Harwell Laboratory, U.K.

Contract No.: FI1W/0090/2

Working Period: January 1987 - December 1987

Project Leader: Dr. P.W. Tasker

A. Objectives and Scope

The primary aim of this work is to develop research models which examine in detail the approximations and assumptions implicit in the assessment models that are used to analyse repository behaviour. The assessments models are necessarily relatively simple. They must make assumptions in many areas including the time evolution of the repository chemistry, the influence of corrosion products on local chemistry etc. The research models use data from experimental programmes to study these points in detail.

The near field has a complex chemistry which determines the solubility of radionuclides. This chemical environment changes both with time and spatially throughout the near-field region. The engineered barriers are very different chemically to the surrounding geology and so will not only degrade with time but may also cause a front of perturbed chemistry to progress into the surrounding regions. All these points involve the space and time evolution of chemistry but where they have been considered previously, the coupling between transport processes and chemistry have largely been neglected. Yet these processes underlie most of the assumptions in the simple near-field models. The conditions of primary interest to our programme concern the waste contained in a steel canister and buried in a concrete environment.

B. Work Programme

B.1 Development of the CHEQMATE computer code which couples chemical equilibria (via. the PHREEQE code/1/) with ionic migration.

B.2 Incorporation of ionic advection in flowing systems into the CHEQMATE code.

B.3 Extension of both the chemical and migration parts of CHEQMATE to regimes of concentrated solutions.

B.4 Application of CHEQMATE to coupled chemistry and transport problems relevant to the near field of a repository, for example the space and time evolution of the oxidation potential in the backfill pore water and the influence of the introduced chemical conditions within a repository on the surrounding geology.

C. Progress of Work and Obtained Results
State of Advancement

The CHEQMATE code has been extended to increase the range of techniques available for coupled chemical/migration models of the near field of a repository (B.1). Particular improvements include the addition of the facility to model migration of ionic species through a series of media with different transport properties (i.e. porosities and diffusion coefficients) and also a method of simulating dilution effects in a real repository, by modelling migration through a spherical geometry. The code has also been extended to include a constant groundwater flow in one dimension (in the rectangular geometry) (B.2). The extended versions of CHEQMATE have been used in the first stages of a model of the evolution of the groundwater chemistry in a host rock under the influence of an ingress of alkaline pore water from a cement backfill (B.4). Some preliminary investigations have been made into extension of the chemical equilibria part of the code to model concentrated solutions. (B.3).

Progress and Results

1. Development of the CHEQMATE code (B.1)

The original version of the computer code CHEQMATE (CHemical EQuilibrium with Migration And Transport Equations) combined chemical equilibria (via. the PHREEQE code/1/) with one-dimensional ionic diffusion and electromigration through either a stationary fluid or a saturated porous medium. The code has been extended to include the facility to model migration across interfaces between porous media of different physical properties, such as the boundary between the backfill and host rock. It has also been modified to allow a more realistic simulation of the dilution effects associated with a full three-dimensional geometry, by modelling ionic migration through a spherical system.

2. Addition of Advection to the CHEQMATE code (B.2)

As a first stage, a constant pore water flow has been added to the version of CHEQMATE in a rectangular geometry. This has involved adding ionic advection and dispersion terms to the transport equations.

3. Extension of CHEQMATE to Regimes of Concentrated Solutions (B.3)

Some preliminary studies have been carried out to assess the range of techniques within the chemical equilibration part of the code (i.e. the PHREEQE program) to correct activity coefficients for ionic strength. These correction methods are only strictly valid in solutions of strength less than 0.5M, but some can give reasonable approximations at much higher concentrations. Some alternative methods which may provide better representations of concentrated solutions are being investigated.

4. Investigation of the Evolution of the Groundwater Chemistry Around a Repository (B.4)

An important aspect in an assessment of the rate of release of nuclides from a repository is the perturbation to the groundwater chemistry in the host rock caused by the presence of the engineered barriers. In the U.K., current plans for a low- or intermediate-level waste repository comprise a deep repository with a largely cementitious backfill material. The equilibrium water composition within the backfill will therefore be highly alkaline and significantly different to the surrounding groundwater chemistry. Ionic migration processes such as diffusion will tend to level out such variations over a period of time and lead to the progression of a plume of calcium hydroxide from the edges of the repository into the pores of the surrounding rock. The progress of this plume, and later of any escaping radionuclides, will also be influenced by any flow of groundwater through the backfill and rock. An ingress of alkalinity into the host rock may result in important changes to the chemical and physical properties; the cation-exchange capacity within the mineral structure may be affected which will influence the sorption characteristics of the nuclides. Also the permeability and porosity of the rock may be changed which could affect the migration of nuclides out of the repository.

The first stage of a model of the evolution of the groundwater within a clay rock surrounding a repository has been completed. Although the site of a repository in the U.K. has not as yet been decided, many rock formations contain substantial amounts of clay minerals, so this preliminary model may have considerable relevance to a repository assessment. However, the model is sufficiently flexible that other rock types may be considered if a good thermodynamic description of the composition is available. The model uses the extended versions of the CHEQMATE code and aims to predict the evolution of the porewater composition and precipitates in the clay by modelling a section of repository extending across the concrete/clay interface. The thermodynamic model of clay comprises an idealised clay mineral equilibrated with calcite and water, and models the buffering capacity in terms of sequential substitution of cations at the clay surface by calcium ions. As a first approximation, it is assumed that calcium hydroxide equilibrated with water provides a reasonable simulation of the concrete pore water as far as certain ionic strengths are concerned. In the model, we assume a set of 'base case' parameters which define a realistic set of physical and chemical conditions in the system and choose a repository section (extending across the concrete/clay interface) which spans a physical distance of 6m and run the model up to a time of 1000 years. Two base case runs are considered; one with advection of ions in a groundwater flow and one with no flow. The sensitivity of the model's predictions to physical and chemical parameters describing the system are considered. In particular, we have investigated the effect of the buffering action of the clay minerals, the speed of the groundwater flow through the repository and the geometry of the model on the scale of perturbation to the natural chemistry. We have also considered the effect of dissolved carbon dioxide in the pore water on the amounts of precipitates in the clay pores.

The results from this preliminary model suggest that, for a typical set of physical and chemical conditions, the influence of the concrete backfill on the natural pore water chemistry in clay will be significant although the natural buffering action of the clay does retard the progression of this perturbation. The model predicts that a plume of high pH will extend about 3m into the clay after a 1000 years. This may have important consequences to nuclide release rates through factors such as their solubilities, sorption properties etc. The model will help ensure that sorption studies are done under appropriate chemical conditions. The sensitivity studies indicate that the rectangular geometry in the base case model yields an extreme case in terms of the maximum depth of perturbed chemistry in the host rock; dilution effects may be significant depending on the size of the repository. The preliminary model does not indicate any significant beneficial changes to the transport properties within the clay through pore blocking by precipitates over timescales of 1000 years.

List of Publications

1. Sharland, S.M., Tweed, C.J. and Tasker, P.W., 10th International Symposium on the Scientific Basis for Nuclear Waste Management, Boston, MA, 1st-4th December 1986. Proceedings, pp. 683 (American Materials Research Society, Editors J. Bates and W. Seefeldt).

References

/1/ Parkhurst, D.L., Thorstenson, D.C. and Plummer, L.N., U.S. Geological Survey, Water Resources Investigations, 80-98 (1985).

THE INFLUENCE OF ORGANIC COMPLEXING AGENTS UPON THE MOBILIZATION AND MIGRATION OF RADIONUCLIDES FROM ILW CONTAINED IN CEMENT AND BITUMEN UNDER NEAR-FIELD CONDITIONS FOR A REPOSITORY IN A SALT DOME

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

A. Objectives and scope

The chemical behaviour of elements in solutions depends very much on the form of their complexes in these systems. The interest has been focussed on the change of the solubility and of the migration and sorption behaviour of the elements influenced by various organic complexing agents.

In the past the main interest was put upon the influence of natural complexing agents being present in a salt dome. Now the emphasis has been laid upon artificial complexing agents originating from industrial waste which may cause a definite change in the chemical behaviour of the elements under consideration. Therefore further investigations are urgently needed to cope with these problems.

Especially the solubilities of some elements of high interest, namely iodine, cesium, uranium, neptunium, plutonium and americium, has to be determined under the influence of organic complexing agents as for instance dibutylphosphate (DBP), tributylphosphate (TBP), ethylenediamminetetraacetic acid (EDTA), citrate and oxalate. By adding these special chemical compounds the concentrations for saturation of these elements can be determined in the resulting systems.

On the other hand experiments are performed for leaching the problem elements out of the matrices they have been solidified in.

Moreover the change of the migration and sorption behaviour on matrices typical for depositing ILW in salt domes are to be investigated by use of chromatographic column techniques and batch experiments under the influence of the complexing agents aforementioned.

B. Work Programme

B.1 Source term solubility studies

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

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

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

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

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

B.1.6 Solidification of complexed elements in cement and determination of their leachabilities

B.2 Sorption and migration in the near-field

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

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

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

C. Progress of work and obtained results

State of advancement

Changing the original time table the experiments on the determination of the solubilities of the special elements (B.1.1 and B.1.2) were performed just before the migration experiments started. This decision had to be made with respect to the half life of some tracers used, especially ^{232}U and ^{131}I. On the other hand any radiolysis, which might influence the physical behaviour of the solutions had to be excluded. Until now the solubilities of AgI, $AgIO_3$, $CsNO_3$, $Na_2U_2O_7$ and $Pu(OH)_4$ have been investigated in various saturated salt solutions after contacting cement and bitumen under the influence of complexing organics.

In the case of americium the principal problem may be the high solubility of this element to be expected from the low pH of certain salt solutions, which might result in a lack of ^{241}Am to be available. Therefore the possibility of using other trivalent cations for modelling has been taken into consideration.

The development of suitable analytical methods for radionuclides contained in the leachates of the real waste was finished and the investigation of the leachates started.

The work for topics B.1.5 and B.1.6 has also begun. For this research the elements I, Cs, U, Np and Am were solidified in cement after adding complexing organics.

The work for the topics B.2.ff is under progress as scheduled.

Progress and results

B.1 Solubility studies of the source term

The solubilities of AgI, $AgIO_3$, $CsNO_3$, $Na_2U_2O_7$ and $Pu(OH)_4$ were determined in saturated NaCl solution and in the Q-solution.

After contacting matrices of cement and bitumen the solutions are saturated with the complexing organics.

The relevant pH and Eh values of the resulting solutions are listed up in table I. Since in a waste repository a present cement matrix being guarantees the pH value to be constant in this system the pH is adjusted to the solutions under investigation. The pH values used for these experiments are listed up separately in table I.

The compounds to be investigated are added to the solutions, pretreated with the waste matrices. The systems are stirred for several days at 298 K and the samples are measured after filtration with 450 nm-filters.

The results of the investigation into the solubility of AgI can be seen from table II. The solubility of this compound ranges from $5 \cdot 10^{-5}$ mol·dm^{-3} to $6 \cdot 10^{-4}$ mol·dm^{-3}. Only in the Q-solution saturated with DBP and with the corrosion products of bitumen a higher solubility of $1 \cdot 10^{-2}$ mol·dm^{-3} was found.

The solubilities of $AgIO_3$ in the various systems under investigation are listed up in table III. They are higher than those of AgI and are within the range from $2 \cdot 10^{-3}$ mol·dm^{-3} to $1 \cdot 10^{-2}$ mol·dm^{-3}. If DBP and EDTA are present even higher solubilities ranging from $6 \cdot 10^{-2}$ mol·dm^{-3} to $4 \cdot 10^{-1}$ mol·dm^{-3} will be obtained.

The solubilities of Cs can be seen from table IV. They don't vary very much with the various systems saturated with the complexing organics. In the saturated NaCl solution and in the Q-solution contacted with cement the solubilities range only from 1.6 to 1.9 mol·dm^{-3}. In the Q-solution contacted with bitumen the solubilities are a little bit lower. They range from 1.35 to 1.5 mol·dm^{-3}.

The solubilities of $Na_2U_2O_7$ for the systems under investigation are listed up in table V. In most of the systems the solubilities are within the range of 10^{-5} and 10^{-4} mol·dm^{-3}. Under the influence of complexing citrate and EDTA even higher values can be found.

The solubilities of $Pu(OH)_4$ in the systems to be investigated can be seen from table VI. Also in this case EDTA or citrate make the solubilities increase in comparison to the other organics used.

Until now ultrafiltrations have been performed with solutions saturated with AgI and $CsNO_3$, the results of which are shown in the tables VII and VIII. These results prove that the filtration of solutions with membranes, the pore sizes of which range from 450 nm to 2 nm, does not influence the concentration of the elements under investigation.

In order to examine leachates from real waste in respect to their content of fission products and actinides a suitable analytical method was developed, the flow sheet of which can be seen from figure 1.

Solutions, containing ^{131}I, ^{137}Cs, U, ^{237}Np or ^{241}Am were solidified with Portland 35 F-cement together with TBP, EDTA and citrate. These solidified products were leached with saturated NaCl solutions. In table IX the amounts of nuclides used for modelling and those quantities obtained from the leaching processes are presented. As can be seen the greater amount of the fission products added are leached, whereas the majority of the actinides is fixed to the cement matrix.

B.2 Sorption and migration in the near-field

Migration experiments were performed with solutions, saturated with AgI, $CsNO_3$, $Na_2U_2O_7$ and $Pu(OH)_4$.

The labelled solutions were added in form of a puls of approximately 2 cm^3 to the columns. The column was rinsed with the same solution which did not contain any complexing organic agents. The fillament of the columns consisted of NaCl.

The results obtained from the experiments with the columns containing AgI are presented in table X. The data show, that the overwhelming majority of the I^- passes the column, without being retained.

The results from the column experiments with solutions containing Cesium are registered in table XI. In most of the systems the recovery is 50 % of the Cs originally added.

The migration experiments performed with solutions containing uranium gave the results shown in table XII. Only from those systems, which contained EDTA the recovery was found to be 100%. The recoveries from the other systems investigated uptil now ranges from 0 - 25 %.

The recoveries for plutonium are listed in table XIII. In alkaline NaCl solutions contacted with cement these values are comparitively small. The highest value (20 %) was found for plutonium complexed with oxalate. From the other alkaline systems of the same kind recoveries were obtained ranging from 0 to 4 %. In saturated NaCl solutions and in Q-solutions the recoveries deviate very much from each other. Nevertheless a higher recovery seems to exist for those systems containing DBP, TBP and oxalate.

Experiments for determining the equilibrium of the sorption of various problem elements on NaCl were performed with solutions containing AgI and uranium.

Those solutions used for batch experiments were contacted with cement and bitumen first. After this procedure they were saturated with the organic complexing agents. After separating small and even colloidal particles by filtration the concentration of I^- or uranium was determined in these solutions. Finally solid NaCl was added.

The R_s-values for the sorption of I^- on NaCl are registed in table XIV. All of them are near to 0 $cm^3 \cdot g^{-1}$, that means that the overwhelming amount of the I^- stayed in the solution. In general no material was adsorbed at all or only a very small amount.

In table XV the results from the adsorption experiments with uranium are presented. In most cases the R_s-values are below 1 $cm^3 \cdot g^{-1}$ but some of those obtained from systems containing DBP. They are in the range of 4.6 $cm^3 \cdot g^{-1}$ for NaCl solutions contacted with bitumen, 21 $cm^3 \cdot g^{-1}$ in those NaCl systems contacted with cement and 28 $cm^3 \cdot g^{-1}$ in Q-solutions contacted with bitumen.

<u>List of publications</u>

Keiling, Ch., Esser, V., Marx, G., "Migration and sorption behaviour of Actinides in systems of high salinity under the influence of organic complexing agents", presented at the "International Conference on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere" in Munic, September 1987

Keiling, Ch., Esser, V., Hintze, C., Marx, G., "Die Migration von Transuranen und ihre Rückhaltung durch geologische Medien", presented at the 21. GDCh-Meeting in Berlin, September 1987

Table I. pH- und Eh-Values of saturated salt solutions after their contact with the organic compounds

System	org. Ligand	Systems pH	Eh / mV	regulated pH
NaCl/Cement	DBP	1,67	492	12,3
	TBP	12,30	-63	12,3
	EDTA	6,14	264	12,3
	Citrate	12,32	-48	12,3
	Oxalate	12,22	-65	12,3
NaCl/Bitumen	DBP	0,42	321	0,4
	TBP	6,27	200	6,3
	EDTA	3,88	146	3,9
	Citrate	6,90	149	6,9
	Oxalate	6,44	156	6,4
Q-Sol./Cement	DBP	-0,55	516	6,4
	TBP	5,31	363	6,4
	EDTA	1,79	302	6,4
	Citrate	4,95	304	6,4
	Oxalate	5,01	342	6,4
Q-Sol./Bitumen	DBP	-0,79	482	-0,8
	TBP	6,69	275	6,7
	EDTA	2,47	359	2,5
	Citrate	6,55	293	6,6
	Oxalate	6,68	229	6,6

Table II. Solubility of AgI in various saturated salt solutions containing organic complexing agents

Solution	org. Ligand	$[I^-]$ / $mol \cdot dm^{-3}$
NaCl/Cement	without	$2.28 \cdot 10^{-4}$
	DBP	$2.67 \cdot 10^{-4}$
	TBP	$3.53 \cdot 10^{-4}$
	EDTA	$3.42 \cdot 10^{-4}$
	Citrate	$4.45 \cdot 10^{-4}$
	Oxalate	$2.96 \cdot 10^{-4}$
NaCl/Bitumen	without	$2.87 \cdot 10^{-4}$
	DBP	$7.34 \cdot 10^{-5}$
	TBP	$3.14 \cdot 10^{-4}$
	EDTA	$2.70 \cdot 10^{-4}$
	Citrate	$2.19 \cdot 10^{-4}$
	Oxalate	$4.61 \cdot 10^{-4}$
Q-Solution/Cement	without	$6.57 \cdot 10^{-4}$
	DBP	$4.86 \cdot 10^{-5}$
	TBP	$2.17 \cdot 10^{-4}$
	EDTA	$1.11 \cdot 10^{-4}$
	Citrate	$7.38 \cdot 10^{-4}$
	Oxalate	$1.34 \cdot 10^{-4}$
Q-Solution/Bitumen	without	$2.94 \cdot 10^{-4}$
	DBP	$1.00 \cdot 10^{-2}$
	TBP	$6.51 \cdot 10^{-4}$
	EDTA	$2.13 \cdot 10^{-4}$
	Citrate	$2.99 \cdot 10^{-4}$
	Oxalate	$4.07 \cdot 10^{-4}$

Table III. Solubility of $AgIO_3$ in various saturated salt solutions containing organic complexing agents

Solution	org. Ligand	$[IO_3^-]$ / $mol \cdot dm^{-3}$
NaCl/Cement	DBP	$8.25 \cdot 10^{-3}$
	TBP	$2.13 \cdot 10^{-3}$
	EDTA	$6.60 \cdot 10^{-3}$
	Citrate	$4.68 \cdot 10^{-3}$
	Oxalate	$1.16 \cdot 10^{-2}$
NaCl/Bitumen	DBP	$3.07 \cdot 10^{-1}$
	TBP	$2.45 \cdot 10^{-3}$
	EDTA	$1.31 \cdot 10^{-2}$
	Citrate	$1.87 \cdot 10^{-3}$
	Oxalate	$1.13 \cdot 10^{-3}$
Q-Solution/Cement	DBP	$1.87 \cdot 10^{-1}$
	TBP	$6.14 \cdot 10^{-3}$
	EDTA	$6.14 \cdot 10^{-2}$
	Citrate	$7.98 \cdot 10^{-3}$
	Oxalate	$9.57 \cdot 10^{-3}$
Q-Solution/Bitumen	DBP	$4.09 \cdot 10^{-1}$
	TBP	$3.28 \cdot 10^{-3}$
	EDTA	$1.17 \cdot 10^{-1}$
	Citrate	$6.95 \cdot 10^{-3}$
	Oxalate	$3.51 \cdot 10^{-3}$

Table IV. Solubility of $CsNO_3$ in various salt solutions containing organic complexing agents

Solution	org. Ligand	[Cs] / $mol \cdot dm^{-3}$
NaCl/Cement	TBP	1.63
	DBP	1.71
	EDTA	1.57
	Citrate	1.69
	Oxalate	1.69
NaCl/Bitumen	TBP	1,74
	DBP	1,95
	EDTA	1,62
	Citrate	1,78
	Oxalate	1,87
Q-Solution/Cement	TBP	1.74
	DBP	1.55
	EDTA	1.72
	Citrate	1.70
	Oxalate	1.68
Q-Solution/Bitumen	TBP	1,48
	DBP	1,44
	EDTA	1,36
	Citrate	1,38
	Oxalate	1,45

Table V. Solubility of $Na_2U_2O_7$ in various salt solutions containing organic complexing agents

Solution	org. Ligand	[Uranium] / $mol \cdot dm^{-3}$
NaCl/Cement	DBP	$4.62 \cdot 10^{-5}$
	TBP	$1.05 \cdot 10^{-5}$
	EDTA	$5.54 \cdot 10^{-4}$
	Citrate	$3.06 \cdot 10^{-4}$
	Oxalate	$2.05 \cdot 10^{-4}$
NaCl/Bitumen	DBP	$5.44 \cdot 10^{-6}$
	TBP	$7.79 \cdot 10^{-5}$
	EDTA	$1.37 \cdot 10^{-3}$
	Citrate	$7.27 \cdot 10^{-4}$
	Oxalate	$7.77 \cdot 10^{-5}$
Q-Solution/Cement	DBP	$2.52 \cdot 10^{-4}$
	TBP	$1.22 \cdot 10^{-4}$
	EDTA	$1.13 \cdot 10^{-4}$
	Citrate	$1.09 \cdot 10^{-3}$
	Oxalate	$1.34 \cdot 10^{-4}$
Q-Solution/Bitumen	DBP	$2.73 \cdot 10^{-4}$
	TBP	$1.43 \cdot 10^{-5}$
	EDTA	$3.89 \cdot 10^{-4}$
	Citrate	$2.69 \cdot 10^{-3}$
	Oxalate	$1.60 \cdot 10^{-5}$

Table VI. Solubility of $Pu(OH)_4$ in various saturated salt solutions containing organic complexing agents

Solution	org. Ligand	[Pu] / $mol \cdot dm^{-3}$
NaCl/Cement	without	$2.5 \cdot 10^{-8}$
	DBP	$1.5 \cdot 10^{-7}$
	TBP	$1.7 \cdot 10^{-8}$
	EDTA	$1.0 \cdot 10^{-5}$
	Citrate	$1.4 \cdot 10^{-5}$
	Oxalate	$4.4 \cdot 10^{-7}$
NaCl/Bitumen	without	$1.7 \cdot 10^{-7}$
	DBP	$4.7 \cdot 10^{-7}$
	TBP	$1.2 \cdot 10^{-8}$
	EDTA	$5.2 \cdot 10^{-5}$
	Citrate	$1.2 \cdot 10^{-6}$
	Oxalate	$6.0 \cdot 10^{-9}$
Q-Solution/Cement	without	$3.5 \cdot 10^{-7}$
	DBP	$9.4 \cdot 10^{-6}$
	TBP	$3.4 \cdot 10^{-7}$
	EDTA	$1.7 \cdot 10^{-6}$
	Citrate	$4.9 \cdot 10^{-5}$
	Oxalate	$1.3 \cdot 10^{-6}$
Q-Solution/Bitumen	without	$1.2 \cdot 10^{-6}$
	DBP	$6.3 \cdot 10^{-7}$
	TBP	$3.4 \cdot 10^{-7}$
	EDTA	$2.4 \cdot 10^{-7}$
	Citrate	$1.4 \cdot 10^{-5}$
	Oxalate	$3.5 \cdot 10^{-7}$

Table VII. Results of ultrafiltration experiments with I^--containing solutions

System	org. Ligand	Relative quantity of I^- in solution after filtration Poresize: 450 nm	2 nm
NaCl/Cement	DBP	100 %	100.0 %
	TBP	100 %	100.0 %
	EDTA	100 %	81.4 %
	Citrate	100 %	92.1 %
	Oxalate	100 %	95.8 %
NaCl/Bitumen	DBP	100 %	92.2 %
	TBP	100 %	87.0 %
	EDTA	100 %	80.6 %
	Citrate	100 %	90.2 %
	Oxalate	100 %	100.0 %
Q-Sol./Cement	DBP	100 %	87.2 %
	TBP	100 %	100.0 %
	EDTA	100 %	95.8 %
	Citrate	100 %	83.0 %
	Oxalate	100 %	100.0 %
Q-Sol./Bitumen	DBP	100 %	93.5 %
	TBP	100 %	100.0 %
	EDTA	100 %	84.6 %
	Citrate	100 %	84.1 %
	Oxalate	100 %	99.3 %

Table VIII. Results of ultrafiltration experiments with Cs^+-containing solutions

System		Poresize / nm 450	200	100	50	10	2
NaCl/Cement /	TBP	100	99.7	99.7	99.2	98.5	93.3
	DBP	100	99.5	96.4	95.9	95.2	93.8
	Citrate	100	99.5	98.7	98.6	97.5	96.9
	EDTA	100	98.4	98.1	97.3	96.7	93.6
	Oxalate	100	100	100	100	100	99.8
Q-Sol.Cement/	TBP	100	100	99.8	99.5	98.7	97.9
	DBP	100	99.8	99.8	99.3	98.4	96.7
	Citrate	100	100	99.4	99.2	99.0	97.9
	EDTA	100	99.6	99.5	99.3	98.0	97.8
	Oxalate	100	100	100	100	99.4	99.3

Table IX. Results of the leaching experiments on simulated cement waste

Element	Amount of the elements solidified in cement / mol	Contacttime / d	leached amount / %
Iodine	$5.45 \cdot 10^{-3}$	8	100
Cesium	$5.40 \cdot 10^{-3}$	35	92.6
Uranium	$5.00 \cdot 10^{-7}$	14	9.3
Uranium	$5.61 \cdot 10^{-3}$	27	0.3
Neptunium	$3.88 \cdot 10^{-6}$	37	0.0
Americium	$1.26 \cdot 10^{-10}$	35	0.0

Table X. Results of the migration experiments on iodide. (The filling of the columns consisted of NaCl)

Mass added / mol	System	Porosity / % Vol/Vol	Recovery / %	K_D / $cm^3 \cdot g^{-1}$
$4.1 \cdot 10^{-7}$	NaCl/Cement/DBP	36	100	0
$3.6 \cdot 10^{-3}$	NaCl/Cement/TBP	35	92	-
$3.2 \cdot 10^{-7}$	NaCl/Cement/EDTA	34	100	0
$3.4 \cdot 10^{-7}$	NaCl/Cement/Citrate	35	91	-
$4.1 \cdot 10^{-7}$	NaCl/Cement/Oxalate	37	100	0
$3.9 \cdot 10^{-7}$	NaCl/Bitumen/EDTA	38	96	-
$5.3 \cdot 10^{-7}$	NaCl/Bitumen/Citrate	38	99	0.02
$1.9 \cdot 10^{-7}$	Q_Sol./Cem./DBP	40	66	-
$3.6 \cdot 10^{-7}$	Q-Sol./Cem./TBP	37	100	-
$4.2 \cdot 10^{-7}$	Q-Sol./Cem./EDTA	38	94	-
$5.6 \cdot 10^{-7}$	Q-Sol./Cem./Citrate	35	80	0
$4.4 \cdot 10^{-7}$	Q-Sol./Cem./Oxalate	38	100	-
$1.6 \cdot 10^{-7}$	Q-Sol./Bit./EDTA	40	100	-
$4.2 \cdot 10^{-7}$	Q-Sol./Bit./Citrate	38	96	-
$3.9 \cdot 10^{-7}$	Q-Sol./Bit./Oxalate	40	95	0

Table XI. Results of the migration experiments on cesium. (The filling of the columns consisted of NaCl)

Mass added / mol	System	Porosity / % Vol/Vol	Recovery / %	K_D / $cm^3 \cdot g^{-1}$
$4.7 \cdot 10^{-3}$	NaCl/Cement/DBP	36	26	-
$2,3 \cdot 10^{-3}$	NaCl/Cement/TBP	35	65	0
$2,9 \cdot 10^{-3}$	NaCl/Cement/EDTA	34	86	0
$3,0 \cdot 10^{-3}$	NaCl/Cement/Citrate	36	58	-
$9,3 \cdot 10^{-4}$	NaCl/Cement/Oxalate	36	58	0
$1,9 \cdot 10^{-3}$	NaCl/Bitumen/DBP	36	67	-
$4,6 \cdot 10^{-3}$	NaCl/Bitumen/TBP	36	68	-
$5,2 \cdot 10^{-3}$	NaCl/Bitumen/EDTA	36	68	-
$3,6 \cdot 10^{-3}$	NaCl/Bitumen/Citrate	36	81	-
$3,6 \cdot 10^{-3}$	NaCl/Bitumen/Oxalate	37	48	0
$3,4 \cdot 10^{-3}$	Q-Sol./Cem./DBP	36	49	0
$4,6 \cdot 10^{-3}$	Q-Sol./Cem./TBP	33	69	0
$3,4 \cdot 10^{-3}$	Q-Sol./Cem./EDTA	38	64	0
$2,1 \cdot 10^{-3}$	Q-Sol./Cem./Citrate	32	95	0
$4,0 \cdot 10^{-3}$	Q-Sol./Cem./Oxalate	39	55	0
$2,9 \cdot 10^{-3}$	Q-Sol./Bit./DBP	35	45	0
$5,2 \cdot 10^{-3}$	Q-Sol./Bit./TBP	32	75	0
$1,6 \cdot 10^{-3}$	Q-Sol./Bit./EDTA	38	83	0
$3,1 \cdot 10^{-3}$	Q-Sol./Bit./Citrate	36	57	-
$3,6 \cdot 10^{-3}$	Q-Sol./Bit./Oxalate	37	41	-

Table XII. Results of the migration experiments on uranium. (The filling of the columns consisted of NaCl)

Mass added / mol	System	Porosity / % Vol/Vol	Recovery / %	K_D / $cm^3 \cdot g^{-1}$
$9.01 \cdot 10^{-8}$	NaCl/Cement/DBP	33.9	21.1	0.004
$5.07 \cdot 10^{-9}$	NaCl/Cement/TBP	32.7	11.2	0.01
$5.97 \cdot 10^{-7}$	NaCl/Cement/Citrate	30.8	19.5	0.2
$4.06 \cdot 10^{-7}$	NaCl/Cement/Citrate	36.0	25.0	0.19
$1.11 \cdot 10^{-6}$	NaCl/Cement/EDTA	32.7	100.0	0.0
$2.01 \cdot 10^{-8}$	NaCl/Cement/Oxalate	33.3	0.0	—

Table XIII. Results of the migration experiment on Plutonium. (The filling of the columns consisted of NaCl)

Mass added / mol	System	Porosity / % Vol/Vol	Recovery / %	K_D / $cm^3 \cdot g^{-1}$
$1.8 \cdot 10^{-11}$	NaCl/Cement/DBP	34	0.1	0
$1.6 \cdot 10^{-9}$	NaCl/Cement/TBP	35	0.6	0
$7.7 \cdot 10^{-7}$	NaCl/Cement/EDTA	36	1.3	-
$4.5 \cdot 10^{-7}$	NaCl/Cement/Citrate	38	3.8	-
$7.4 \cdot 10^{-9}$	NaCl/Cement/Oxalate	36	19.7	0
$3.4 \cdot 10^{-11}$	NaCl/Bitumen/DBP	35	60.0	0.1
$2.1 \cdot 10^{-8}$	NaCl/Bitumen/TBP	38	88.0	-
$8.6 \cdot 10^{-8}$	NaCl/Bitumen/EDTA	36	11.2	-
$4.5 \cdot 10^{-8}$	NaCl/Bitumen/Citrate	38	3.8	0.1
$1.8 \cdot 10^{-9}$	NaCl/Bitumen/Oxalate	34	13.4	0.06
$8.4 \cdot 10^{-8}$	Q-Solution/Cement/DBP	36	25.6	-
$2.4 \cdot 10^{-8}$	Q-Solution/Cement/TBP	34	9.6	0.02
$5.9 \cdot 10^{-9}$	Q-Solution/Cement/EDTA	38	13.0	-
$7.6 \cdot 10^{-8}$	Q-Solution/Cement/Citrate	35	5.6	-
$1.2 \cdot 10^{-9}$	Q-Solution/Cement/Oxalate	38	100	0
$2.4 \cdot 10^{-8}$	Q-Solution/Bitumen/DBP	36	50.6	-
$9.4 \cdot 10^{-9}$	Q-Solution/Bitumen/TBP	34	19.8	-
$1.0 \cdot 10^{-7}$	Q-Solution/Bitumen/EDTA	37	11.7	0.04
$1.3 \cdot 10^{-8}$	Q-Solution/Bitumen/Citrate	40	33.6	-
$3.0 \cdot 10^{-8}$	Q-Solution/Bitumen/Oxalate	36	33.7	-

Table XIV. Sorption of I^- on solid NaCl under the influence of complexing organics

Solution	org. Ligand	Volume / cm^3	Mass of NaCl / g	Rs / $cm^3 \cdot g^{-1}$
NaCl/Cement	without	15	3.0001	0.27
	DBP	15	3.0024	0.10
	TBP	15	3.0002	0.05
	EDTA	15	3.0024	0.04
	Citrate	15	2.9997	0.06
	Oxalate	15	2.9997	0.20
NaCl/Bitumen	without	15	2.9994	0.00
	DBP	15	3.0000	0.09
	TBP	15	3.0019	0.03
	EDTA	15	2.9993	0.00
	Citrate	15	3.0088	0.05
	Oxalate	15	3.0033	0.07
Q-Sol./Cement	without	15	2.9997	0.09
	DBP	15	3.0025	0.41
	TBP	15	3.0019	0.03
	EDTA	15	2.9993	0.00
	Citrate	15	3.0088	0.05
	Oxalate	15	3.0033	0.07
Q-Sol./Bitumen	without	15	3.0014	0.19
	DBP	15	3.0025	0.30
	TBP	15	2.9998	0.02
	EDTA	15	2.9991	0.01
	Citrate	15	3.0007	0.05
	Oxalate	15	3.0007	0.00

Table XV. Sorption of Uranium on solid NaCl under the influence of complexing organics

Solution	org. Ligand	[Uranium] / $mol \cdot dm^{-3}$	Volume / cm^3	Mass of NaCl / g	Rs / $cm^3 \cdot g^{-1}$
NaCl/Cement	DBP	$1.4 \cdot 10^{-6}$	10	3.0082	21.27
	TBP	$1.0 \cdot 10^{-5}$	10	3.0164	0.11
	EDTA	$5.5 \cdot 10^{-4}$	10	2.9986	0.20
	Citrate	$3.1 \cdot 10^{-4}$	10	3.0069	0.23
	Oxalate	$2.1 \cdot 10^{-4}$	10	2.9981	0.08
NaCl/Bitumen	DBP	$5.4 \cdot 10^{-6}$	10	3.0006	4.59
	TBP	$5.1 \cdot 10^{-5}$	10	3.0049	0.13
	EDTA	$1.4 \cdot 10^{-3}$	10	3.0114	0.00
	Citrate	$4.4 \cdot 10^{-4}$	10	2.9966	0.00
	Oxalate	$7.8 \cdot 10^{-5}$	10	3.0067	0.13
Q-Sol./Cement	DBP	$2.5 \cdot 10^{-4}$	10	3.0160	0.01
	TBP	$1.2 \cdot 10^{-4}$	10	2.9998	0.27
	EDTA	$1.1 \cdot 10^{-4}$	10	3.0124	0.00
	Citrate	$1.6 \cdot 10^{-4}$	10	3.0134	0.00
	Oxalate	$1.3 \cdot 10^{-4}$	10	3.0118	0.00
Q-Sol./Bitumen	DBP	$2.7 \cdot 10^{-4}$	10	2.9993	28.63
	TBP	$1.4 \cdot 10^{-5}$	10	3.0012	0.05
	EDTA	$2.8 \cdot 10^{-5}$	10	3.0168	0.01
	Citrate	$2.7 \cdot 10^{-3}$	10	3.0099	0.08
	Oxalate	$1.6 \cdot 10^{-5}$	10	3.0014	0.00

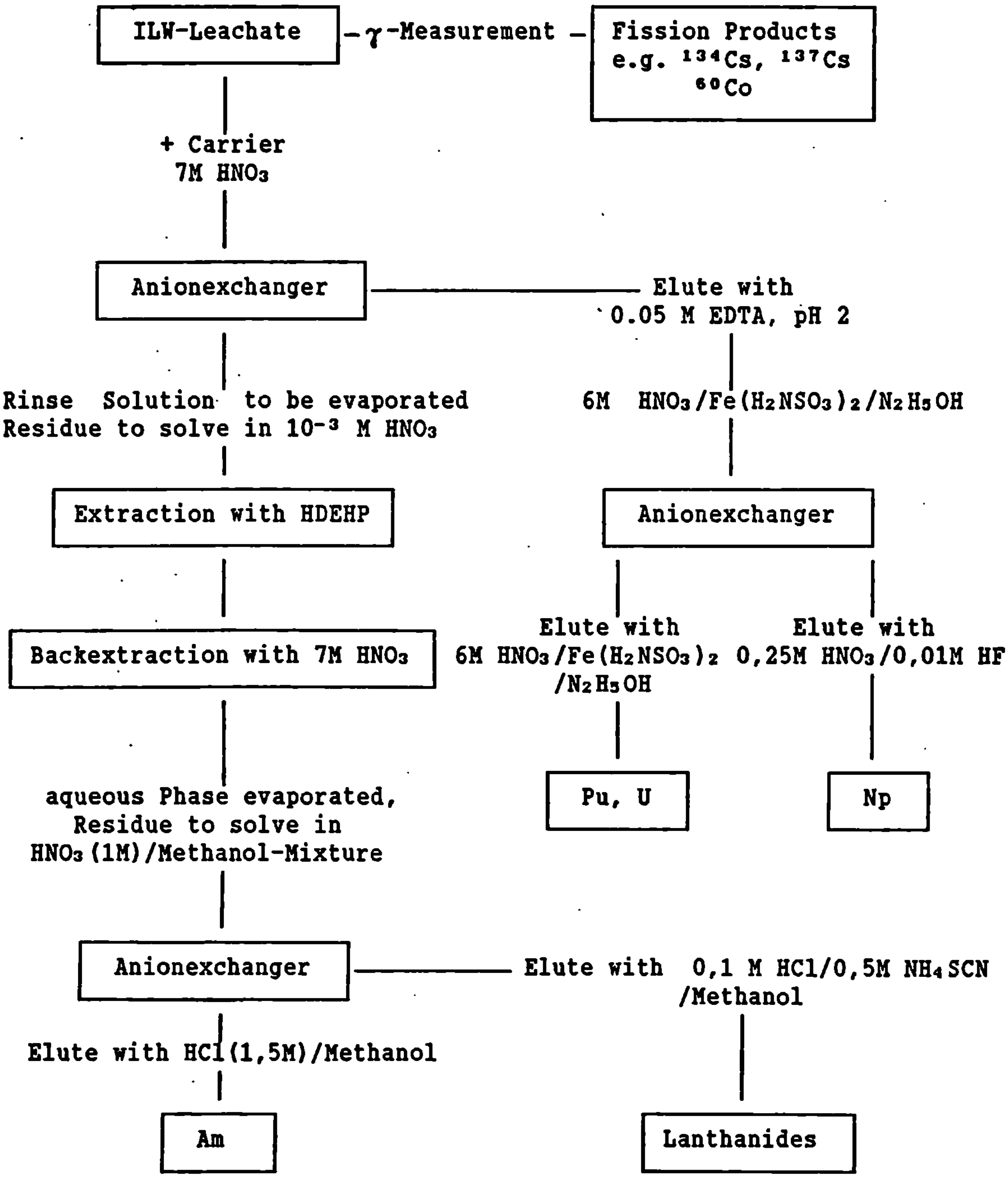

Figure 1. Chemical Procedure for the Separation of Actinides from real waste leachates

INVESTIGATION OF LLW AND MLW CEMENT PRODUCTS RESULTING FROM REPROCESSING

Contractor: Kernforschungszentrum Karlsruhe GmbH
Institut für Nukleare Entsorgungstechnik (INE)
Contract N°: FI1W/0092-D(B)
Duration of contract: July 1, 1986 - December 31, 1989
Project Leader: P. Vejmelka

A. Objectives and scope

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

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

B. Work Programme

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

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

C. Progress of work and results

State of advancement

To determine the equilibrium concentrations of relevant radionuclides for the system cemented waste form/salt solution, laboratory experiments with Pu, Am and Np doped samples using Q-brine and NaCl-solution were performed. Based on the results, the source term for the activity release in the near field of the waste package can be formulated. The results obtained for the experiments with Q-brine indicate that in this case the equilibrium concentration for Pu, Am and Np depends on the activity inventory of the samples and therefore an adsoprtion equilibrium is the relevant process. In NaCl solution the equilibrium concentrations are more or less independend from the activity content of the samples and are comparable low (10^{-8}-10^{-10} Moles/l). This is due to the high pH value (12-13) in this system and the equilibrium concentration depends on the low solubility of the actinide compounds in the high pH-system.

Additional to the laboratory experiments, leach experiments with real 200 l cemented waste forms (low level) using Q-brine at 40°C as leachant were started. The aim of the investigations is to determine the influence of the fabrication conditions on the activity release.

First results for the release of Cs-137 under the experimental conditions are available (leach period 100 days).

Progress and results

In order to determine the equilibrium concentrations for Pu, Am and Np-compounds in the system cement/salt solution, cement samples with different contents of the actinide elements were stored in Q-brine (rich in $MgCl_2$) and NaCl-solution at room temperature (2 g waste form in 30 ml brine). To accelerate the equilibrium adjustment, crushed samples with a high specific surface were used. In parallel reference samples without cement stone were stored under similar conditions.

From our corrosion and leach experiments it is known that in Q-brine fast corrosion reactions occur with the formation of basic Mg-chlorides, $CaSO_4$ phases and Friedel's salt /1/. By the used waste form/brine-ratio the equilibrium pH-value remains at 6.5, due to the buffer capacity of the excess $MgCl_2$ in the system.

After defined time periods, samples were taken from the liquid phase, filtered using an Amicon system (1.5 nm) and the activity was measured either using Liquid-Scintillation-Counting and/or γ-measurement and α-spectroscopy.

In Q-brine the resulting equilibrium concentrations for the investigated range of the actinide inventory depend on the activity inventory of the samples. We therefore conclude that a sorption equilibrium determines the activity concentration. As an example, Fig. 1 gives the results obtained from the experiments with Am-241.

Due to the sorption equilibrium the concentration of Am in Q-brine in present of cement stone (pH ~ 6.5) is 1-2 orders of magnitude less than the reference onces without cement stone.

In NaCl-solution, the actinide concentrations are independent from the activity content of the samples and are all in the same range of 10^{-8}-10^{-10} Moles/l. In this case, in contrast to the Q-brine system, the equilibrium concentration is determined by the much lesser solubility in the high pH-system (pH 12-13) being approximately 4 orders of magnitude less than in the pH 6 range.

Comparison of the results obtained using simulated samples show a good agreement with the results from experiments using real waste form samples. In summary the results show that for real ILW-cemented waste forms the actinide equilibrium concentrations in both systems (Q-brine and NaCl brine) are relatively low and are in the range of 10^{-8}-10^{-10} Moles/l.

The leach experiments with two real 200 l cemented waste forms (low level) using Q-brine as leachant at 40°C were started in July 1987. The aim of the investigations is to determine the influence of the preparation conditions on the activity release. Fig. 2 show the installed leaching equipment. The composition of the samples is given in table I. Table II gives the radiochemical composition and table III the chemical composition of the used LLW-evaporator concentrate.

Directly after preparation of the samples in the KfK in-drum cementation facility, six 100 ml samples were taken from each drum for laboratory investigations. Three samples were used to measure the compressive strength, the obtained values are 14 ± 2 N/mm². First leaching results are available for a leach period of 100 days, but for a detailed description of the leach characteristic more results are necessary.

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Investigation of the corrosion resistance of different composed cemented waste forms, Finnish-German Seminar on Nuclear Waste Management, 1986 ESPOO, Sept. 23-25, 1986, Finnland.

Table I Composition of the real 200 l cemented waste forms

Ordinary Portland Cement (PZ 45 F)	156.3 kg
Water	98.5 kg
Salt	26.2 kg
Total weight	281.0 kg
density	1.70 kg/l

Table II Radiochemical composition of the 200 l cemented waste forms (sampling date November 15, 1984)

H-3	2.9 E 6	Bq/sample
Na-22	6.2 E 6	
Mn-54	1.35 E 7	
Co-60	6.9 E 7	
Sr-90/Y-90		
Zr-95	4.9 E 7	
Nb 95	1.35 E 8	
Ru-106/Rh-106	2.9 E 9	
Sb-125	5.3 E 8	
Cs-134	7.9 E 7	
Cs-137/Ba-137	7.2 E 8	
Ce-144/Pr-144	8.5 E 8	
Am-241	5.8 E 8	
Σ Alpha	1.14 E 9	
Σ Beta	8.5 E 9	
Pu	0.38 E-1	g/sample
U	157	

Isotopic composition

Pu-238	1.0	U-235	0.31
Pu-239	62.58	U-238	99.69
Pu-240	26.08		
Pu-241	6.24		
Pu-242	4.10		

Table III Chemical composition of the LLW-evaporator concentrate used for the preparation of the 200 l-waste forms

Na^{+}	101.3	g/l
Ca^{2+}	0.07	
Fe^{3+}	0.17	
Cr^{3+}	0.05	
Ni^{2+}	0.41	
Cl^{-}	22.45	
F^{-}	2.85	
SO_4^{2-}	18.81	
NO_3^{-}	55.44	
density	1.202	kg/l
pH-value	11.9	
drying residue (105°C)	250.0	g/l

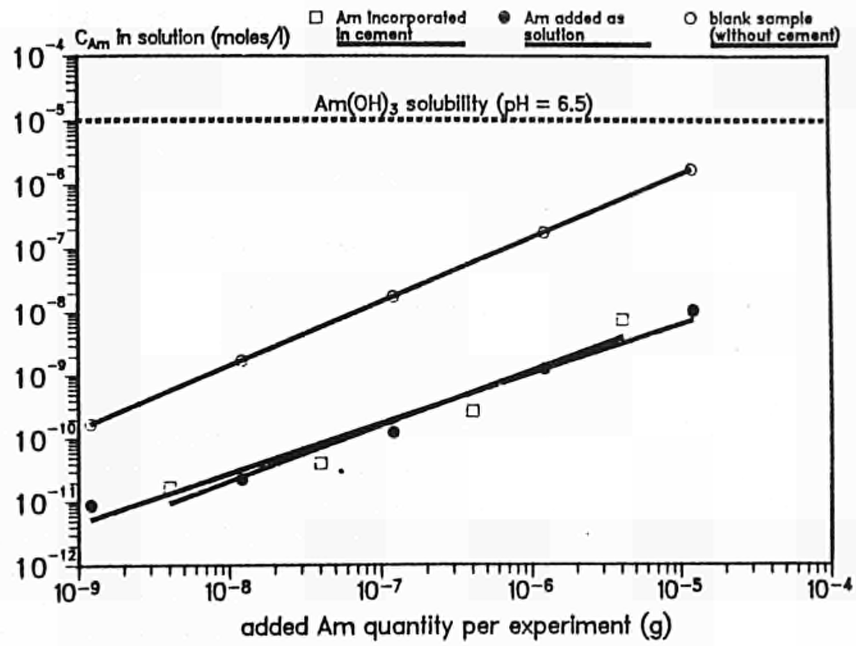

Fig. 1: Am-241 equilibrium concentrations in the system cemented waste form/Q-brine at room temperature for samples with different Am-content (2 g cement, 30 ml Q-brine).

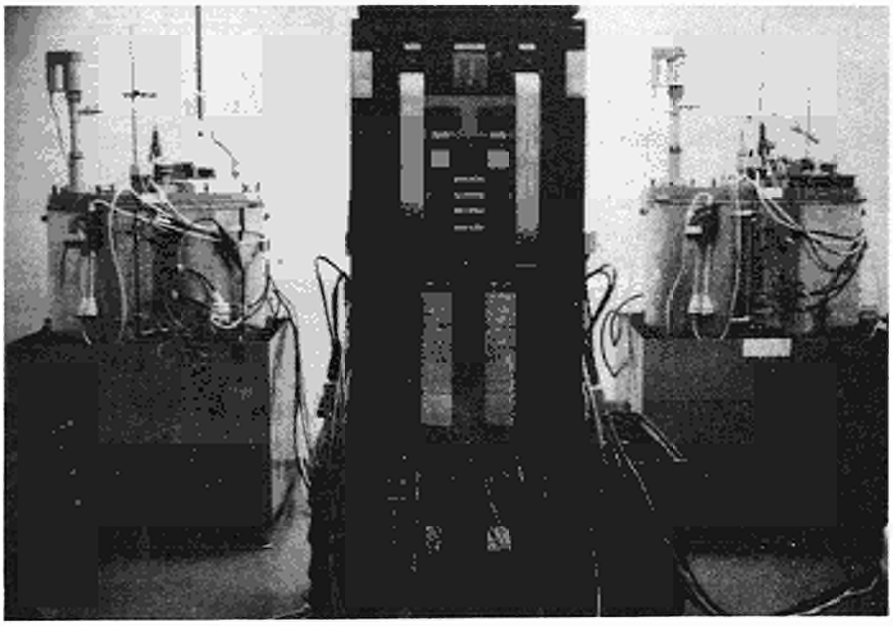

Fig. 2: Leaching equipment for the investigation of real 200 l LLW-cemented waste forms in Q-brine at 40°C.

THE EFFECTS OF RADIATION ON INTERMEDIATE LEVEL WASTE FORMS

Contractor: UKAEA, Harwell, U.K.

Contract No.: FI.1W.0093 U.K.(H)

Duration of Contract: July 1986 - December 1987

Project Leader: D.C. Phillips

A. OBJECTIVES AND SCOPE

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

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

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

B. WORK PROGRAMME

B.1 Selection and procurement of specimens.

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

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

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

B.5 Irradiation in vented containers.

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

B.7 Conclusions and feedback.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Summary

Accelerated gamma and alpha irradiation experiments have been carried out on RMA 11.1, simulated combustible plutonium contaminated material (PCM) in a cement matrix, at a number of dose rates and under various environmental and confinement conditions. It has been demonstrated that under some circumstances, at the laboratory scale, this waste form can swell sufficiently to rupture its container and may disintegrate. A major component of PCM is polyvinylchloride (PVC). Cement pore water extracted from gamma irradiated samples of PVC encapsulated in cement had a pH of 9.8, after 9 MGy, a considerable reduction below the value of 13.0 obtained from unirradiated controls. Reduced pH could adversely affect the retention of actinides by the cement matrix. Gamma radiation experiments on a simulate of RMA 5, mixed ion exchangers in a polymer matrix, demonstrated that this waste form maintained its integrity during irradiation. Some cemented inorganic waste forms (e.g. RMA 2) and some cements based on BFS/OPC can fragment under irradiation. One possible reason for this is the accumulation of radiolytic gases to high pressures in pores in the cement. A technique has been developed for measuring gas permeability in wet cement systems and has been used, with other porosity measurement techniques, to compare the behaviour of different formulations to explore the problem of gas pressurisation. The results indicate that pore size distribution may be important. Accelerated α irradiation experiments have also been carried out on RMA 10, incinerator ash immobilised in cement. Data on gas evolution, mechanical integrity and dimensional stability have been generated for each of the above waste forms; and samples of RMA 3, organic ion exchangers in cement, have been manufactured for subsequent gamma radiation experiments.

Progress and results

1. Selection and procurement of specimens (B1)

During this year work has concentrated on RMA 3, 5, 10, 11.1 and their respective matrices. Inactive simulates of RMA 3 and 11.1 have been made at Harwell, and of RMA 5 have been supplied by the CEGB, for accelerated gamma irradiation experiments. Alpha active samples of RMA 10 and RMA 11.1 have been produced at Harwell containing different levels of ^{238}Pu to produce a range of high α dose rates from x10 to x1000 higher than the real waste form. Samples of BFS/OPC and PFA/OPC have also been manufactured for investigation of matrix materials.

2. Gamma-damage experiments (B2, B4)

Accelerated gamma radiation experiments have been carried out on inactive simulates of RMA 5 and RMA 11.1; on cemented individual components of the RMA 11.1 waste stream; and on a number of different BFS/OPC and PFA/OPC cements.

Irradiation of RMA 5 and 11.1 was carried out on samples confined in vented containers, to simulate storage conditions, and on free-standing, unconfined specimens under both dry and water saturated conditions, to simulate extremes of disposal conditions. A range of specimen sizes from 4 cm diameter to 15 cm diameter were irradiated at dose rates of approximately 0.1 Gy s^{-1}. The confined samples of RMA 11.1 swelled sufficiently to rupture the seams of their metal containers at doses in the range 400 to 800 kGy. Unconfined samples irradiated dry displayed some shrinkage while those irradiated wet swelled and appeared on the verge of disintegration at 800 kGy. The irradiated samples of RMA 5 which were either confined or unconfined and irradiated dry gave similar results to earlier work on this and other polymer matrix waste forms /1//2//3/, with only small changes in volume and their integrity maintained: the novel feature of these tests was the irradiation of water saturated specimens, which displayed no significant dimensional changes and no indication of deterioration at 500 kGy.

In the irradiation tests on some of the individual components of RMA 11.1 four different types of sample were studied: powdered cellulose, shredded cellulose, powdered PVC, and shredded PVC, each in a matrix of the same PFA/OPC formulation. The unconfined samples, of 5 cm diameter, were irradiated dry at 2.8 Gy s^{-1}. At 3 MGy the shredded PVC samples showed signs of fragmenting and by 9 MGy had totally disintegrated; the shredded cellulose samples exhibited some cracking at 9 MGy; the powdered cellulose and PVC samples had maintained their integrity at this dose. Cement pore water was extracted from the irradiated specimens and unirradiated controls. The pore extract obtained from the unirradiated samples showed no significant change in pH, indicating that little chemical degradation of the organics occurred in the timescale of the experiments: in contrast the pore extract from the shredded PVC samples fell from approximately 13.0 to 9.8.

Irradiations of BFS/OPC and PFA/OPC cement samples resulted in spallation and cracking of some of the BFS/OPC formulations. X-ray and thermal analysis did not reveal any changes in microstructure as a result of irradiation. Mercury intrusion porosimetry measurements indicated that there may be a correlation between cement pore size distributions and the tendency for matrix fragmentation: formulations which fragmented had a simple distribution of small pores, while those which did not had a bimodal distribution of pore sizes. Similar measurements are currently underway on samples of RMA 2, cemented borate wastes, which have been shown in earlier work to disintegrate under irradiation /4/.

Detailed analyses have been carried out of the gases evolved and absorbed by many of the above samples on irradiation.

3. Alpha-damage experiments (B3, B4)

Alpha irradiation samples were prepared containing levels of ^{238}Pu which gave dose rates of 3.1×10^{-3} Gy s^{-1}, 7.0×10^{-2} Gy s^{-1} and 6.4×10^{-1} Gy s^{-1}. The samples of RMA 11.1 contained the simulated waste in a powdered form rather than the shredded form of full-scale waste, in order to produce a more homogeneous simulate on the small scale of these experiments. Samples were of 3 cm and 5 diameter. At 9 MGy the compressive strength of these RMA 11.1 simulates had declined from approximately 2.5 MPa to approximately 1.5 MPa but there was no indication of any spontaneous disintegration. Alpha irradiated samples of RMA 11.1 containing shredded waste have much lower compressive strengths of $\sim$ 0.2 MPa at the same dose /5/. No significant changes in volume occurred on irradiation of the cured waste form. Alpha irradiation of RMA 10 simulate resulted in a decrease in strength from approximately 20 MPa to approximately 5 MPa after 30 MGy. Detailed measurements of gas evolution and absorption under oxygen and inert atmospheres have been carried out on the above specimens.

4. Irradiation in vented containers (B5)

The results of experiments to investigate the effect of varying degrees of confinement of waste forms during irradiation were described, for polymer matrix waste forms, in the previous Annual Summary Reports and reference /3/. Further data on this are being accummulated as described in Section 2 above.

5. Basic mechanisms (B6)

A possible cause of the disintegration of some OPC/BFS cements and some waste forms, and the probable cause of the swelling of RMA 11.1, under irradiation, is the gas pressurization of the cement matrix. In order to be able to investigate this a technique has been developed which enables measurement of the permeability of gases through fully wet, hydrated cement. The apparatus has been tested and demonstrated on a variety of cement grouts ranging from ages of 10 days to 5 years. Samples of a wider range of properties have been produced for further investigation of the relationship between gas permeability and dimensional instability during irradiation.

6. Conclusions and feedback (B7)

A considerable amount of data has been generated and will continue to accumulate as the irradiations progress. Analysis of the gases evolved is providing information of value in the design of repository and disposal sites, with respect to ventilation requirements, as well as of value in interpreting the basic mechanisms and their rates within the materials. An example of the latter is the failure to detect significant quantities of HCl or Cl_2 escaping from RMA 11.1. Measurements of pH and chloride ion concentration in extracted pore water show that these products of radiolysis of PVC are trapped by, and alter the properties of, cement. The swelling under certain conditions of RMA 11.1 with subsequent container rupture or waste form disintegration is an important observation, but the extrapolation from these high dose-rate small-scale experiments to the real case of large scale lower dose-rates is not stranghtforward. Previous work has shown that for some waste forms the effects of gas bubble swelling can be correlated for different dose-rates (I) and container sizes (L) through an IL^2 model /6/. Preliminary comparisons indicate that the accelerated γ irradiation experiment has an IL^2 value approximately a factor of ten greater than that estimated for the full-scale waste form. However the different distributions of radiation damage, and the differences in G values between α and γ irradiation, make a simple comparison of IL^2 values suspect. In addition to the experimental work described here, assistance has been given to the Commission in selecting reference waste forms and defining appropriate specifications for them.

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Physico-chemical characterization of bituminized Eurochemic medium level waste

Contractor: S.C.K./C.E.N. Mol, Belgium
Contract N°: FI1W/0094
Duration of Contract: 1/08/1986-31/12/1989
Project Leader: P.Ph. Van Iseghem

A. Objectives and Scope

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

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

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

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

B. Work Programme

B.1. Effect of specimen size

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

B.2. Effect of pressure

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

B.3. Ageing behaviour

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

C. Progress of work and obtained results (period January-December 1987)

State of advancement

The specimens required for the corrosion tests were delivered by Belgoprocess. They consist on inactive bitumen samples of various size (between 0.75 ml and 11.5 l), and active samples (about 1 ml each).

The corrosion tests on the inactive samples were started during the second half of 1987. Data for two test durations (14 and 90 days) are available. The corrosion tests on the active samples will start beginning of 1988.

Data on some physico-chemical properties were obtained on real Eurobitum samples, aged for 51 months (produced: November 1982). The samples were found to have hardened, and the thermal behaviour in the vicinity of the flash and self ignition point changed slightly.

Progress and results

Effect of specimen size on the corrosion and swelling behaviour

Two inactive, full size Eurobitum drums were selected. The drums were produced during the cold test runs of the Eurobitum plant, using similar waste components and bitumen as in the active operation. The homogeneity and composition (total salt, $NaNO_3$, water) of these drums were checked, and found to be excellent.

Samples of the requested size were manufactured by retrieving bitumen from the drums, and heating (above the softening point) crucibles filled with bitumen. This way, the following quantity of cylindrical (height to diameter ratio of 3/2) samples were produced: 18 samples of 11.5 l, 24 (0.5 l), 18 (16.3 ml) and 24 (0.75 ml). The corresponding sample surface area to sample volume ($SA.v^{-1}$) ratio's are (in cm^{-1}) 0.25, 0.70, 2.20 and 6.25.

A two liter sample was sent to RISØ (see RISØ contribution to the CEC programme).

Corrosion tests are underway on these samples in two different media (distilled water, and a mixture of 100 g Boom clay per liter distilled water). The test temperature is 23°C, and durations are 14, 90 and 365 days. Some preliminary results (durations 14 and 90 days) are:

- Swelling for all samples is smaller than 1 vol %; the surfaces of the corroded bitumen samples are covered with some white (crystalline) precipitates.
- Mass losses are smaller than 1 %.
- Minor pH changes with progressing corrosion are recorded.

Chemical analysis of the leachates is in progress.

Effect of pressure on the corrosion and swelling behaviour

Some of the Eurobitum specimens sampled on line were selected, and made available to the S.C.K. by Belgoprocess. The samples were produced during 1980-1981. Sixty samples requested by the S.C.K. were of about 0.86 ml volume (yielding a $SA.v^{-1} = 6.25\ cm^{-1}$), and were prepared by slicing the sampled Eurobitum specimens (of about 5 ml volume). For each of these 5 ml samples analytical data exist, relating to the total salt content, water content, density, U content, α activity, β activity (and the Cs-137 and Sr90 specific activities).

The following corrosion tests are in preparation:

(a) Tests on active Eurobitum samples at ambient pressure, 23°C, in two media: synthetic interstitial clay-water (SIC) and concentrated clay/SIC mixture (CCSICM). Test durations vary between 14 and 365 days.

(b) Similar tests as in (a), but at a pressure of 4 MPa representative of the clay repository.

To correlate with the results from the tests on inactive simulants, tests are planned on inactive simulants in SIC and CCSICM, for specific specimen volumes of 0.7 and 6.25 cm^{-1}.

These corrosion tests will be interpreted in terms of mass loss, dimensional stability, and chemical/radiochemical analysis of the leachate.

Ageing behaviour

The ageing of some fully active Eurobitum samples produced in November 1982 has been evaluated. Compared with the data at time zero and one year ageing the following differences were observed:

* The softening point increases from 101 to 104°C, and the penetration decreases from 20.0 tot 18.8 x 10^{-1} mm. This suggests some hardening of the waste form.
* The flash point increases from 262 to 272°C, but the self ignition point decreases from 312 to 293°C.

The next analysis of the ageing behaviour is foreseen for mid of 1989 (about 6.5 years).

List of publications

(1) Physico-chemical characterization of bituminized Eurochemic medium-level waste - Annual report 1986 (R2738)
Presented at the CEC progress meeting for task 3, sections 1+5 (Cadarache, April 1987).

(2) Physico-chemical characterization of bituminized Eurochemic medium-level waste - Semestrial progress report January-June 1987.
Presented at the CEC progress meeting for task 3, section 1-2-3-5 (Fontenay-aux-Roses, October 1987).

FULL SCALE LEACHING TESTS, LYSIMETER TESTS, SCALE EFFECT

Contractor : CEA, CEN-Cadarache, France
Contract No. : F11W/0095/1 Task 3
Working period : January 1987 - December 1987
Project leader : A. SAAS
Executant of task 3 : J.C NOMINE, CEN-Saclay

A. OBJECTIVES AND SCOPE

The task 3 deals with the following areas of applied research : full scale leaching tests, laboratories lysimeter tests and the study of the scale effect in the leachability of radioactive blocks.

B. WORK PROGRAMME

B.1 Knowledge of the transfer of radionuclides by leaching between full-scale packages of real active waste encapsulated in different matrice and the biosphere.
B.2 Lysimeter tests on inactive or active doped samples.
B.3 Does a "scale effect" exist, which will permit from laboratory measurements of the leachability of small blocks of embedded wastes, the extrapolation of the results to real blocks ?

C. PROGRESS OF WORK AND OBTAINED RESULTS

During the period January - December 1987, substantial results on the above mentionned objectives have been obtained, especially in the field of full size leaching tests and lysimeter experiments.

Full scale leaching test (B-1)

Full scale leaching experiments have been carried out ;

i. experiments is going on for some blocks
ii. the leaching process has been stopped for others
iii. experiments on new blocks have been launched.

i. KFK cement. A concentrate block of 170 l containing either specimen alpha or beta-gamma emitters ; the focus is on the amount of cesium and total salts evacuated after more 500 days = 20 and 9 % respectively.

ii. Two tritiated cement-composite blocks were fabricated with dismantling wastes issued from a hot cell of CEN-Saclay. After 300 days, the total Cs leached fraction located between 1.5 and 2.8 10^{-6} ; it must be emphasized that one of the block was superficially cracked, a fact which seems to have no significant influence on the Cs release.

iii. 4 x 200 l blocks issued from CEA research centers containing either ciment and evaporator concentrates or cement-sludges and concentrates (alpha emitters only) are under investigation. After 90 days, no really significant release of radionuclides has been observed.
2 x 200 l blocks containing bitumen and evaporator concentrates with beta-gamma and alpha traces, fabricated at the bituminizing facility of CEN-Saclay began to be leached 90 days ago. After this period, the following values were noted for the total fraction leached : $^{137}Cs \sim 10^{-5}$, $^{60}Co \sim 3\ 10^{-3}$ (a high value), $^{90}Sr \sim 10^{-4}$, alpha : non significant, dry extract : 5 %. A beginning of swelling has been observed.

Lysimeter experiments (B-2)

Laboratory scale lysimeters have been studied, fabricated and experimented in an inactive way. The efficiency of the apparatus has been demonstrated. Some experiments, conducted with a 90%/10% sand-clay mixture, as representative of an engineered barrier, showed a good confinment of the cesium contained in the concrete samples.

Scale effect (B-3)

The continuation of the experiment shows that after 735 days for the actual total duration, the differences on the values of the annual activity fraction released (F.A.L) by leaching between the samples (200, 20, 4 x 20 and 0,2 l for memory) are not high. The total fraction leached obtained are plotted in the next table.

BLOCK	$\Sigma \frac{a_n}{A_o}$ at 735 days	V $cm.d^{-1}$ at 735 days
200 liters	8.83×10^{-3}	1.19×10^{-4}
20 "	2.60×10^{-2}	1.72×10^{-4}
2 J "	5.33×10^{-2}	1.65×10^{-4}
2 A "	5.37×10^{-2}	1.66×10^{-4}
2 C "	6.58×10^{-2}	1.94×10^{-4}
2 S "	4.80×10^{-2}	1.42×10^{-4}
0.2 "	5.66×10^{-2}	8.35×10^{-5}

EMBEDDED WASTES AND LEACHATES

Contractor CEA : CEA CEN CADARACHE FR

Contract n° F : 11 W/0095/1 - task 3

Working period : 1986 - 1989

Project leader : A. SAAS

Executant : C. POLETIKO CEN CADARACHE

A - OBJECTIVES AND SCOPE

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

For such measurements we must obtain a liquid sample, this implies a complete destruction of each matrix.

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

B - WORK PROGRAMME

B.1 - Full destruction of embedded thermosetting resins.

B.2 - Measurement of pure bêta emitters (^{63}Ni, ^{55}Fe, ^{99}Tc...).

B.3 - Mineralization of bitumen matrices and solubilization of sludges used to coprecipitate nuclides.

B.4 - Solubilization of cement matrices.

B.5 - Measurement of ^{14}C and ^{3}H in all matrices.

B.6 - Method for concentration and separation of alpha emitters from each solution of mineralization.

B.7 - Solutions of gamma emitters, at low concentration (such as ^{94}Nb).

C - PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement :

In 1987 we did the isolation of iron 55 as scheduled in B.2 programme. The second determination was the isolation and measurement of ^{93m}Nb and ^{94}Nb as scheduled in B.7 programme.

Progress and results :

After mineralization of samples a specific chemical separation has been done for iron 55 measurement.

The specificity of iron is to precipitate with ammonia, the yield is close to 100 % at pH ≅ 10.

Iron 55 has an X ray in 6 keV vicinity. The best ways to measure this isotope is :

- liquide scintillation for low activities (i.e. < 100 Bq/l),
- X ray spectrometry for higher activities.

Some samples have been analyzed :

Inconel, ion exchange resins for nuclear wastes and also environmental samples (from nuclear power plant rejection).

Results were in good agreement with ^{60}Co and ^{63}Ni which are also activation products. Detection limit is close to 1 Bq per sample.

Concerning niobium, gamma spectrometry does not permit to evaluate 94 and 93m isotopes due to low activities of these isotopes ; a chemical separation is required.

An procedure has been developped, which permits a full extraction of niobium with TBP. ^{94}Nb is then measured with a germanium h.P detector and ^{93m}Nb, X rays, is measured with a germanium planar detector. Ion exchange resins have been successfully tested.

Detection limits are :

1 Bq per sample for ^{94}Nb,

10 Bq per sample for ^{93m}Nb.

<u>Liste of publication</u> :

- Technical report for ^{55}Fe (Internal CEA + CCE).
- Technical report for ^{93m}Nb and ^{94}Nb (Internal CEA + CCE).

3.B. High active and alpha waste forms characterization

Investigation of the Long Term Behaviour of HLW Glass Under Conditions Relevant to Final Storage

Contractor: Fraunhofer-Institut für Silicatforschung (FhG-ISC), Würzburg, F.R.G.

Contract No.: FI1W/0028
Working period: May 1986 - October 1988

Project leader: H. Roggendorf

A. Objectives and Scope

Borosilicate glasses are proposed as waste form for the final disposal of High Level Waste (HLW) by the Federal Republic of Germany. Between 1980 and 1985 extensive studies on the corrosion mechanisms of the inactive HLW glass type SM 58 in a salt brine were performed by the contractor (contract nos. WAS-232-81-53 D (B) and WAS-323-83-53 D (B)). A theoretical study /1/ on reported corrosion data (for different glasses and different corrosion conditions) showed that most HLW glasses corrode according to a very similar pattern. The main mechanisms are:

- network dissolution,
- formation of reaction product layers on top of the glass, and
- ion exchange.

The following model was developed from these results: In fresh leachants corrosion starts with an initial rate r_0 linearly depending on t. Due to the accumulation of reaction products in the leachate, this initial rate slows down and reaches finally a long term rate r_∞, which again is linearly depending on t. Long term corrosion conditions can be achieved in the laboratory by enlarging the sample surface area to solution volume ratio s. The product s•t is a parameter taking into consideration that in corrosion tests with higher s values saturation with glass corrosion products is reached in a shorter time.

At present the interest is focused on the following open points: The data at high s•t values should be approved by additional experiments. Only a few data could be collected up to now about the composition of leachates, especially salt brines, saturated with glass corrosion products, and the influence of the surface composition of the remaining glass on the corrosion rate is still unknown. The last point is important for high s•t values, because it is expected the depth of the ion exchange zone to be increased when the corrosion rate decreases. The aim of the current contract is to clear the questions indicated above and to investigate the corrosion mechanisms of the new reference HLW glass SON 68. The corrosion tests will be performed in cooperation with the Hahn-Meitner-Institut (HMI), Berlin.

B. Work Programme

B.1. Corrosion pre-tests for the optimization of analytical techniques.
B.2. Supplementary corrosion tests.
B.3. Optimization of analytical techniques (Photoelectron spectroscopy (XPS), acid etching).
B.4. Optimization of preparation methods.
B.5. Preparation and measurement of standard samples with XPS.
B.6. Surface analysis of corroded glass samples.
B.7. Preparation and sampling of saturated leachates at test temperature with subsequent chemical analysis.
B.8. Evaluation of test results.

C. Progress of work and obtained results

Summary

During 1987 several series of corrosion tests have been performed. For these tests two versions of the SON 68 glass were used, the original SON 68 from COGEMA and a substitute from HMI, Berlin. The SON 68 substitute was used for 90 tests in which glass chips and glass powder were corroded together in three different salt brines. The results provided an overview on the corrosion behaviour of SON in salt brines.

Another set of 12 tests with the original SON 68 under similar conditions was performed at HMI, Berlin. The investigation of the surface chemistry of these samples started at the end of 1987 at FhG-ISC.

Additional corrosion experiments have been carried out in solution 1 at 190 °C (Table I). In these tests surface area, solution volume, and corrosion time were used in order to vary the s•t-value (s: ratio of surface area to solution volume; t: corrosion time) without powder addition.

For solution analysis an autoclave system was built up which allows the sampling of leachates during the corrosion tests. These tests will be started at the beginning of 1988.

The general work progress is as follows:

B.1. and B.2.: are completed
B.3. : partly completed (acid etching), partly delayed,
B.4. : progressing normally,
B.5. and B.6.: delayed,
B.7. : progressing normally.

Progress and results

1. Corrosion pre-tests and supplementary corrosion tests (B.1. and B.2.)

Chips of the HLW glass SON 68 (composition in Table I) with a size of 12 x 9 x 2 mm^3 were corroded in salt brines (composition in Table II) at 110, 150, and 190 °C for 30 and 120 d. The ratio s of the glass surface area to the leachant volume was varied between 0.033 and 100 cm^{-1} by adding glass powder with adjusted particle sizes to the tests. For each combination of leachant and temperature 10 corrosion tests were performed. The corrosion progress was determined by balancing the glass chips and by analyzing the boron and lithium content of the leachates. The s ratio was corrected approximately for the decrease of surface area during the corrosion test.

A straightforward interpretation led to the following results:

- the long term corrosion process depends linearly on s•t in the solutions 1 and 2
- and follows a square root time law in solution 3, but
- the observed temperature dependance of the corrosion tests was contradictory and could not be explained by simple reaction kinetics.

In the meantime an additional set of corrosion tests with the glass SON 68 in solution 1 at 190 °C has been performed. The aim was to gather more data for these specific corrosion conditions over a wide range of s•t. This was achieved by varying the leachant volume, the corrosion time, and the surface area of the glass sample. Figure 1 shows these data in a double logarithmic plot as mass of reacted glass per leachant volume m_g (q indicates the determination by balancing) vs. s•t. Allthough the data points are scattering a bit (s•t is only approximating an universal time parameter), one may assume that the corrosion process proceeds linearly with time at a given s value until the leachate is saturated with respect to a reaction product. Then the corrosion rate slows down until a lower value is reached. The corrosion proceeds then again linearly with time until the leachate is saturated with respect to a new reaction product.

It looks as if five distinct s•t ranges can be distinguished:

1. $0.03\ cm^{-1}\cdot d \leq s\cdot t \leq 0.3\ cm^{-1}\cdot d$; m_q depends linearly on s•t; $r = 0.63\ mg\ cm^{-2}\cdot d^{-1}$.
2. $0.3\ cm^{-1}\cdot d \leq s\cdot t \leq 4\ cm^{-1}\cdot d$; m_q is more or less constant.
3. $4\ cm^{-1}\cdot d \leq s\cdot t \leq 25\ cm^{-1}\cdot d$; m_q depends linearly on s•t; $r = 0.051\ mg\ cm^{-2}\cdot d^{-1}$.
4. $25\ cm^{-1}\cdot d \leq s\cdot t \leq 90\ cm^{-1}$; m_q is more or less constant.
5. $90\ cm^{-1}\cdot d \leq s\cdot t \leq 800\ cm^{-1}\cdot d$; m_q depends linearly on s•t; $r = 0.0079\ mg\cdot cm^{-2}\cdot d^{-1}$.

Above $800\ cm^{-1}\cdot d$ only few data points are available, but they indicate a new range with $r = 0.0036\ mg\cdot cm^{-2}\cdot d^{-1}$, if the value at $s\cdot t = 2450\ cm^{-1}\cdot d$ is determined correctly.

These findings indicate that the corrosion model of an initial corrosion rate r_0 slowing down to a final corrosion rate r_∞ should be expanded to allow more than one solubility limitation.

With that expanded corrosion model in mind the earlier corrosion data were evaluated again. The corrosion rates found for the corrosion of the HLW glass SON 68 in solutions 1 and 2 for different s•t ranges are listed in Table III. The results of this new evaluation were:

- for each set of corrosion data (same temperature and leachant) more than one s•t range was found with a respective corrosion rate r depending linearly on s•t;
- data for different corrosion times can be compared on a common s•t scale only at 190 °C;
- it is not always possible to compare data for the same s•t value to get informations about the temperature dependence of the corrosion reaction;
- the underlined data at 110 °C, 150 °C, and 190 °C for corrosion in solution 1 which were determined for different s•t ranges fit to the same thermal activated reaction (activation energy 18 kJ/mole);
- it seems to be that the long term corrosion conditions are achieved in the discussed tests only at 190 °C.

As said before the corrosion process in solution 3 follows a square root time law. Figure 2 shows this for 150 °C. Again the data for different corrosion times do not follow the same $\sqrt{s\cdot t}$-law, even not at 190 °C. The square-root time law indicates the influence of diffusion processes either in the glass surface region or in the solution.

2. Corrosion tests (B.2.)

To prepare samples for surface analysis 12 corrosion tests were performed at the HMI. The test parameter were chosen to get samples for the short, medium, and long term range of the corrosion process. Table IV shows the test parameters applied. The data from these HMI tests agree very well with the data measured at FhG-ISC. This is demonstrated in Figure 3 for the corrosion at 190 °C in solutions 1 and 2.

3. Surface analysis (B.3. and B.5.)

A set of 15 standard samples for quantitative XPS analysis of the surface composition of corroded SON 68 glass chips has been melted. These standards have a general composition similar to SON 68, but in each of them, the compositions were varied. Due to faults in the XPS equipment the measurements are delayed. But the first standard samples have been investigated. The XPS analysis was performed in combination with Ar ion milling. After each milling step the surface was analysed with XPS. This procedure was continued until the signals of the individual elements reached a constant level. For Si and O the standard deviation for more than 10 measurements at various depths was lower than 1 %. For most other elements the standard deviation was about 10 %. Zn was an exception with rather poor results due to the low Zn content of the glass and the low sensitivity of XPS for Zn. As a first impression quantitative determinations should be possible for Si and Ca, with less certainly for Na. The results for Boron were rather poor and should be investigated further.

References

/1/ CONRADT, R., ROGGENDORF, H., and OSTERTAG, R., Report of the Commission of the European Communities, Report EUR 10680 EN (1986).

Table I. Composition of the HLW glass SON 68 in wt. %

SiO_2	B_2O_3	Na_2O	Li_2O	Al_2O_3	CaO	Fe_2O_3	ZrO_2	ZnO	rest
45.5	14.0	9.9	2.0	4.9	4.0	2,9	2.7	2.5	11.4

Table II. Composition of the leachants in wt. %

solution	NaCl	KCl	$MgCl_2$	$MgSO_4$	$CaSO_4$	$CaCl_2$	K_2SO_4
1	1.45	4.73	26.80	1.40	0	0	0
2	0.31	0.11	33.03	0	0.005	2.25	0
3	25.90	0	0	0.16	0.21	0	0.23
rest is water							

Table III. Corrosion rates r for the corrosion of the HLW glass SON 68 in salt solutions

solution	θ in °C	s•t ranges in $cm^{-1}\cdot d$	corrosion times in d	corrosion rate r in $mg\cdot cm^{-2}\cdot d^{-1}$
1	110 °C	0 - 2600	30	0.0035
1	110 °C	0 - 12000	120	0.00081
1	150 °C	0 - 2600	30	0.0036
1	150 °C	0 - 1100	120	0.0021
1	190 °C	0.03 - 0.3	x	0.63
1	190 °C	4 - 25	x	0.051
1	190 °C	90 - 800	x	0.0079
1	190 °C	> 800	x	0.0036
2	110 °C	0 - 2500	30	0.0058
2	110 °C	0 - 10000	120	0.0020
2	150 °C	0 - 2600	30	0.0039
2	150 °C	0 - 1100	120	0.0022
2	190 °C	0 - 700	x	0.0097
2	190 °C	600 - 2500	x	0.0032

x at 190 °C the data for different corrosion times can be compared on a common s•t scale

Table IV. Test parameters for the corrosion of the HLW glass SON 68 in salt brines; tests performed at HMI, Berlin; m_q is the amount of reacted glass per leachment volume determined by balancing the glass chips

Test	solution	θ in °C	s in cm^{-1}	t in d	m_q in $mg \cdot cm^{-3}$
W1	1	190	0.1	82	0.25
W2	1	190	10	158	5.5
W3	2	190	0.1	82	0.22
W4	2	190	10	159	4.6
W5	3	190	1	81	1.1
W6	3	190	100	130	12
W7	1	150	10	243	4.0
W8	2	150	10	249	2.7
W9	3	150	100	251	4
W10	1	110	10	242	1.7
W11	2	110	10	248	2.0
W12	3	110	100	250	15

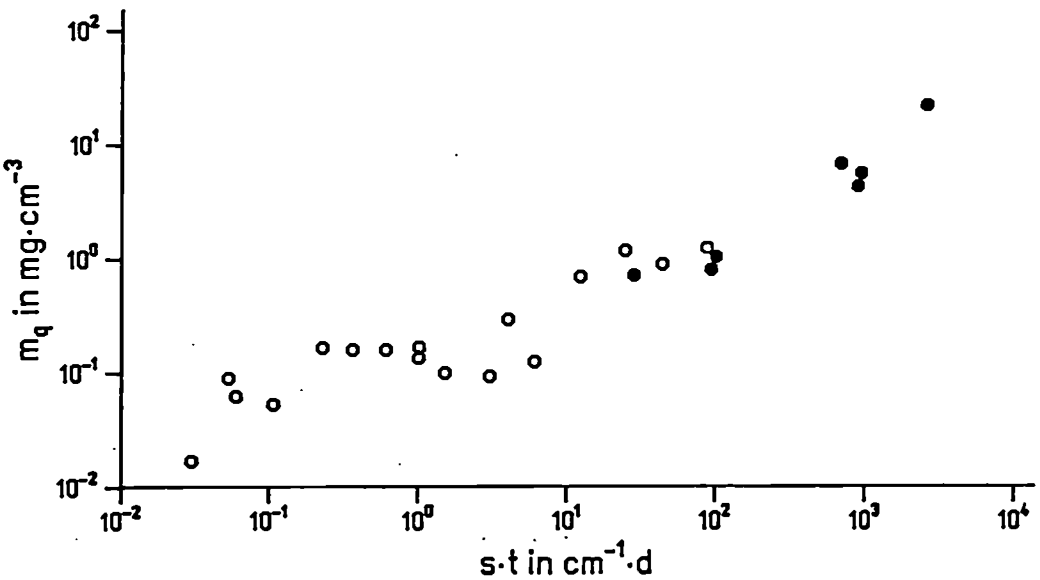

Figure 1. Amount of reacted glass per leachant volume m_q as a function of the product s•t for the corrosion of the HLW glass SON 68 in solution 1 at 190 °C; s: ratio of glass surface area to leachant volume; t: corrosion time;

o : corrosion test with glass chips only;

● : corrosion test with glass chips and glass powder

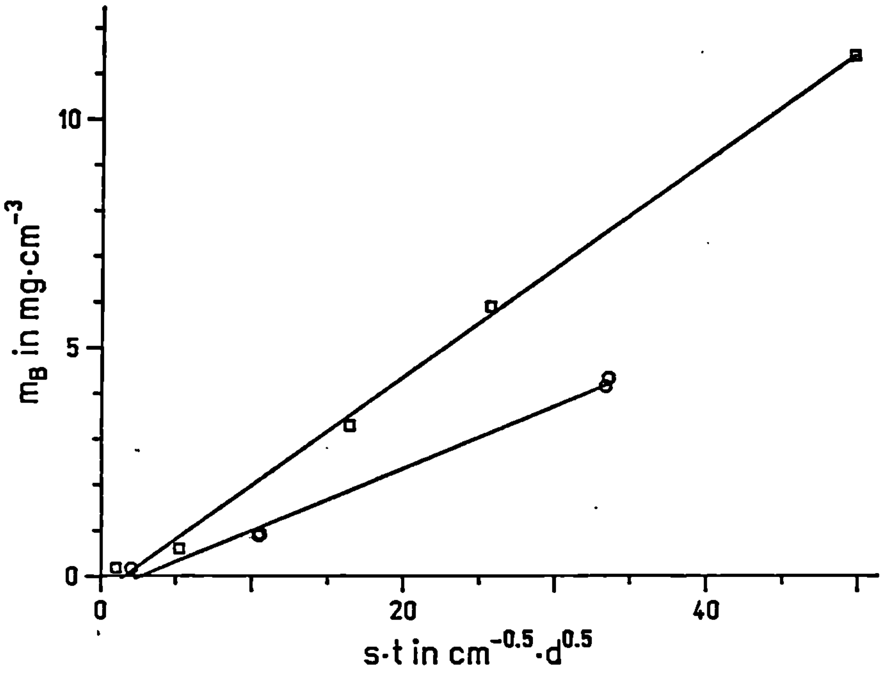

Figure 2. Amount of reacted glass per leachant volume, m_B (determined by boron analysis of leachate) as a function of $\sqrt{s \cdot t}$ for the corrosion of the HLW glass SON 68 in solution 3 at 150 °C;
□ : 30 d; O : 120 d

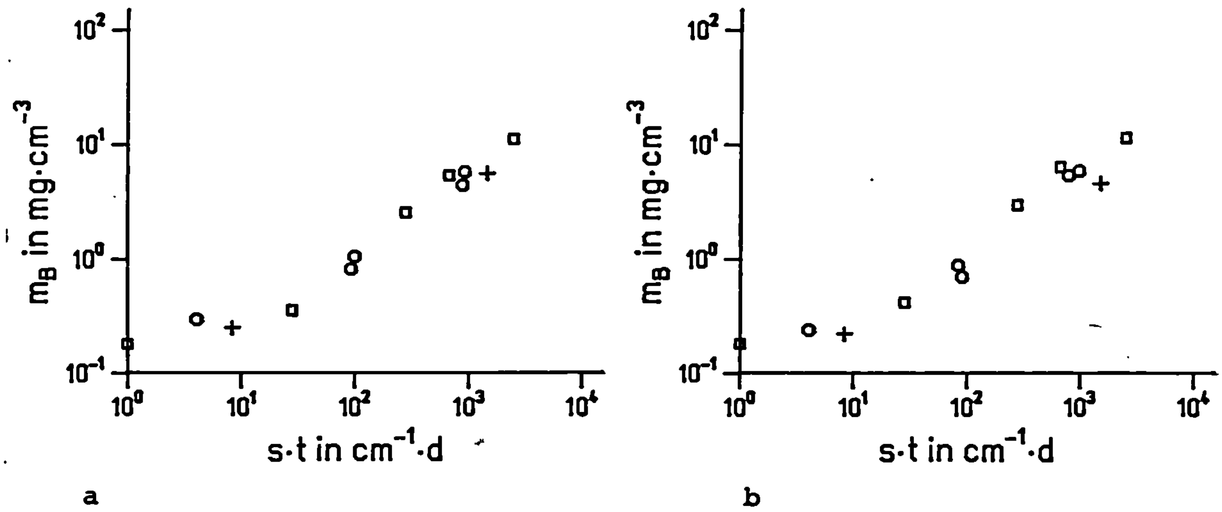

Figure 3. Amount of reacted glass per leachant volume, m_B (determined by boron analysis of leachate) as a function of s•t for the corrosion of the HLW glass SON 68 in solution 1 (a) and solution 2 (b) at 190 °C;
□: 30 d; O : 120 d; + : HMI test

Radiolytic Oxidation

Contractor: UKAEA, Harwell Laboratory, UK
Contract No: FI1W/0029
Duration of Contract: September 1986 - March 1989
Project Leader: F.T. Ewart

A. OBJECTIVES AND SCOPE

Preliminary studies in the UK and USA have suggested that alpha and gamma radiation fields can increase the oxidation state of some elements important to radioactive waste management. This programme will establish the significance of these effects as a mechanism for causing enhanced aqueous concentrations in the near-field of a repository. Because of the flux of radiation necessary to cause these oxidation state changes, the effects are only likely to be found in cemented ILW or vitrified HLW; the programme therefore addresses only these waste forms.

In part of this programme a model of radiolytic effects will be constructed which is compatible with the geochemical codes that are used for modelling repository behaviour. This model will be used to interpret the results obtained in the experimental studies.

B. WORK PROGRAMME

B.1. Effects of gamma irradiation on neptunium and uranium solubility limits
B.2. Electrochemical study of the dissolution of oxides of Tc, Np, Pu and Am.
B.3. Effect of enhanced alpha radiation on the solubility of elements selected by studies under B.2.
B.4. Effect of radiolysis on sorption of Tc, Np and Pu.
B.5. Study of overall effects of radiation, waste, matrix and backfill.
B.6. Effect of colloids.
B.7. Modelling studies.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Further studies on the effect of gamma irradiation on the solubility of neptunium have been made. These have provided more evidence that the irradiation of neptunium(IV) in contact with water below pH12 results in the oxidation of the radionuclide to a more soluble form. Irradiation in concrete equilibrated water above pH12 shows no increase in the concentration of neptunium to levels above the detection limit of 3×10^{-8}M. These studies are near completion. Solubility data for uranium(IV) and uranium(VI) are currently uncertain and gamma irradiations of the U(IV) system have been delayed until improved results are available.

The electrochemical cell has been constructed and has been commissioned inactively. Current effort in this part of the programme is directed at the fabrication of an active working electrode.

The overall effects experiments have been set up and are equilibrating. The analyses of these experiments are scheduled for the beginning of 1989 after approximately one year.

Sorption studies have commenced with a BFS/OPC substrate. The radionuclide chosen for the initial work is technetium. Early results suggest that gamma irradiation of a solution of pertechnetate in contact with 3:1 BFS/OPC under argon results in precipitation of technetium from solution. This behaviour would be characteristic of the reduction of Tc(VII) to a less soluble oxidation state.

Computer based modelling studies of radiolytic oxidation have addressed the need to ensure that the kinetic model, which best describes the process of radiolysis, is also compatible with the thermodynamic approach adopted by most speciation models. The kinetic model has been adapted to simulate a reduced number of reactions representing only thermal chemical processes, under selected conditions corresponding to those in typical thermodynamic modelling using the PHREEQE code. Modelling studies are continuing with the radiolytic effects superimposed on the thermal chemistry for the speciation of plutonium ions.

The current state of work progress is as follows:

B.1. B.2. Progressing normally.
B.3. Delayed, will start early 1988.
B.4. Originally delayed, now progressing normally.
B.5. Progressing normally.
B.6. Not yet started.
B.7. Progressing normally.

PROGRESS AND RESULTS

1). Gamma Irrradiation and Solubility (B.1.)

Neptunium

Work on the gamma irradiation of Np(IV) hydroxides is nearing completion /1/, /2/. All the experiments this year have been sampled by filtration through Amicon Centricon-30 filters (30,000 molecular weight cut-off) and analysed by liquid scintillation counting. A large set of experiments have been irradiated at a low dose rate of $40Gy.hr^{-1}$ by external ^{60}Co sources to an accumulated dose of 1.7×10^{5} Gy over a period of approximately ten months. The results of these experiments are summarised in Table I. The maximum concentration of neptunium obtainable in solution in these experiments was 7×10^{-5}M, some samples approach this level. Irradiation at the high pH of the concrete water failed to raise the concentration of Np above the detection limit of $3 \rightarrow 6 \times 10^{-8}$M and stainless steel appears to play a role in decreasing the concentration in other waters. Neptunium(IV) has also been precipitated from solution in the presence of sodium dithionite as a holding reductant to minimise any possibility of oxidation prior to irradiation. Irradiation of this solid in bentonite water under argon confirms previous results; the solution level rises as the total dose increases. These results are summarised in Table II.

2. Sorption (B.4)

Solutions of technetium(VII) in contact with a representative grouting composition of 3:1 BFS/OPC have been gamma irradiated. Solid/liquid separation is performed by filtration through Amicon Centricon-30 filters and samples analysed for technetium by liquid scintillation counting. Irradiation under argon to an accumulated dose of 4.3×10^4 Gy results in precipitation of Tc from solution and results in artificially high distribution ratios of up to 4×10^5ml g^{-1}, calculated from the loss of radionuclide from solution. If air is present during irradiation low values for R_d of 4→40ml g^{-1} are obtained, these are similar to values for unirradiated experiments under air or argon. This behaviour suggests that pertechnetate, irradiated in solution under argon, in contact with BFS/OPC, is being reduced to a less soluble form. These initial results may mean that oxidation of Tc in the lower oxidation states in gamma fields is unlikely to occur for waste encapsulated in BFS/OPC matrices.

3. Overall Effects (B.5)

The overall effects experiments, which simulate the near-fields of representative intermediate and high level waste repositories, have been started. A total of 20 experiments have been mounted in stainless steel vessels. Some modifications were made to the conditions proposed in the original technical annex due to the delay in commencing this part of the programme. The hydroxides of the radionuclides (Tc, Pu, Np) were used rather than the oxides to enable the system to equilibrate more rapidly. It was originally hoped to use ratios of materials eg. bentonite:glass which would be related to those proposed for the 'Round Robin' leach test. Due to the smaller scale of our experiments the ratio of water to solids has been increased to guarantee sufficient recovery of the aqueous phase for analysis at the conclusion of the experiments.

4. Modelling Studies (B.7)

The computer based modelling studies have concentrated on relating the kinetic model of radiolysis to the thermodynamic equilibrium models which are commonly used to simulate the thermal chemistry of radionuclide ions. The thermodynamic model chosen for comparison was the PHREEQE code, as specified in the programme technical annex, section 2.1. The radiolytic model which had been developed during 1986 for plutonium speciation included a comprehensive set of thermal and radiolytic processes, with reaction rate constants based on literature values for radionuclide species /3/ and water radiolysis /4/. This model was stripped of all radiolytic processes and the thermal reaction rate constants were re-evaluated to be consistent with the equilibrium constants given in PHREEQE /5/. The control of Eh by notional species was also included. Results of a PHREEQE simulation for a plutonium solution under typical conditions were replicated exactly by the kinetic model. The simulations included, optionally, interaction of solution species with solid (mineral) phase compounds or purely solution chemistry. With this compatibility assured, the radiolytic model has been revised and work is in progress on combined radiolytic and thermodynamic simulations. Preliminary indications are that a γ dose rate of 500 Gy. hr^{-1} causes appreciable changes in plutonium speciation.

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Table I

Irradiation of Np(IV) Hydroxide, Low Dose Rate ((i),(ii))

Water	Solid Present	Amount of Solid /g	pH After Irradiation	Eh/mV vs H_2 after Irradiation	Filtered [Np]/M	Unfiltered [Np]/M
Bentonite	None	-	8.5	+340	4×10^{-6}	6×10^{-5}
	Bentonite	0.1	8.9	+370	3×10^{-5}	9×10^{-5}
	Bentonite	0.1	8.8	+380	4×10^{-5}	9×10^{-5}
	Stainless steel	1.0	8.5	+200 → -70	8×10^{-7}	4×10^{-5}
Concrete	None	-	12.5	+220 → +20	$<6 \times 10^{-8}$	$<6 \times 10^{-8}$
	Concrete	1.0	12.7	+160 → - 80	$<6 \times 10^{-8}$	$<6 \times 10^{-8}$
	Concrete	1.0	12.4	+170 → - 30	$<3 \times 10^{-8}$	$<4 \times 10^{-8}$
	Stainless steel	1.0	12.6	+170 → - 330	$<3 \times 10^{-8}$	2×10^{-6}
Granite	None	-	8.3	+70	2×10^{-6}	5×10^{-5}
	Granite	1.0	8.8	0 → -60	5×10^{-7}	3×10^{-5}
	Granite	1.0	8.6	+180 → +160	7×10^{-6}	4×10^{-5}
	Stainless steel	1.0	8.2	-95 → -85	3×10^{-7}	4×10^{-5}
AnalaR + NaOH	None	-	7.9	+370 → +300	2×10^{-7}	4×10^{-5}
	Stainless steel	1.0	8.1	-20 → -30	6×10^{-7}	4×10^{-5}
	Stainless steel	1.0	8.0	+170 → +60	2×10^{-6}	3×10^{-5}
	Stainless steel	1.0	11.6	-360 → -490	2×10^{-6}	4×10^{-5}

Notes

(i) Dose rate = 40 Gy/hr

(ii) Accumulated Dose = 1.7×10^5 Gy

(iii) Many redox measurements were unstable showing a slow drift, this is indicated in the table

Table II

Gamma Irradiation of Np(IV) Precipitate*

Water	Dose /kGy	Final pH	Final Eh/mV	Filtered [Np] /M
Bentonite	0	9.5	+250	<3.2 x 10^{-8}
		9.6	+240	<3.2 x 10^{-8}
	6.2	9.3	+560 → +320	2.5 x 10^{-6}
		9.2	+460 → +330	3.5 x 10^{-6}
	12	8.0	+600	3.9 x 10^{-6}
		8.0	+600	7.4 x 10^{-6}
	19	8.5	+630	1.3 x 10^{-5}
		8.5	+620	9.7 x 10^{-6}
	25	8.7	+600	1.2 x 10^{-5}
		8.7	+600	1.2 x 10^{-5}
	36	8.7	+300	1.8 x 10^{-5}
		8.5	+300	1.5 x 10^{-5}
Concrete	0	11.1	+380	<3.2 x 10^{-8}
		11.1	+380	<3.2 x 10^{-8}
	48	10.5	+550	5.5 x 10^{-6}
		10.1	+450	1.4 x 10^{-6}

Dose rate = 0.26 kGy hr^{-1}

* Neptunium(IV) precipitated in the presence of sodium dithionite as holding reductant.

Table III

Sorption of Technetium on 3:1 BFS/OPC

Size[1] Range	Atmos.	Total Contact Time/ Days	Irrad. Time/ Hrs.	Dose /kGy	Starting Concn. of Tc/M	Final Conc. of Tc/M	R_d[2] /ml.g^{-1}
F	Air	1	-	-	7.4×10^{-5}	4.5×10^{-5}	13
		1				3.5×10^{-5}	23
		7				4.9×10^{-5}	10
		14				3.8×10^{-5}	19
		14				3.9×10^{-5}	19
C	Ar	9	-	-	7.8×10^{-5}	5.8×10^{-5}	7
		9				5.6×10^{-5}	8
F		9				3.4×10^{-5}	25
		9				3.2×10^{-5}	28
C	Air	19	170	44	7.5×10^{-5}	6.2×10^{-5}	4
		19				5.9×10^{-5}	5
F		19				2.5×10^{-5}	41
		19				3.1×10^{-5}	28
C	Ar	14	167	43	7.8×10^{-5}	4.6×10^{-9}	3.4×10^{-5}
		14				3.9×10^{-9}	4.0×10^{-5}
F		14				3.0×10^{-7}	5.2×10^{-3}
		14				6.4×10^{-6}	2.2×10^{-2}
C	Ar	9	97	25	7.8×10^{-5}	1.0×10^{-5}	1.3×10^{-2}
		9				8.2×10^{-6}	1.7×10^{-2}
F		9				3.9×10^{-5}	19
		9				3.3×10^{-5}	27

Notes

(1) F = fines, size range <0.125 mm
C = coarse material, size range 2-5 mm

(2) Values of distribution ratios for irradiated experiments under argon may be artificially high due to precipitation of technetium

BASIC MECHANISMS OF AQUEOUS CORROSION OF WASTE GLASSES

Contractor: CEA, CEN-Valrho, SDHA, F
Contract No: FI1W-0030
Duration of Contract: August 1986 - July 1989
Project Leader: N. Jacquet-Francillon

A. OBJECTIVES AND SCOPE

Although a major research effort has been undertaken during the last decade on aqueous corrosion of nuclear glasses |1| |2| our understanding of the basic corrosion mechanisms is essentially phenomenological and many important questions remain unanswered. This understanding is indispensable to ensure that the mechanisms taken into account in corrosion models correspond effectively to those governing the long term release of radionuclides.

The experiments proposed here are parameter studies of simple glass-water systems designed to investigate the effects of saturation, leaching under hydrothermal conditions, corrosion at the interface layer, and the behavior of technetium and the actinides.

B. WORK PROGRAM

B1 Investigation of the apparent solubility limit of SON 68 glass for different SA/V values. (Are the steady-state concentrations in solution related to the glass itself, to the gel or to newly formed crystalline phases?)

B2 Hydrothermal leaching and analysis of the crystalline phases formed between 50°C and 250°C.

B3 Examination of the interface or ionization layer between the surface layers and the sound underlying glass.

B4 Determination of the concentration profiles in the surface layers for the principal actinides.

B5 Filtration study of the physicochemical form in which plutonium is found in the leachates.

B6 Investigation of technetium behavior.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

- Solubility: The experiments were conducted for a full year, and have now been completed. A true solubility limit was not reached in any case since the silicon concentration continued to increase slightly. At high values of (SA/V x time), corrosion rates as low as 5×10^{-4} $g \cdot m^{-2} d^{-1}$ were measured.

- Hydrothermal Leaching: The experiments at all three temperatures have been completed. At 50°C, 150°C and 250°C corrosion was found to progress in a linear manner. A large number of newly formed crystalline phases were observed at 250°C as well as very extensive sample deformation.

- Corrosion Front: The initial transmission electron microscope examinations showed that the "corrosion front" obtained by Soxhlet leaching was less than 500 Å thick.

- Actinide Concentration Profiles: Under Soxhlet conditions most of the plutonium and americium were confined in the surface gel layer although a solubility limit did not appear to be reached in solution. Leachate filtration studies have not yet begun.

- Technetium Leaching: The experiments with durations up to 91 days have been completed; others lasting up to one year are still in progress. In oxidative conditions, technetium was found to be a mobile element both in distilled water and in "Volvic" mineral water.

Progress and Results

1. Solubility (B.1)

A new series of experiments was undertaken at 90°C at three different SA/V ratios, with three specimens in each case placed in sealed tubes to prevent water loss. The experimental duration was extended to one year.

The results confirm that the silicon concentration in solution is highly dependent on the SA/V ratio. This was attributed to SA/V-related changes in the pH. Results expressed as the product of (SA/V x time) thus differ for each SA/V ratio considered (Figure 1).

Nevertheless, no true silicon solubility limit was reached, even at SA/V ratios as high as 8000 m^{-1}: the solution is therefore not in equilibrium with the glass, the gel or a neoformed silicate phase. Extremely low corrosion rates were obtained under these conditions (Table I) indicating that the long-term rate obtained with low (SA/V·t) values may be overestimated.

2. Hydrothermal Leaching (B2)

The experiments involved alteration of monolithic specimens with a large surface area (SA/V = 350 m^{-1}) in "Volvic" water at 50, 150 and 250°C under a pressure of 10 MPa.

- Solution Analysis Data: The results are shown in Figure 2. The most notable finding is the linear evolution of the corrosion at all three temperatures after the usual slowdown during the first few days. Comparable results were obtained in double distilled water |2| suggesting that perhaps this linear corrosion corresponds to a glass hydration mechanism independent of the solution concentration.

- Identification of Neoformed Mineral Phases: No crystals were observed by optical or electron microscopy on the sample leached at 150°C although X-ray analysis using a linear localization detector showed minute amounts of minerals from the analcime-pollucite series together with hydrated calcium silicates (3.04 Å and 2.34 Å lines could not be positively identified).The 250°C specimen showed significant crystallization under optical and electron microscope observation, and the following species were identified by X-ray diffraction: minerals of the analcime-pollucite series, gyrolite and okenite (hydrated calcium silicates), and clayey materials resembling smectite (12.5 Å reflections). It may be noted that crystal development was considerably higher in Volvic mineral water than in double distilled water for the same time and temperature.

3. Corrosion Front Examination (B3)

Ultramicrotome samples were prepared for transmission electron microscopic examination of the surface layer on a sample leached for 28 days under Soxhlet conditions. This technique provides sufficient resolution to analyze points only 200 Å apart. No transition was observed between the glass and the gel layer, only a clear separation at nanometer scale. The analysis findings at 200 Å on the glass side of the interface indicated the same composition as the bulk glass.

The thickness λ of the corrosion front can be expressed simply by the following relation: $\lambda = D/V$, where D is the mobile element interdiffusion coefficient and V is the glass corrosion rate. Since V is very high in Soxhlet experiments, it is not surprising to find an extremely thin corrosion layer.

The remainder of the program will investigate static leaching samples with high SA/V ratios for which the corrosion rate V is several orders of magnitude lower, and on which the interface layer should be substantially thicker.

4. Actinide Concentration Profiles (B4)

Four SON 68 glass samples doped with 0.85 wt% of ^{237}Np, ^{239}Pu, ^{238}Pu and ^{241}Am oxides were leached for 28 days under Soxhlet conditions. The surface layers were generally similar to those obtained on inactive samples, comprising an inner layer enriched in Zr, La, Ce, Nd, Cr, P, Mn and Fe, and an outer layer also enriched in Mn, P and Fe but especially in Ni, Cr, Zn and Al.

The actinides were found in both layers, but primarily in the inner layer. The actinide enrichment was much higher for Pu and Am than for neptunium. The slight differences observed between ^{238}Pu and ^{239}Pu may be attributable to radiolysis, and will have to be confirmed by another series of tests before any conclusions can be drawn.

5. Technetium Leaching (B6)

Samples with a 50 m^{-1} SA/V ratio were leached under static conditions in teflon containers. The results are summarized in Table II. In oxidative conditions the technetium leach rate exceeded the overall mass leach rate: technetium therefore behaves like a mobile element.

The technetium and mass leach rates in Volvic water were lower during the first few days. This may be explained by the initial silicon concentration in solution which is about 23 ppm in Volvic water. After 28 days the mass leach rates were identical and no significant difference in technetium behavior attributable to the nature of the water was observed.

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Table I - Final Rate after 1 Year at 90°C versus SA/V Ratio

SA/V (m^{-1})	$g \cdot m^{-2} d^{-1}$	
50	0.0090)	ref |1|
350	0.0030)	
400	0.0012)	this study
2000	0.0004)	
8000	0.0006)	

Table II - Technetium Leaching at 90°C: Normalized Mass Loss ($g \cdot m^{-2} d^{-1}$)

Duration (days)	Technetium		Mass Loss	
	Distilled Water	Volvic	Distilled Water	Volvic
3	0.21	-	0.13	-
7	0.43	0.22	0.20	0.07
14	0.16	-	0.10	-
28	0.09	0.14	0.05	0.05
56	0.05	-	0.03	-
91	0.04	0.05	0.024	0.02

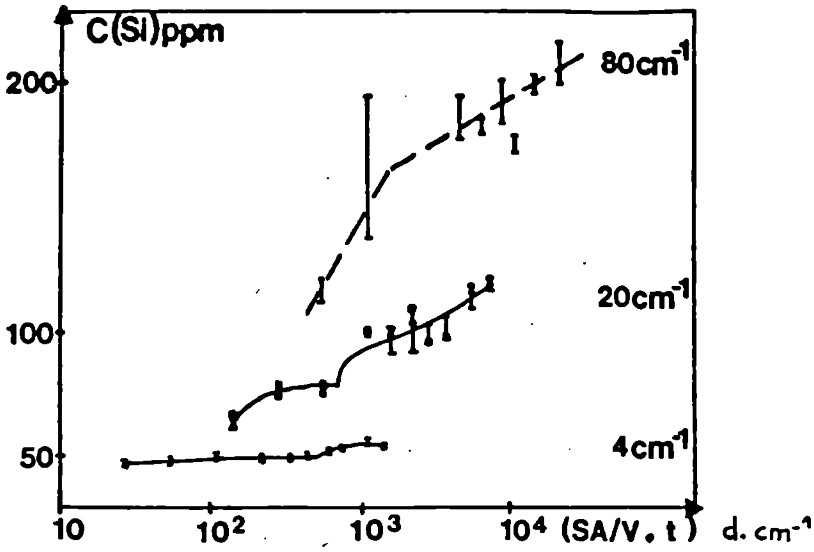


FIGURE 1 : SILICON CONCENTRATION VERSUS (SA/V.t) FOR DIFFERENT SA/V RATIOS (2nd TEST SERIES)

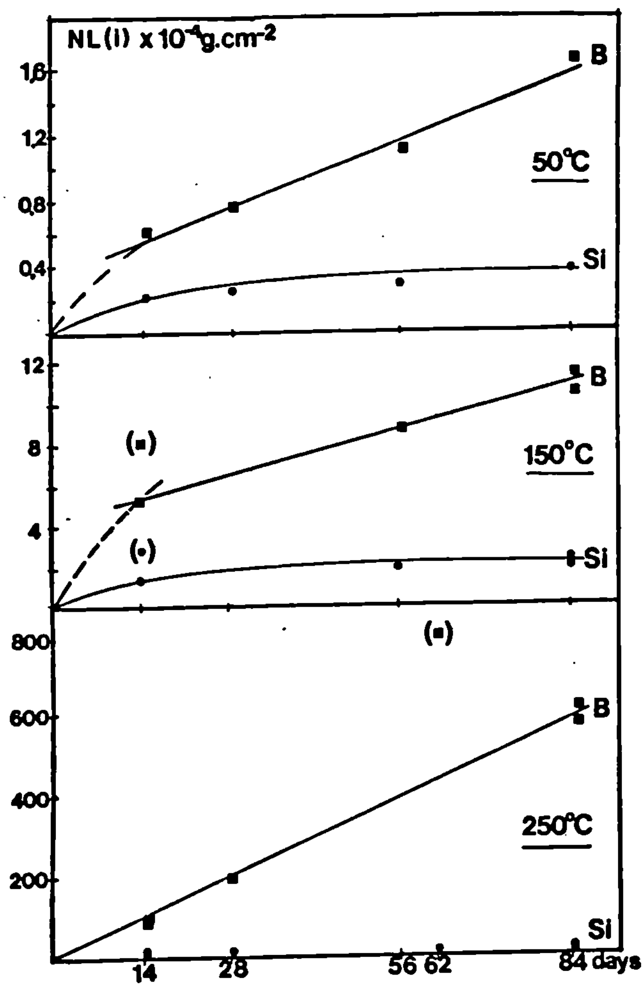


FIGURE 2 : NORMALIZED MASS LOSS FOR BORON AND SILICON AT 50°C, 150°C, AND 250°C

TESTING THE ALTERATION OF WASTE GLASSES UNDER GEOLOGICAL STORAGE CONDITIONS

Contractor:	CEA, CEN-Valrho, SDHA, F
Contract No:	FI1W-0096
Duration of Contract:	September 1986 - August 1988
Project Leader:	N. Jacquet-Francillon

A. OBJECTIVES AND SCOPE

A large number of parameters must be taken into account to predict glass alteration behavior in a geological repository: flow rate, temperature, pressure, pH, Eh, CO_2 content, radiolysis, water composition, nature of the surrounding rock, backfill material, possible corrosion products, etc. Laboratory parameter studies have been conducted for many years and are indispensable to an understanding of the glass alteration mechanisms and the effects of each parameter. However, none of the parameters is independent of the others and although investigating them separately is not sufficient, a systematic study of all possible combinations would be prohibitive. Under these circumstances parameter experiments must be completed by integral tests which simulate all of the parameters of a granitic repository as realistically as possible.

The objective of this program is to conduct a series of integral leaching experiments meeting this criterion. The program is expected to provide information in the following areas:

- equilibrium concentrations which tend to occur when all of the environmental materials are present;
- glass alteration rate under steady-state conditions;
- effect of smectite (considered for storage in France) on glass alteration: previous experiments showed the determining effect of the nature of the clay used as a backfill material;
- identification of newly formed compounds under integral test conditions;
- actinide behavior in a complex geological medium: leaching rate and physicochemical form.

B. WORK PROGRAM

B1 Two non-radioactive experiments with simulated SON 68 glass using monolithic and fractured blocks to simulate an industrial glass block.

B2 Four experiments with alpha-doped glasses: the glass samples will be spiked with uranium-thorium, neptunium, plutonium and americium, respectively.

B3 Four mini-experiments with moist clay on nonradioactive glass and on plutonium-doped glass.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

SON 68 18 17 L1C2A2Z1 glass was leached for 18 months under integral conditions simulating a granitic repository with an engineered barrier of sand and smectite backfill. Initial results include the following:
- Contrary to what was observed in pure water, glass corrosion progressed for 16 months although the total silicon concentration quickly reached a steady-state value. The corrosion rate diminished considerably after 16 months.
- Extensive fracturation of the glass block (x12) led only to a slight (x1.4) increase in the quantity of corroded glass.
- The actinide concentration in solution appeared to diminish in time, probably because of a very low release rate together with strong fixation on the environmental materials.
- The apparent leach rates were lower than for mobile elements in the glass matrix by two orders of magnitude for Np, three orders of magnitude for Pu and five orders of magnitude for Am.
- The glass was significantly altered in moist clay (about 15 times more than in pure water after 28 days at 90°C) and the plutonium retention factor in the layer was much lower.

The current status of the work program is as follows:
- B1: Two thirds of the experiments are nearing completion; the results remain to be examined.
- B2: All the experiments are nearing completion.
- B3: All the experiments have now begun.

Progress and Results

1. Inactive Experiments (B1)

Three inactive experiments have been undertaken: one on a monolithic glass block (TAV 7 - 2 years) and two others with fractured blocks (TAV 9 - 3 years, and TAV 11 - 8 months). The fracturation ratio was estimated at 12:1 based on granulometric screening of a fractured glass block, and Soxhlet leaching tests are now in progress with other samples to confirm this value.

Results: Results covering the first 18 months are now available for TAV 7 and TAV 9. Most of the concentrations reached virtually steady-state values after 4 months of leaching (Figure 1). The ratio of the boron and molybdenum concentrations between the fractured and unfractured tests was constant at about 1.4:1. When the potential leaching surface area was increased by a factor of 12 after fracturing, the altered glass quantity increased in far lower proportions. Two explanations may be advanced for this phenomenon: the corrosion rate may be controlled by a solubility limit, or the cracks may quickly be obstructed by the development of the altered layers. Morphological analyses are planned in this area.

2. Alpha-Doped Glass (B2)

Four tests were carried out: TAV 12 (an inactive control specimen), TAV 13 (^{237}Np-doped glass), TAV 14 (^{239}Pu) and TAV 15 (^{241}Am). All four experiments will be terminated at the end of January 1988 after eighteen months of leaching time.

Results: The pH was constant throughout the test: alpha radiolysis related to the high specific activity of the americium-doped glass did not have a significantly long term effect on the pH.

The activity values measured on the filter and filtrate are indicated in Table I. The specific activity was relatively constant for TAV 13 (^{237}Np) and TAV 14 (^{239}Pu). In test TAV 15 (^{241}Am) the activity was very low except for the first two days: this may have been due to slight contamination, or americium may be fixed more quickly by the environmental materials than it is leached from the glass.

The apparent actinide leach rate in a simulated granitic repository environment was the same as in double distilled water:

$$L(^{241}Am) < L(^{239}Pu) < L(^{237}Np).$$

3. Moist Clay (B3)

The same experimental device was used as for contract No 30 (90°C at 10 MPa). All the planned tests have now begun. Seven durations were selected for the inactive tests: 14 & 28 days, 2, 3, 4, 5 and 6 months. Three radioactive tests have also been initiated with ^{239}-doped glass. Preliminary tests conducted with different smectite/water ratios showed that the thickness of the alteration layer was virtually the same after 28 days.

Results

- Inactive Tests: Results are available for 14, 28 and 60 days. The mass loss values indicate a practically constant daily leach rate (1.0×10^{-4} $g \cdot cm^{-2} d^{-1}$). The altered layer was 10 to 20 microns thick after one month on polished cross sections observed under a scanning electron microscope, and similar in appearance to the layer formed after 28 days of Soxhlet leaching at 100°C.

- Radioactive Tests: After 28 days the doped glass was significantly altered and little plutonium retention was observed in the surface layer. The mass loss $NL_{(m)}$ was 28×10^{-4} $g \cdot cm^{-2}$ and the Pu retention factor $FR = NL_{(m)}/NL_{(Pu)}$ was 5.4. The clay had to be rinsed several times to recover the activity trapped by the moist smectite (Table 2) which seems to have a high Pu retention capacity.

Table I - Radioactive Test:
Filter and Filtrate Activity (in Becquerels)
Referenced to 1 cm^3 of Solution
(C = conditioning pot; L = leaching pot)

Durée en mois		^{237}Np		^{239}Pu		^{241}Am	
		C	L	C	L	C	L
0	Filtrat	0,09		0,03		⩽0,01	
	Filtre	⩽0,01		0,05		0,74	
2	Filtrat	2,15	0,11	⩽0,02	0,89	0,70	0,56
	Filtre	⩽0,01	1,22	<0,01	52	18,5	27
4	Filtrat	⩽0,013	0,96	⩽0,02	1,3	1,26	0,85
	Filtre	⩽0,01	0,56	0,06	23	0,89	16
6	Filtrat	⩽0,01	1,22	0,78	3,4	0,74	2,2
	Filtre	0,03	0,96	1,85	30	0,70	1,3
8	Filtrat	⩽0,01	0,89	⩽0,01	2,8	<0,01	1,2
	filtre	⩽0,01	0,22	<0,01	37	<0,01	0,96
10	Filtrat	⩽0,01	<0,07	⩽0,01	1,8	<0,01	0,85
	Filtre	<0,10	5,55	⩽0,10	55	⩽0,40	8,5
12	Filtrat	⩽0,01	0,67	⩽0,10	2,0	⩽0,07	1,4
	Filtre	⩽0,10	2,41	⩽1	81	⩽0,40	7,8
14	Filtrat	⩽0,01	0,56	<0,01	1,4	<0,01	1,0
	Filtre	<0,01	0,17	0,05	4,1	<0,01	0,4

Table II - Moist Clay Experiments:
Activity Recovered during Successive Rinses

1st sample rinse (water only)	96.2 Bq
2nd sample rinse (water + brush)	174 10^3 Bq
Leaching pot rinse	1.7 x 10^3 Bq
1st clay rinse	91.8 x 10^3 Bq
2nd clay rinse	56.6 x 10^3 Bq
3rd clay rinse	57.3 x 10^3 Bq
Total recovered activity:	381 x 10^3 Bq

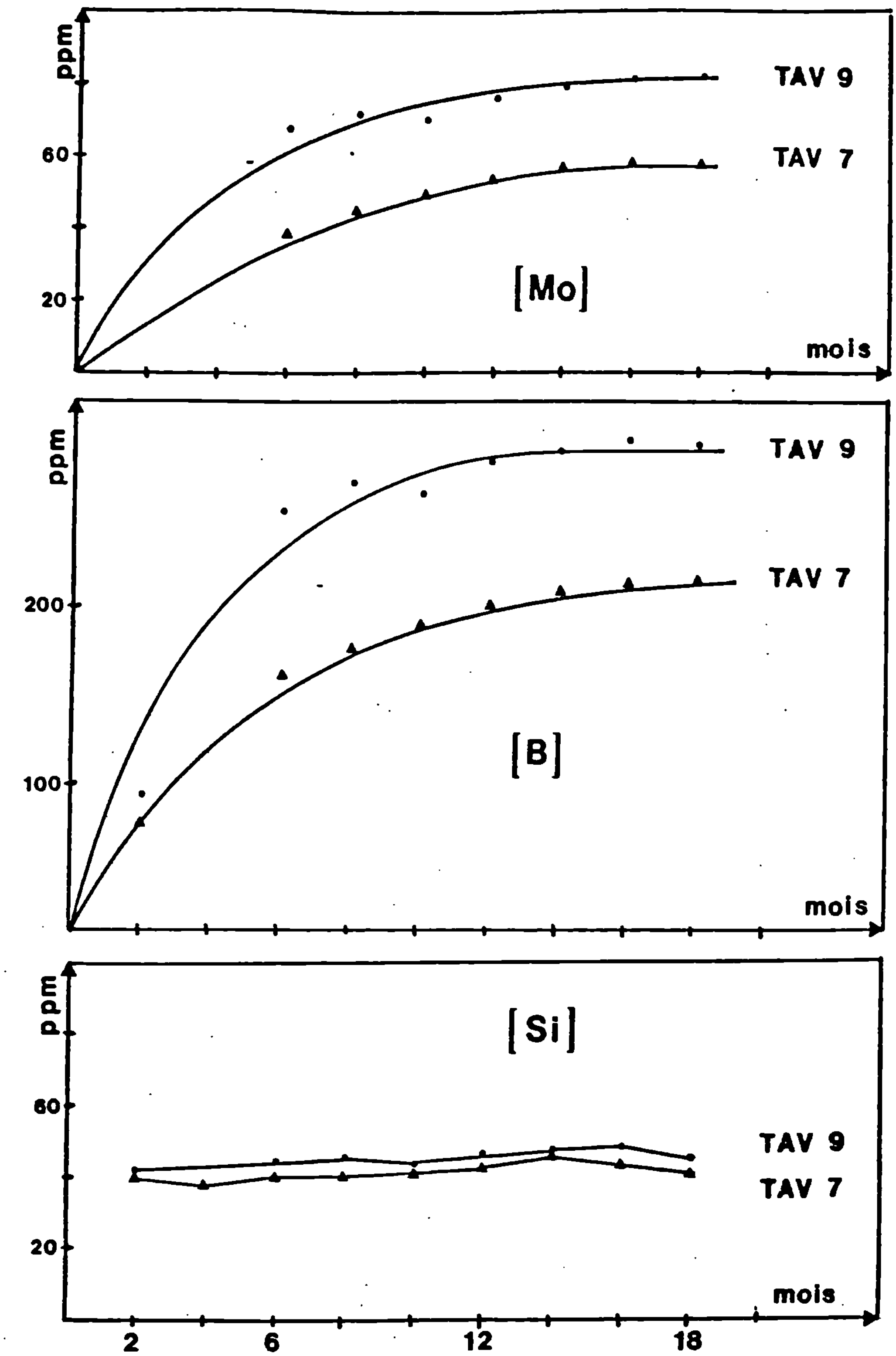


Figure 1 - Inactive Tests
Evolution of Si, B and Mo Concentrations in the Leaching Pot

Radionuclide Release from Solidified High Level Waste

Contractor: UKAEA. Chemistry Division, Harwell Laboratory, UK.
Contract No: FI.1W.0097.UK(H)
Duration of Contract: July 1986 - December 1989
Project Leader: J.A.C. Marples

A. Objectives and Scope

The aim of the research is to ensure that vitrified waste forms in general and the UK's reference glass MW in particular are suitable for eventual disposal in either hard-rock or clay.

Studies are in progress of the leaching behaviour of these glasses and the release of radioisotopes from them. In particular, measurements have been made of the concentrations, under a range of conditions that could occur after disposal, of the radiologically important elements Tc, Np, Pu and Am. It is assumed that the release of these elements from the repository must be less than this concentration multiplied by the water flow-rate through the repository.

Studies are also in progress of the glasses radiation stability to ensure that this will not cause problems.

B. Work Programme

B.1. Leaching behaviour of reference materials and solubility of selected radioisotopes.
B.2. Effect of radiation and radiolysis.
B.3. Effect of product quality on the release rate.

C. Progress of work and results obtained

Summary

Using doped glasses, the concentrations of Tc, Np, Pu and Am have been measured, over a period of a year, in equilibrium with the various possible components of a future repository for vitrified high-level waste. In most of the experiments, the conditions were made to be reducing as they are expected to be so after disposal. These equilibrium concentrations have been found to be comparable to, but usually somewhat greater than the 'limiting concentrations' which, in drinking water, would lead to an annual dose of 1mSv. Initial concentration measurements from a similar experiment using fully-active waste, were somewhat higher than those from the doped glasses for Np and considerably so for Am and Pu.

The density of Pu-238 doped MW glass is decreasing on an exponentially saturating curve in a similar way to that shown by other similar glasses. The predicted linear expansion at saturation is 0.14%. The leach rate of the glass decreases slightly with radiation dose.

The general progress of the work is as follows:

. B.1. and B.2. are progressing normally.

. B.3. The technical necessity for this section is being considered. The product quality was found not to affect the leach rate and so is unlikely to affect the equilibrium concentrations that will determine the release rate.

Progress and results

1. Leaching behaviour of reference materials and solubility of selected isotopes

One possible scenario for the disposal of the vitrified waste is as follows: the steel canisters in which the glass is cast will be surrounded by an overpack of thick cast iron or thin Ti alloy. The overpacked cylinders will be emplaced in galleries or boreholes deep undeground and held in place with a backfill either of clay or of a Portland-cement concrete. This backfill will restrict the access of water and, particularly in the cement-based case, will condition the water to a high pH. The overpack will will be expected to protect the vitrified waste for several hundred years until the activity of the main fission products (Cs-137 and Sr-90) has decayed away. In the period between a few hundred and many thousands of years, potentially the most hazardous radioactive elements in the vitrified high-level waste are Am, Pu, Np and Tc.

The release of one of these elements from the repository cannot be greater than the product of the water flow through it, multiplied by the 'equilibrium concentration' of that element. This equilibrium concentration is the concentration of the element in the presence of all the components of the repository and will result from a combination of the solubility and sorption of that element.

Samples of glass were made up containing a full inactive simulate of the high-level waste. These were doped with isotopes of the four radioelements and after crushing (to speed up the approach to equilibrium) were mixed with possible components of the repository and with water and loaded into capsules. The loading was carried out in an argon - 5% hydrogen filled glove-box to enable the reducing conditions, that will occur in a repository, to be established. The capsules were held in an oven at, normally 60°C, for periods of up to a year before they were opened and the water overlying the solids sampled and analysed.

The results for each element are compared below with the 'limiting concentration' (LC). This is the concentration of the element which in drinking water would lead to an annual radiation dose of 1mSv to someone drinking 2 litres per day. For the four radioactive elements these are:

Tc-99: 6.5×10^{-8} molar

Np-237: 2.0×10^{-10} molar

Pu-239(80%) + Pu-240(20%): 1.7×10^{-12} molar

Am-241: 4.6×10^{-14} molar.

For Tc, the observed concentrations in the repository simulation tests were below the limiting concentrations when conditions were reducing and when iron filings were used to represent the overpack. Under oxidising conditions or with a titanium overpack the equilibrium concentration ranged up to about 150 times the limiting value. The presence of iron appeared to be important, suggesting the possible formation of a Tc-Fe compound or complex.

For neptunium, the observed concentrations were slightly higher than the limiting value when a cementitious backfill was used. With a clay or bentonite backfill, the concentrations were up to a few hundred times higher.

For plutonium, the concentrations were below the limiting value for both cement and bentonite backfills. The only occasion when a significantly higher value occurred (10xLC) was when a clay backfill was used, which gave a pH of only 5.5.

The concentrations found for americium were about 40 to 80 times the limiting value with, again, the clay backfill and, to a lesser extent, the bentonite backfill giving higher results (up to 4000xLC).

The initial results of a similar test using fully-active glass with a cementitious backfill have given rather higher concentrations for the three actinides: Neptunium: 15xLC, plutonium: 10xLC and americium: 180xLC.

In addition to the equilibrium concentration measurements, a coupon of glass was also included in some of the capsules so that the mass-loss leach rates could be measured. After 12 months, the value with a bentonite backfill was $3 \times 10^{-6} g.m^{-2}.sec^{-1}$, a little more than would be observed in an MCC-1 test. With most cementitious backfills, the results were 10x lower than this whilst with a cement-fuel ash backfill the leach rate was at least 400x lower, ie less than $10^{-8} g.m^{-2}.sec^{-1}$.

The density of the UK reference glass MW, doped with 2.5.% Pu-238, has continued to decrease with radiation dose, giving a predicted linear expansion at saturation of 0.14%. The leach-rate has actually also decreased slightly wth radiation dose but only by about the amount of the expected precision of the results.

LONGTERM BEHAVIOUR OF TRU-WASTE BEARING CERAMICS

Contractor	:	Kernforschungszentrum Karlsruhe GmbH / FRG Institut für Nukleare Entsorgungstechnik (INE)
Contract N°	:	FI1W/0098-D (B)
Working Period.	:	January 1987 - December 1987
Project Leader	:	A. Loida

A. OBJECTIVES AND SCOPE

Alumosilicate-based ceramics are suitable matrix materials for the immobilization of TRU-waste. The feasibility of this conditioning method has been demonstrated by synthesizing alumosilicate ceramics, loaded with original TRU-waste up to 20 wt.-% on lab-scale. The final products consists of a mixture of mullite ($Al_6Si_2O_{13}$) and corundum (Al_2O_3), as well as actinide oxides and fission product alloys and oxides. The leach rates for actinides show values between 10^{-8} and 10^{-9} g/cm²d after the ISO-draft.

Aim of the current programme is to get information on the long time behaviour of such ceramics with respect to radiation and hydrolytic influences.

Changes in microstructure and hydrolytic stability as a function of long storage time, induced by high α-dosis and thus accelerating mutual interactions, will be recorded.

The goal of this programme is achieved by performing "time-lapse" experiments. That means doping the ceramics with a short-living α-emitting radionuclide, so the desired high α-dose is transmitted to the matrix within short times.

B. WORK PROGRAMME

B.1 : Synthesis of samples:
- ceramics (type KAB 78), loaded with 30 wt.-% of dissolver residues
- ceramics (type KAB 78), loaded with 20 wt.-% of $Pu(238)O_2$.

B.1.1 : Preparation of these samples for ceramographic and leaching investigations.

B.2 : Characterization of these samples as a function of time (α-dosis).

B.3 : Leaching of these samples at elevated temperature in Q-brine.

B.4 : Characterization of these samples after the leaching experiments and after reaching the α-dosis required.

C. PROGRESS OF WORK AND RESULTS OBTAINED

1. Synthesis and Preparation of Samples (B.1, B.1.1)

Due to its availability, Plutonium(-238)O_2 with an amount of 20 wt.-% has been incorporated into the ceramic matrix, which consisted of a mixture of 66 wt.-% reactive corundum, 17 wt.-% kaolinite, and 17 wt.-% bentonite. Another series of specimens for comparing investigations consisting of the same type of matrix, loaded with 30 wt.-% of dissolver residues from the reprocessing of fast breeder reactor fuel has been prepared simultaneously. In both cases, the firing temperature was 1300°C.

Density, open porosity and α-activity have been determined as follows:

ceramic KAB 78

Loaded with	20 wt.-% $Pu(-238)O_2$	30 wt.-% dissolver residues
density	3.63 g/cm³	3.43 g/cm³
open porosity	< 2 vol%	< 2 vol%
specific α-activity	1.0 E11 Bq/g (2.733 Ci/g)	1.33 E9 Bq/g (0.036 Ci/g)

2. <u>Sample Characterization (B.2)</u>

The ceramographic sample characterization has been performed by means of X-ray-diffractometry, optical and electron microscopy. The crystalline phase compositions has been determined as

- corundum (Al_2O_3), mullite ($Al_6Si_2O_{13}$) and PuO_2, considering the ceramic KAB 78 containing 20 wt.-% $Pu(238)O_2$,
- corundum (Al_2O_3), traces of mullite ($Al_6Si_2O_{13}$), $(U,Pu)O_2$, ε-phase and RuO_2 with respect to the KAB 78 ceramics containing 30 wt.-% of original dissolver residues.

During the first year the internal absorbed α-dose of the Pu(238) ceramics reached 2.80 E 11 rads. At the beginning, in the middle and at the end of the year the data of the X-ray-peaks of the Pu(238) ceramics were reanalyzed with respect to the α-values, peak aereas, intensity factors and half-width-values. In function of time no significant changes of these data could be found so far.

By means of electron microscopy well selected regions of the "time-lapse" sample have been recorded with emphasis on the registration of their pores′ and cracks′ dimensions and their elemental distributions in function of the increasing internally absorbed α-dose.

3. <u>Leaching Tests (B.3</u>

A series of leaching tests after the ISO-draft have been performed, using the KAB 78 Pu(238) ceramics. The average leachrate for plutonium was found to be about 1 E-7 g/cm²d after a total leaching time of 160 days, using Q-brine and distilled water as leaching solutions.

Leaching and corrosion experiments with these samples at 200°C, using autoclave technique have already been started. The first run having had a duration of six weeks has just come to an end.

CHARACTERIZATION OF HLW GLASS SAMPLES

Contractor: HMI, Berlin, FRG
Contract N°: FI1W-0099-D(B)
Working Period: October 1986 - December 1989
Project Leader: G. Malow

A. OBJECTIVES AND SCOPE

In the frame of the two preceding European joint programs on "Testing and Evaluation of the Properties of Various Potential Materials for Immobilizing Highly Radioactive Waste" starting in 1975 a lot of data on the characterization of simulated solidified high level waste forms has been acquired. Thermal, mechanical and radiation stability and the chemical stability under the attack by various aqueous media were tested. The experiments have been performed under waste repository relevant conditions and under simplified laboratory conditions selected to investigate the corrosion mechanism. In the present research program the fully radioactive Cogema glass R7T7 proposed as a reference glass will be investigated in the hot cell facility. The results will be compared with those obtained for non-radioactive glass samples in order to find out whether there are significant differences due to radiation and to the different way of glass manufacture. Due to a delay in the melting of the highly radioactive glass, the experiments cannot be started. Therefore, a short term post-investigation of the highly radioactive glass from the PAMELA plant has been proposed. The aim being a check-up of the active LEWC glass SM513LW11.

B. WORK PROGRAMME

B.1. HAW glass R7T7 or SON68.18.17.L1C2A2Z1 will be produced in Valrho, France, and delivered with nominal composition and production conditions.
B.2. Quality control outside the hot cells.
B.2.1. Chemical composition of the bulk glass by EPMA measurements and comparison with nominal composition.
B.2.2. Homogeneity of glass and unsoluble phases in the glass melt by EPMA and SEM.
B.3. Crystallization and devitrification at the temperature of maximum crystallization velocity.
B.4. Preparation of imbedded, polished samples for B.2.1., B.2.2. and B.3.
B.5. Leaching and corrosion behaviour under static conditions at higher temperature.
B.6. Leaching experiments
B.6.1. Experiments in autoclaves between 110° and 190°C in saturated salt brines.
B.6.2. Preparation of samples: chips and possibly powder.
B.6.3. Short and long term leaching experiments, i.e. between <30 d and ~1000 d.
B.7. Analysis of the leachates by ICP optical spectroscopy.
B.8. Investigation of HAW glass.
B.8.1. Mass loss measurements of leached glass samples.
B.8.2. SEM and EPMA investigation of the surface layers and identification of crystalline phases.

C. PROGRESS OF WORK AND OBTAINED RESULTS

1. COGEMA glass SON68.18.17.L1C2A2Z1

Due to a delay in the melting of the highly radioactive glass in Valrho, France, the start of the investigation of the active glass R7T7 has been scheduled for 1988. Therefore results cannot be reported at this time.

The research programme has been started with the installation and testing the new equipment of the hot cell facility to perform the experiments listed in the work programme.

The quality control of the glass will be performed using scanning electron microscopy for the homogeneity of the glass and unsoluble phases in the glass melt. Electron microprobe will be used for measuring the chemical composition of the glass and the crystal phases formed during the annealing of the glass at the temperature of maximum crystallization velocity.

The corrosion of the glass will be measured at 150 and 190°C under static conditions in saturated NaCl-$CaSO_4$ and KCl-$MgCl_2$-Na_2SO_4 solutions and with container material present. The leachates will be analysed by ICP for the elements Sr, Zr, Mo, Ba, La, Ce, Nd, Cr, Fe, Mn, Ni and the glass formers Si and B. The surface will be investigated by SEM and EPMA and enrichments and depletions of elements in the surface layer will be measured. The question of long-term extrapolation of corrosion rates will be addressed by discussing the leaching mechanism.

2. PAMELA glass SM513LW11

- Specification

Samples of the high active PAMELA glass SM513LW11 have been shipped to HMI. Annealing experiments and sample preparation for microscopy have been started. Some properties of the inactive glass described /1/ should be used for the comparison of the results of the active and inactive glasses. The thermal stability, i.e. crystallization tendency was determined by a TTT diagram (time-temperature-transformation) /1/. The observed crystal phases were titanite, pyroxenes, amphiboles and SiO_2 polymorph.

Some corrosion tests like MCC-1P /2/ and EC Static High Temperature Leach Test /3/ were performed. A comparison of the results with those of other common nuclear waste glasses showed that all corrosion rate are in the same area. The waste oxide content of the highly active glass is about 11 weight % and the specific activity: α: 2.1 E 07 Bq/g, β: 3.7 E 09 Bq/g, Cs-137: 2.7 E 07 Bq/g and Am-241 1.2 E 07 Bq/g.

- Crystallization

The crystallization behavior of the high active glass was investigated at 620, 780 and 820°C for 3, 30 and 100 days. The highest crystallization yield was found after 100 days at 620°C. Figure 1 is a secondary electron micrograph with two various crystalline phases. The small bright crystals are probably titanite as found in the inactive glass /1/. Figure 2a shows the column diagram from the SEM-EDS analysis of annealed glass samples for various temperatures and times. Figure 2b shows the column diagrams of the large dark crystals after 3, 30 and 100 days at 620, 720 and 820°C. The composition and the appearence of the crystals suggest amphiboles and pyroxenes when compared with the results from the inactive glass /1/. Summarizing it may be concluded that the crystallization of the highly active glass is much the same than that of the inactive simulated glass.

REFERENCES

/1/ SCHIEWER, E., "The Borosilicate Glass for 'Pamela'", Radioactive Waste Management and the Nuclear Fuel Cycle, Vol. 7 (2), April 1986, pp. 121-138.
/2/ MCC-1P Static Leach Test Method, Nuclear Waste Materials Handbook (US Department of Energy, DOE/TIC-11400, 1981)
/3/ Rep. EUR 9772 (1985)

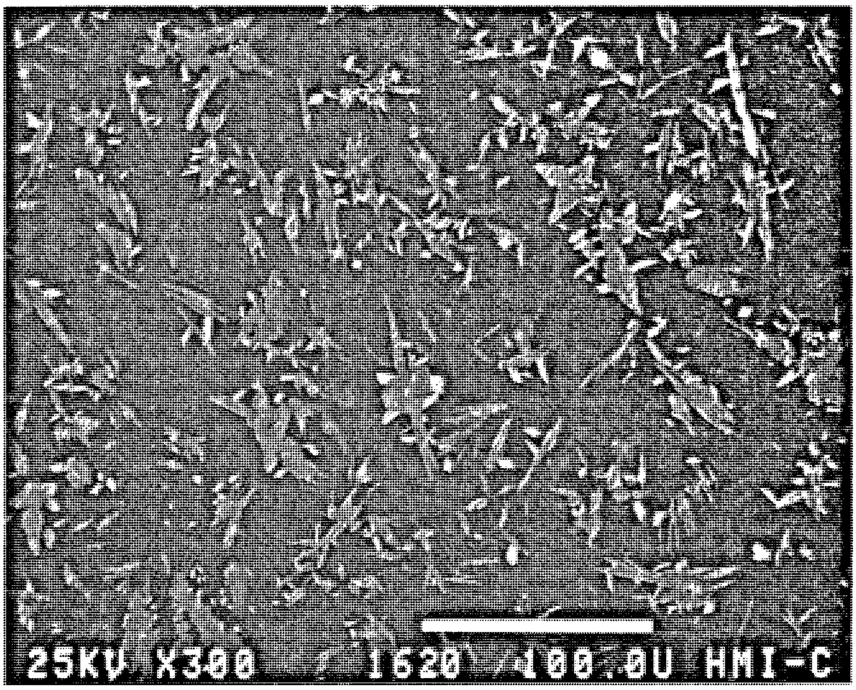


Figure 1 SEM micrograph of HLW glass SM513LW11 annealed at 620°C for 100 days. (White bar = 100 μm)

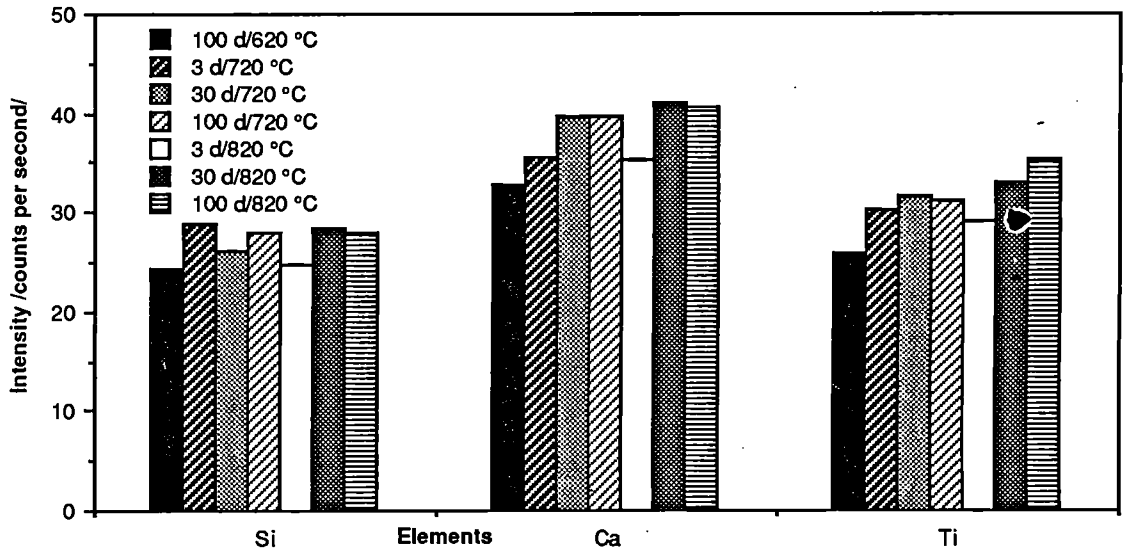


Figure 2a X-ray intensities of elements from SEM-EDS analysis of the annealed HLW glass SM513LW11. Annealing times: 3, 30 and 100 days. Annealing temperatures: 620, 720 and 820°C. From analysis of the small, bright crystals in Figure 1.

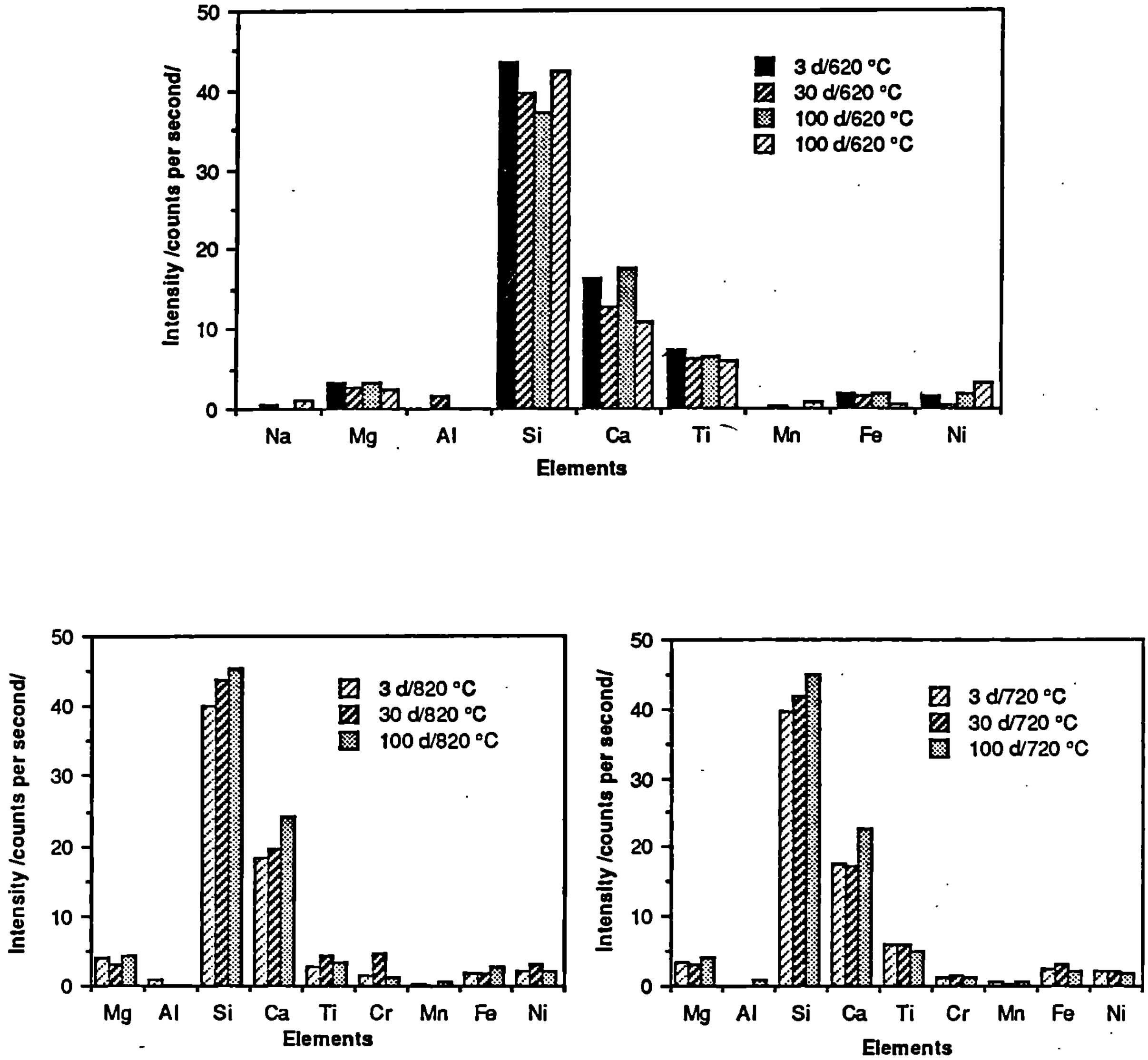


Figure 2b X-ray intensities of elements from SEM-EDS analysis of the annealed HLW glass SM513LW11. Annealing times: 3, 30 and 100 days. Annealing temperatures: 620, 720 and 820°C. From analysis of the large, dark crystals in Figure 1.

Laboratory and in-situ interaction between simulated waste forms and clay

Contractor:	S.C.K./C.E.N., Mol, Belgium
Contract N°:	FI1W/0100
Duration of Contract:	August 1986 - December 1987
Project Leader:	P.Ph. Van Iseghem

A. Objectives and Scope

The present programme is a continuation of the research carried out in the framework of the second CEC R&D programme (81-84; covered by contracts no. 302-83-15 WASB and 324-83-55 WASB). A large amount of important indications on the corrosion behaviour of various candidate HLW and TRUW reference waste forms in static conditions, including e.g. the influence of SA/V (surface area to volume), temperature and clay, and on the leaching behaviour of Pu from the TRUW waste form was obtained. In situ experiments in a surface clay quarry were performed. The preparations for the γ irradiation tests and the in situ experiments in the underground laboratory in clay were nearly finished.

The programme aims to elucidate the corrosion mechanisms of some reference HLW and TRUW glasses in clay media. This must enable one to propose a source term for the radionuclide release into the near field, and to model the long term interaction between glass and clay. The study includes both laboratory (inactive and tracered glasses; without and with external γ radiation) and in situ experiments. Four reference high-level waste (the AVH SON68, the Pamela SM513 and 527, and the Italian BEL-15) and alpha waste (WG124) glasses are being studied.

One part of the programme is carried out by ENEA Casaccia (Item B.4).

B. Work Programme

B.1. Corrosion experiments on waste glasses SON68, SM513, SM527 and WG124 in various clay media (without, with different amounts of clay), with attention to the leaching of the matrix components Si, B, Na, Fe, ..., and of the radionuclides Pu, Cs, Sr, Tc, Np, Am. Most experiments are performed at 90°C for periods until two years, in carefully controlled redox conditions.

B.2. Corrosion experiments on waste glasses SON68, SM513 and SM527 in clay media, in an external γ radiation field of 10^5 rad h^{-1}, without and with the simultaneous presence of container material (maximum test duration 1000 h).

B.3. In-situ experiments on various candidate HLW and TRUW reference glasses in direct contact with clay (first samples will be retrieved in 1988), or in the clay derived atmosphere (2 and 6 months results will become available in 1987).

B.4. Laboratory interaction tests on the Italian BEL-15 reference glass with clay media, to determine its quality as compared with other candidate glasses, and to simulate the in-situ experiments.

C. Progress of Work and obtained Results

State of Advancement

Most of the inactive corrosion experiments are underway for about 8 months. The tests in clay derived liquids will start beginning of 1988. The corrosion tests on Pu-Cs-Sr tracered glasses SON68, SM513 and SM527 are underway since more than one year; solubility tests and corrosion experiments under oxidizing conditions will start beginning 1988; the preparation and corrosion testing of Tc-Np-Am tracered glasses will be initiated during the second half of 1988, in combination with the additional experiments foreseen in the 1988-1989 contract (contract no FI1W/0179).

A first series of γ-irradiation experiments has been finished, with a maximum irradiation dose of about 0.63×10^8 rad. Two new irradiation tests were performed, in conditions of increased clay concentration (500 instead of 100 g per l water), and with synthetic interstitial claywater as liquid phase. The presence of canister material in the corrosion experiments will be included in the 1988-1989 tests.

The in-situ tests in contact with clay were further operated; the first retrieval is foreseen for September 1988 (two years). The tests in the clay derived atmosphere were started beginning 1987. Serious problems were encountered due to an unexpectedly large water intrusion; new sample loadings will be installed during 1988. Laboratory simulation tests of the in-situ interaction with clay were continued (90 and 170°C, without and with pressure).

The corrosion of the Italian BEL-15 reference glass in distilled water and Italian or Belgian synthetic claywater has been studied (91 days maximum duration). The tests in clay loaded solutions are in preparation. The corrosion of the glass in repository simulating conditions is underway since about 4 months (termination foreseen in summer 1988).

Progress and Results

1. Corrosion mechanisms in clay media

All experiments were carried out in clay-water mixtures, in which the water is the synthetic interstitial claywater ("SIC"), and whose redox condition is similar to the one in the clay host ($E_h \leq -200$ mV).

1.1. Inactive experiments (glasses SON68, SM513, SM527, WG124)

The corrosion experiments in two clay/SIC mixtures (10 and 500 gl^{-1}) are underway since about 8 months; they are interpreted in terms of mass losses, pH-E_h, and chemical analysis of the leachates (after high speed centrifugation, 15×10^3 rpm, to separate clay from the solution). Surface analysis by electron microprobe on the samples corroded for 80 days is in progress.

* The mass loss data indicate mass losses up to more than 15 times larger in the concentrated clay solution. This is due to accumulation of certain leached glass components (B, Mo, Li, Ca) in the liquid part of the leachate. It is also supposed that sorption of other leached glass components (Si, Al, Ti, ...) on the clay will contribute to larger leaching in the concentrated clay solutions.
* The concentrations of Si, Al, Fe, Ti in the liquid fraction of the leachate are almost constant, or even decrease (Al) with time, irrespective of the clay concentration. Even so, the concentration of Si is larger in the diluted clay solutions.

The corrosion experiments evaluating the role of the surface layer w.r.t. corrosion were started during the first half of 1987. The six months samples were retrieved, weighed, and layers were removed (in some cases; after removal the samples are being further corroded). Evaluation will be carried out after a minimum of 9 months (overall corrosion duration). The tests at 190°C will be performed again, with a more suitable time schedule. Corrosion durations of 6 months were found to be too long in some cases, indeed.

1.2. Radioactive (tracer) experiments (glasses SON68, SM513, SM527)

Experiments on these glasses, tracered with Pu-239, Cs-134 and Sr-90, in the 500 gl^{-1} clay/SIC mixture (CCSICM) are underway for more than one year. Data until 8 months (for SON68 and SM513) show that Pu and Sr stop leaching from the glasses beyond a few months, although the glasses (and also Cs) continue to be corroded. The mobile Pu fraction (i.e. with size smaller than 10^5 MWU) reaches a maximum value of about 2 x 10^{-9} mol L^{-1}, and decreases with continued test duration (e.g. after 240 days: about 10^{-11} mol L^{-1}). The largest fraction of the radionuclides leached is sorbed on the clay; the distribution coefficient, K_d, is not constant with time.

Surface layers of about 15 (SON68) or 25 µm (SM513) have formed within the first month of corrosion, constitued mainly by Si, Al, Ti, Zr and rare earths (such as Nd).

2. Influence of an external γ radiation field

A first irradiation campaign has been finished, by performing a fifth irradiation test in conditions identical to the previous ones (see summary report for 1986), but increasing the irradiation time until 1000 h (yielding a total dose of about 0.63 x 10^8 rad). The systems irradiated at 90°C consisted of clay/water mixtures, without or with a glass sample present (SM513, SON68, or SAN60). Radiolytic gases formed are mainly H_2, and to a minor extent CO_2. The production of H_2 fits roughly literature data concerning water ($G(H_2) \cong 0.45$) and Boom clay ($G(H_2) \cong 0.10$). Safety problems related with the H_2 production were considered as well.

Comparison of the corrosion of the waste glasses in or out of the irradiation field has been reconsidered, by conducting "blank" corrosion tests in the same conditions of temperature, medium, redox condition, and $SA.V^{-1}$. This way it was found that glass corrosion was reduced in the presence of the irradiation field by a factor of 2 to 3 (and, that $SA.V^{-1}$ influences corrosion in clay media irrespective of irradiation).

Interpretation of the corrosion experiments in terms of elemental leaching behaviour is in progress.

A second irradiation campaign has been started, using the same irradiation infrastructure and parameters, but changing the solutions. The clay to water ratio was increased to more realistic proportions, and synthetic interstitial water was used as the liquid fraction. Two irradiations are nearly finished, for irradiation periods of 335 and 1000 h. Again, these tests will be interpreted in terms of radiolytic gas production, pH - E_h changes, and glass corrosion.

3. In-situ experiments

The four tubes for the experiments in direct contact with clay are in operation since the first half of 1986; the first retrieval is foreseen for mid 1988 (one 90°C tube). During 1987 temperature distribution along the tubes was recorded; at the back-end of the tubes relatively large deviations from the target temperatures are measured (e.g. 130°C, relative to 170°C). The temperature profiles are constant with time.

The experiments in contact with clay derived atmosphere are in operation since December 1986 (host temperature), or April 1987 (90 and 170°C). Six different waste glasses and some canister materials (see contract FI1W/0033) were loaded. The strongly increased water flux through the stainless steel filters into the tubes observed upon heating of the tubes, seriously hampered the experiments, in so far that experiments were performed rather in claywater during 1987. A suitable pumping system will be installed beginning of 1988, whereafter new samples will be introduced to investigate the interaction with clay derived atmosphere.

Laboratory simulation of the in-situ clay contact tests was continued; the tests are performed at 90 and 170°C, at ambient or repository (4 MPa) pressure. The data until 180 days duration show that corrosion rates decrease with time at 90°C, but are almost constant at 170°C. Glass corrosion at repository pressure is about twice as large as at the ambient pressure. Surface analytical techniques were experienced in view of the analysis of in-situ corroded samples; it has been found that surface layers between 5 and 25 µm thick may be expected at the interface between glass and clay.

4. Compatibility between the Italian BEL-15 glass and clay

4.1. Short term interaction with clay media

The MCC1 (Materials Characterization Center) standard test, matrix D (maximum duration 91 days) time schedule, was used to characterize the chemical stability in distilled water (DW), Belgian or Italian synthetic interstitial claywater (SIC), or a 500 gl^{-1} Belgian or Italian clay/SIC mixture. The data for DW show rapid saturation of the leachate at 90°C, and continued leaching at 40°C, but at decreasing rate. SEM-EDXA analysis reveals no layer formation. A detailed analysis of the SIC corrosion tests is in progress; surface analysis, however, shows a considerable layer formation, including some Ca or Mg rich compounds (precipitates).
The tests in clay/SIC mixtures are in preparation.

4.2. Clay contact test

Three apparatus have been manufactured to perform clay contact tests, i.e. to corrode the BEL-15 glass in a condition representative for the in-situ condition. Three test durations were selected: 4, 8 and 12 months; temperature is 90°C, and pressure 4.0 MPa. The experiments were started in September 1987; a fraction of the glass surface was surrounded by a stainless steel canister sheet, to include the influence of this material into the test.

List of publications

(1) Laboratory and in-situ interaction between simulated waste glasses and clay - Annual Report 1986 (R-2732).
Presented at the CEC Progress Meeting for task 3, sections 2 + 3 (Geel, March 1987)

(2) The laboratory and in-situ interaction between nuclear waste glasses and clay.
Presented at the second IAEA Resarch Coordination Meeting on the performance of solidified high-level waste forms and engineered barriers under repository conditions (Sydney, April 1987)

(3) Laboratory and in-situ interaction between simulated waste glasses and clay - Semestrial Progress Report January-June 1987.
Presented at the CEC Progress Meeting for task 3, sections 1-2-3-5 (Fontenay-aux-Roses, October 1987)

3.C. Other engineered barriers

Nearfield behaviour of clay barriers and their interaction with concrete

Contractor : CEA, CEN Fontenay-aux-Roses
Contract n° : FI1W - 0031
Working period : May 1986 - December 1986
Project leader : A. LAJUDIE, R. ATABEK

A. OBJECTIVES AND SCOPE

In order to guarantee the safety of underground disposal, coming from spent fuel reprocessing, engineered barriers will be implemented as backfill materials in galleries and access shafts and as buffer materials between the host medium and the waste packages. One of the first requirements for engineered barriers is to minimize water and chemical species transfer. The materials being considered are essentially swelling clays, in particular calcium smectite clays coming from french deposits.

The long term stability of clay materials, as a function of temperature, water salinity and ionic species in solution, has to be evaluated for the different types of host rock (granite, clay and salt).

The final objective of the programme is to take into account material property modification with time in the choice and design of the engineered barriers used for both vitrified and T.R.U. waste disposal.

B. WORK PROGRAMME

B.1 Material choice and experimental condition definition
B.2 Vitrified waste disposal : definition and characterization of clay barriers
B.3 Vitrified waste disposal : temperature effect on clay material properties
B.4 Vitrified waste disposal : hydrothermal degradation of clay materials
B.5 T.R.U. waste disposal : study of concrete durability

C. PROGRESS OF WORK AND OBTAINED RESULTS

Summary

Analyses and preliminary measurements perform on eighteen samples coming from fourteen french clay deposits have led to the choice of two clay materials (reference 4a and 13) which may be used as constituent elements of engineered barrier. The mineralogy of these two clays is now well defined for further investigations. A vitrified waste disposal in granite is taken as the most constraining scenario as far as engineered barrier is concerned. The buffer material properties which are evaluated are directly related to the engineered barrier requirements : thermal conductivity, permeability, water diffusion coefficient,.... Moreover results are obtained on temperature effect on clay material microstructure and properties in both cases : without and with water intake.

B.1 is finished

B.2, B.3, B.4 are progressing normally

B.5. will start in 1988, as planed in the contract.

Progress and results

1. Material choice (B.1.)

Precise mineralogical analyses, performed on clay fraction (≤ 2 μm), give the main component content of the two selected materials, referred to as 4a and 13, coming respectively from sparnacian and oligo-miocene deposits. For example, the samples subjected to hydrothermal degradations (§ B.4) have the following compositions :

	REFERENCE 4a		REFERENCE 13	
Non phyllosilicate minerals	8%	- quartz : 7% - calcite : 1% - goethite:traces	13%	- quartz : 10% - calcite : 3%
Phyllosilicate minerals	92%	- I.K.*Smectite/ kaolinite:87% (52% / 48%) - kaolinite: 5%	87%	- I.S. Smectite/ illite with 69% of smectite - illite

* undifferentiated mixed-layers.

Taking into account the discrepancies due to deposit layer inhomogeneity and measurement dispersion, reference 4a which is the first material to be selected, is defined as follows :

- water content : 9% - 11% (dry state : 105°C, 24 hours in an oven)
- liquidity limit : 95% - 120%
- cation exchange capacity : 50 - 60 meq/100 g of dry clay
- mineralogical composition of the clay fraction (≤ 2 μm) :
  - quartz : 3% - 20%
  - calcite : 1% - 3%
  - kaolinite / smectite mixed-layers : 70% - 90%
  - kaolinite : 1% - 13%

2. Definition and characterization of clay barriers (B.2.)

In the case of vitrified waste disposal in granite which is the french reference scheme, the buffer material being considered is compacted clay matérials. The properties of the prepared material have to be determined as a function of parameters such as dry density (ρ_d) and water content (w) of the material, pressure, temperature and salinity of water. The main properties to be measured are thermal conductivity, permeability, water diffusion coefficient, swelling pressure and swelling ability. Results, obtained at this state of advancement of the contract, concern :

- thermal conductivity (λ in W/m.K) : as is clear from figure 1, thermal conductivity increases with material dry density and water content. Use of additives such as sand and graphite easily improves the thermal conductivity of the engineered barrier. One can keep in mind the following values :

* Reference 4a	: $1.85 < \rho_d < 2.05$ $9.5 < w\ (\%) < 12.5$	$0.9 \leq \lambda \leq 1.1$
* 4a/sand mixture (50/50)	: $1.97 < \rho_d$ mixture < 2.18 w (%) = 7-8	$1.4 \leq \lambda \leq 2.2$
* 4a/sand/graphite mixture (50/45/5)	: $1.97 < \rho_d$ mixture < 2.13 w (%) = 5	$1.7 \leq \lambda \leq 3.0$

- permeability coefficient (K in m/s) : in the case of clay materials, permeability measurements are performed with high hydraulic gradients (5.10^2 - 10^4). It appears from figure 2 that the permeability coefficient of the engineered barrier and dry density of the clay are correlated through the simple relation : $K = 5.35.10^{-8} \exp(-7.2\ \rho_d)$ (at 20°C). Permeability increases if sand is added and the following values can be used :

* Reference 4a :	$\rho_d = 1.95$	$K = 4.10^{-14}$
	$\rho_d = 1.55$	$K = 10^{-12}$
* 4a/sand mixture (50/50) :	ρ_d mixture = 1.89	$K = 3.10^{-13}$
* 4a/sand/graphite mixture (50/45/5) :	ρ_d mixture = 2.0	$K \simeq 3.10^{-13}$

- water effective diffusion coefficient (De in m^2/s) : using tritiated water, values of about 10^{-11} m^2/s and 10^{-10} m^2/s are found respectively for $\rho_d = 1.95$ and $\rho_d = 1.0$. It can be noticed that diffusion process leads to higher water flow than convection process.

3. Temperature effect on clay material properties

As far as granite is chosen without fracture, a dry phase may appear at the early stage of the vitrified waste disposal. Under dry conditions, deshydration of clay materials continuously occurs with the successive departure of (a) hygroscopic water (at the grain surface), (b) zeolitic water (in the sheet spaces), (c) constitutive water (in the sheet structure). Thermogravimetric measurements show that reference 4a looses its constitutive water (which is an irreversible process) at temperature above 190°C. Moreover, it is demonstrated that after one year at 250°C, this clay is able to hydrate rapidly under water but a lost of 17% swelling ability is observed.

4. Hydrothermal degradation of clay materials

Water containing ion species and temperature lead to modifications of the clay structure. Preliminary results, presented on figure 3 for both reference 13 and 4a samples show that a stay at 200 or 250°C during 36 days in pure water does not modify the clay mineralogy. The main difference between the two materials consists in the undifferentiated mixed-layers behaviour : the component content of the mixed-layers remains constant with temperature in the case of Reference 13 (illite/smectite) while it is changed in the case of reference 4a (kaolinite/smectite). The formation of low-charge smectites (SM BC) in the K/S mixed-layers leads to an increase of the clay cation exchange capacity and consequently of the clay sorption properties.

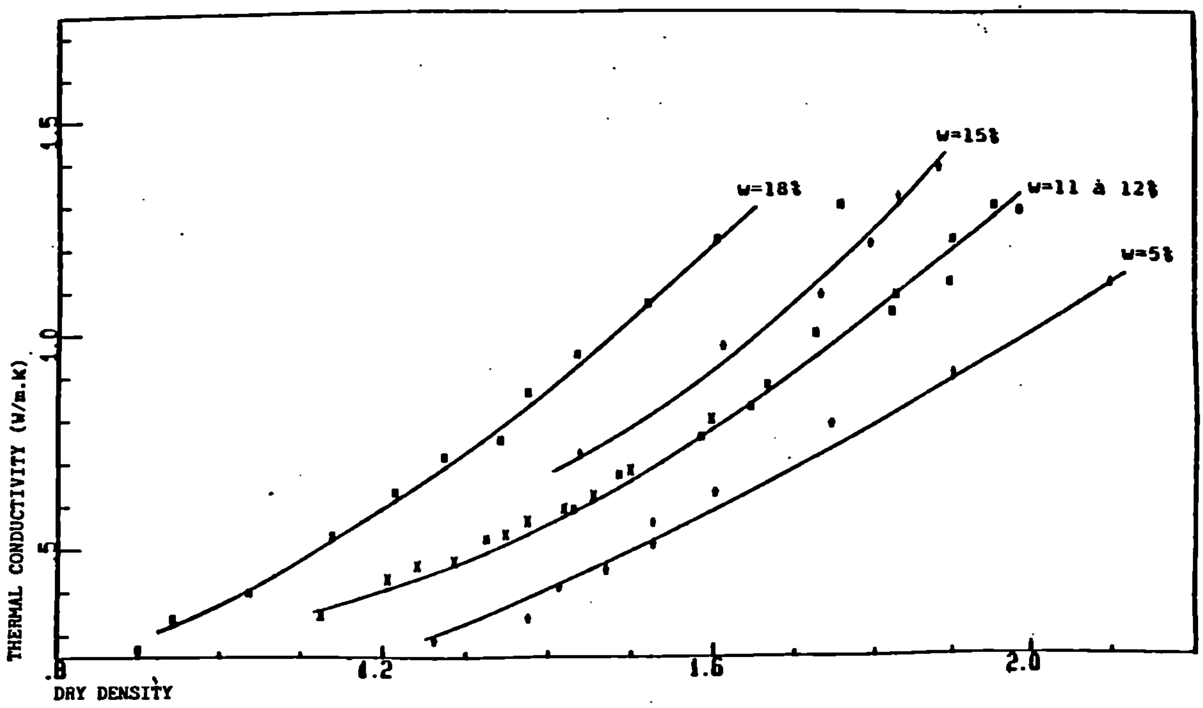


Figure 1 : Thermal conductivity as a function of dry density for reference 4a (20°C) (w = Water content)

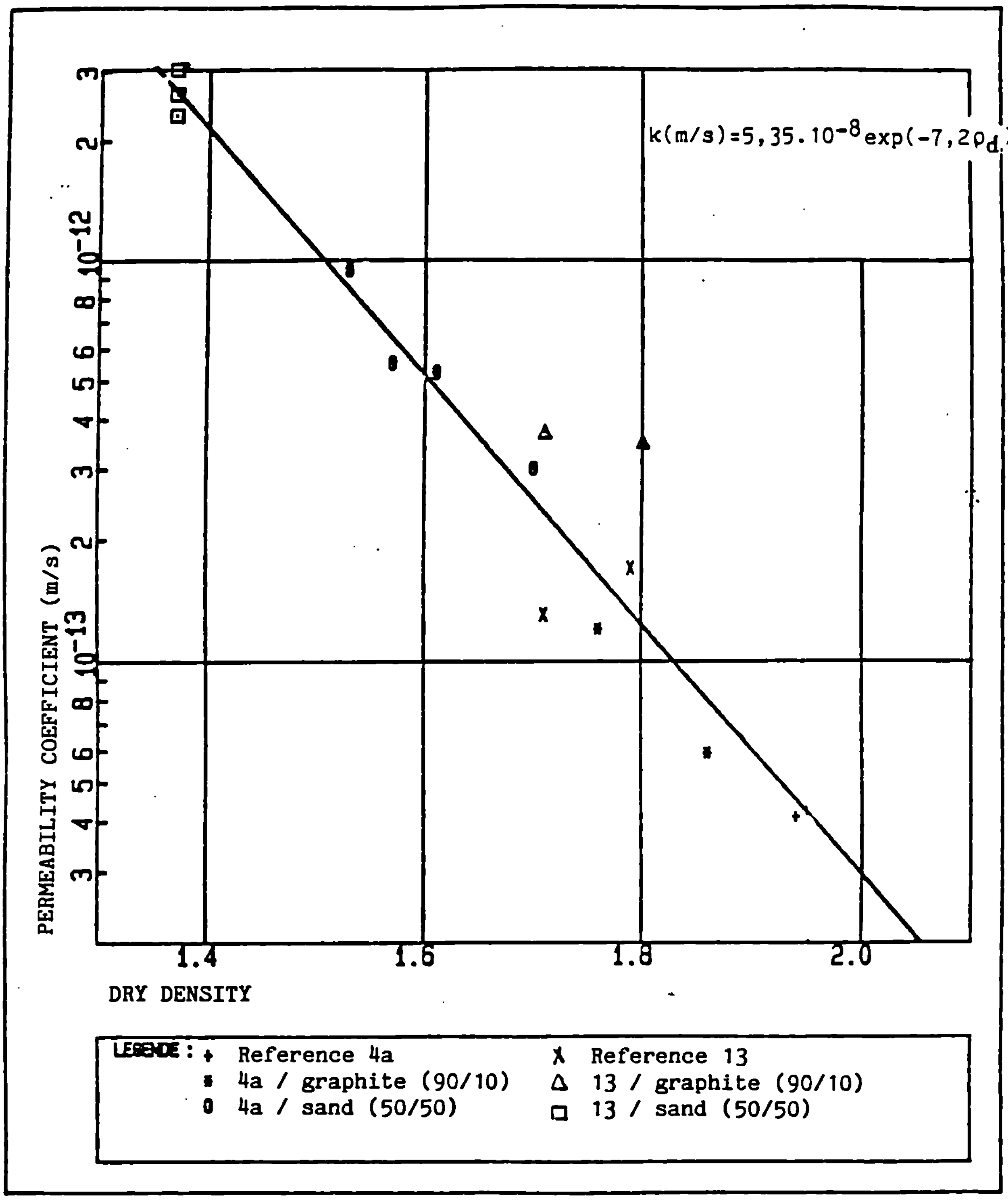


Figure 2 : Permeability coefficient as a function of dry density

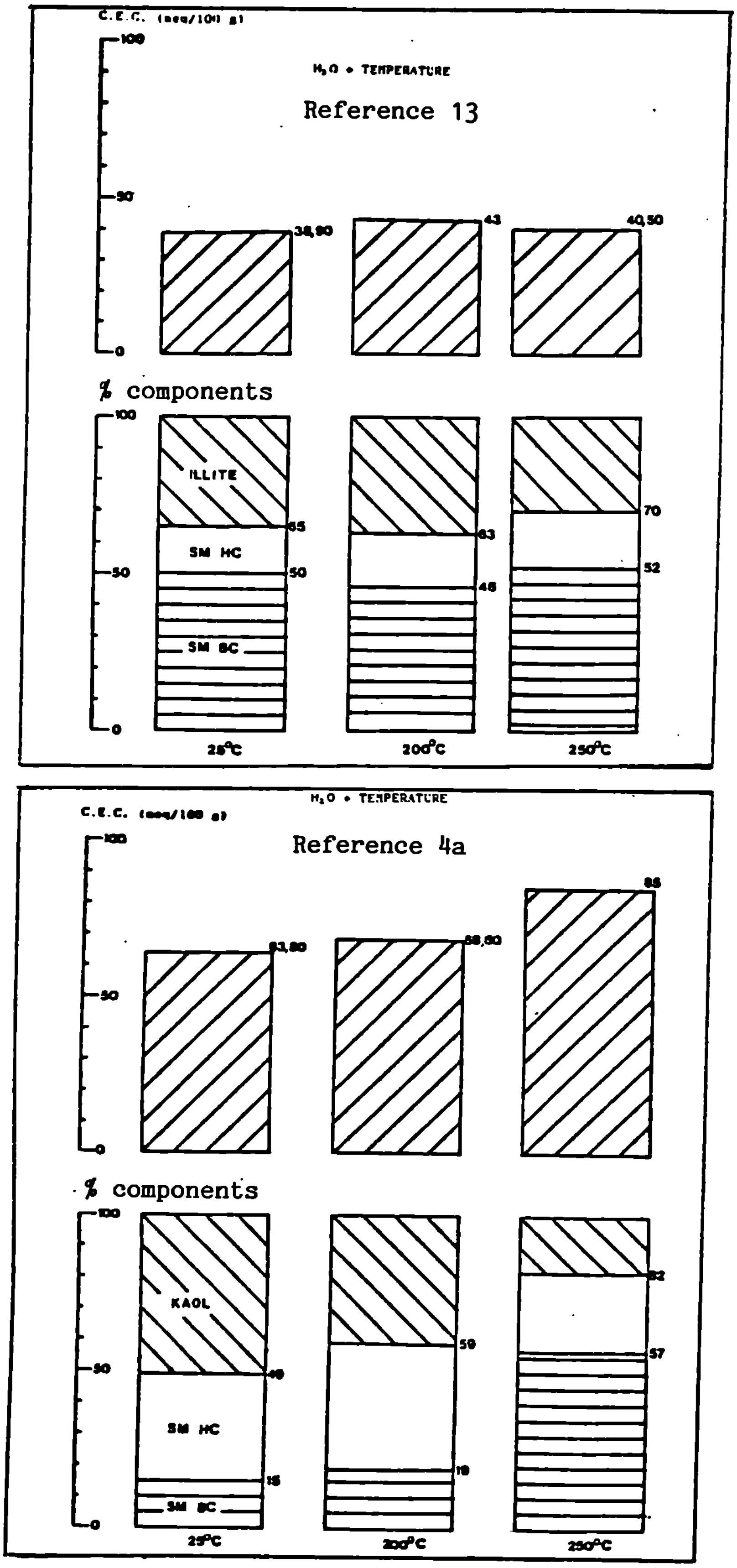


Figure 3 : Hydrothermal degradation of clay materials : temperature effect on cation exchange capacity and component content

CORROSION TESTING OF SELECTED CONTAINER MATERIALS FOR DISPOSAL OF HLW GLASS

Contractor: KfK, Karlsruhe, Federal Republic of Germany
Contract No.: FI1W/0032
Duration of contract: May 1986 - December 1989
Project Leaders: E. Smailos, R. Köster

A. OBJECTIVES AND SCOPE

In order to qualify corrosion resistant packaging materials for disposal of high-level waste forms in rock-salt formations, the corrosion behaviour of a number of materials has been investigated in salt brines (postulated accident conditions) under the preceding EC research task. The results of these studies have shown that unalloyed steels are a promising packaging material. These steels have exhibited so far only general corrosion so that their long-term corrosion behaviour can be reasonably calculated; moreover, it can be expected from their corrosion rates obtained so far in salt brines that the container wall-thickness will be acceptable under a corrosion allowance concept.

These are the goals of the project:

- Definition of the best suited steel (reference steel) for the fabrication of a long-term resistant HLW packaging and the detailed description of the time and temperature behaviour of its corrosion in disposal relevant corrosion media with and without gamma radiation.
- Determination of the corrosion behaviour of Hastelloy C4 subjected to high gamma dose rates under the in-situ conditions prevailing in the Asse salt mine. These are investigations performed in order to complete the results available now.

B. WORK PROGRAMME

B.2.1 Selective laboratory-scale corrosion studies on the three preselected steels, namely fine-grained steel, low-carbon steel, cast steel, with a view to selecting a reference steel.

B.2.1.1 Without gamma irradiation in moist rock salt (rock salt/rock salt brine and rock salt/Q-brine) at 90 °C and 170 °C.

B.2.1.2 With gamma irradiation (10^3 rad/h) at 90 °C in Q-brine.

B.2.2 More detailed laboratory-scale corrosion studies on reference steel subjected to various gamma dose rates (10^2 to 10^4 rad/h) in all three corrosion media enumerated under items B.2.1.1 and B.2.1.2.

B.2.3 Post-test examination of the steels stored in situ (material specimens, welded tube sections) for corrosion attacks at T = 35 °C and 200 °C, rock pressure and high gamma radiation (about 3×10^4 rad/h).

B.2.4.1 Laboratory-scale examinations of the influence of the gamma dose rate (10^2, 10^3, 10^4 rad/h) on corrosion of Hastelloy C4 in Q-brine at 90 °C.

B.2.4.2 Post-test examination of the material specimens and welded Hastelloy C4 tube sections stored in Asse for corrosion attacks. The testing conditions are similar to those under item B.2.3.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Summary

During the period of reporting more in-depth laboratory-scale as well as in-situ corrosion studies have been made on selected HLW packaging materials (unalloyed steels, Ti99.8-Pd, Hastelloy C4, nodular cast iron, Ni-Resist D4, and Si-cast iron). The studies have focused on the unalloyed steels because these steels proved to be the most promising packaging material in the previous studies. In the laboratory-scale experiments the influence has been determined of gamma radiation on the corrosion behaviour of three preselected steels (fine-grained steel, low-carbon steel, cast steel) and Hastelloy C4 in a salt brine (Q-brine) rich in $MgCl_2$ and relevant to accident scenarios in a repository. The experiments were carried out both at realistic dose rates of 1 Gy/h and 10 Gy/h for the thick-walled HLW packaging discussed and at the higher value of 100 Gy/h. The test temperature was 90 °C and the maximum test period was 12 months.

The in-situ experiments involving iron base materials, Ti 99.8-Pd and Hastelloy C4 were performed in the Asse salt mine at T = 120 °C - 210 °C, both without irradiation and in a gamma radiation field of 3×10^2 Gy/h (Co-60 source), within the framework of the German/US Brine Migration Test. Besides, the in-situ corrosion experiments have been continued under various conditions with material specimens and welded tubes of selected materials.

PROGRESS AND RESULTS

B.2.1.1 Corrosion studies on unalloyed steels in moist rock salt (rock salt/rock salt brine and rock salt/Q-brine) without gamma irradiation

Terminated in 1986 (published in the 1986 Annual Report of the Commission of the European Communities)

B.2.1.2, 2.2, 2.4.1 Investigations into the Influence of Gamma Radiation on the Corrosion Behaviour of Unalloyed Steels and Hastelloy C4

The investigations into the influence of the gamma dose rate (1 Gy/h, 10 Gy/h, 100 Gy/h) on the long-term corrosion behaviour of three preselected unalloyed steels and Hastelloy C4 in a salt brine (Q-brine) rich in $MgCl_2$ at 90 °C have been terminated. Similar investigations have started into the rock salt/salt brine two-phase system on fine-grained steel which has been selected as the HLW reference packaging material.

The materials investigated in Q-brine (g/l at 55 °C: 7.1 Na^+; 31.8 K^+; 91.9 Mg^{2+};297.3 Cl^-; 14.4 SO_4^{2-}) had the following compositions (wt.%):

- fine-grained steel: 0.17 C; 0.44 Si; 1.49 Mn; BAL Fe,
- low-carbon steel: 0.1 C; 0.27 Si; 0.66 Mn; BAL Fe,
- cast steel: 0.16 C; 0.61 Si; 1.51 Mn; BAL Fe,
- Hastelloy C4: 15.4 Cr; 15.2 Mo; 0.79 Fe; BAL Ni.

The durations of tests were varied between 50 days and 12 months; the ratio of specimen surface to brine volume (S/V ratio) was 100 m^{-1}. All materials were examined for general corrosion and pitting corrosion. The sensitivity with respect to crevice corrosion and stress corrosion cracking and the influence of welding (TIG welding, electron beam welding) on corrosion were investigated in addition for fine-grained steel and Hastelloy C4.

The results of corrosion of the steels and of Hastelloy C4 have been compiled in Tables I and II. Besides the results obtained under gamma irradiation the corrosion rates measured in previous investigations without irradiation /1/ have been entered for comparison. The essential results can be summarized as follows:

- At gamma dose rates in the range of 1 Gy/h - 100 Gy/h no significant influence of gamma radiation on the corrosion of the steels in Q-brine at 90 °C has been found. The maximum penetration rates of non-uniform corrosion (30 µm/a - 50 µm/a) are intercomparable and imply acceptable corrosion allowances for a thick-walled packaging. After 12 months of testing period no pitting and crevice corrosion or stress corrosion cracking occurred. For these reasons, the unalloyed steels continue to be considered as a promising packaging material.

- The general corrosion of Hastelloy C4 has been low at all dose rate levels (0.1 - 0.4 µm/a) but at 10 Gy/h and 100 Gy/h pitting and crevice corrosion of 20 µm/a has been found. Consequently, adequate gamma shielding will be required if this material will be used as a packaging material.

B.2.3, 2.4.2 <u>In-situ Corrosion Experiments</u>

The material specimens consisting of iron base alloys, Ti 99.8-Pd and Hastelloy C4 stored in the Asse salt mine have been examined for corrosion attacks in the framework of the German/US Brine Migration Test. The specimens placed in about 6 m deep heated, cased boreholes had been exposed to the following corrosive conditions:

- temperature: 120 °C - 210 °C,
- gamma dose rate (Co-60 source): $3x10^2$ Gy/h,
- rock pressure: 28 MPa at the maximum,
- brine migration, gas constituents from the rock salt,
- test period: 900 days at the maximum.

The essential corrosion results obtained in situ can be summarized as follows:

- All materials investigated exhibited high resistance to corrosion under the conditions prevailing in the Brine Migration Test. All material specimens corroded at much lower rates than determined in the previous laboratory-scale tests with brine excess. The reason for the lower corrosion attack of the materials stored under in-situ conditions is considered to be the very small amounts of migrated brine of about 140 ml.
- All materials and above all the materials with passivating oxide layers such as Ti 99.8-Pd and Hastelloy C4, which may corrode selectively already in the presence of minor amounts of brine, had been resistant with respect to any type of local corrosion attack.
- The gamma radiation of $3x10^2$ Gy/h did not exert an influence on the corrosion behaviour of the materials.

In addition to the investigations above the in-situ corrosion experiments have been continued on electron beam welded tubes made of cast steel without and with explosion plated Hastelloy C4 and Ti 99.8-Pd, respectively. The first series was withdrawn after 1.5 years of storage time and is presently subjected to post-test examinations for possible corrosion attacks.

References

/1/ SMAILOS, E., KfK Report 3953 (1985).

List of publications in 1987

SMAILOS, E., KÖSTER R., IAEA Technical Committee Meeting on Materials Reliability in the Back End of the Nuclear Fuel Cycle, Vienna, 2-5 September 1986. Proceedings pp. 7-24 (1987).

SMAILOS, E., SCHWARZKOPF, W., KÖSTER, R., KfK Report 4265 (1987).

SCHWARZKOPF, W., SCHOCH, L., KÖSTER, R., Jahrestagung Kerntechnik, Karlsruhe, 2-4 June 1987. Tagungsbericht pp. 477-480.

Table I General corrosion rates and maximum penetration rates of non-uniform corrosion for unalloyed steels after one year immersion in Q-brine at 90 °C with and without gamma irradiation

Material	Average general corrosion rate (µm/a)				Maximum penetration rate (µm/a)			
	no γ	1 Gy/h	10 Gy/h	100 Gy/h	no γ	1 Gy/h	10 Gy/h	100 Gy/h
Fine-grained steel	31±3	14±4	23±10	37±8	40	30	40	40
Cast steel	40±3	15±4	20±5	-	50	30	30	-
Low-carbon steel	80±2	18±3	23±6	-	90	40	50	-

- = not investigated

Table II General corrosion rates and maximum pitting rates of Hastelloy C4 after one year immersion in Q-brine at 90 °C with and without gamma irradiation

Dose rate (Gy/h)	Average general corrosion rate (µm/a)	Maximum pitting rate (µm/a)
no γ	0.1	-
1	0.05	-
10	0.4	20
100	0.4	20

- = uniform corrosion

CORROSION OF CONTAINER AND INFRASTRUCTURE MATERIALS UNDER CLAY REPOSITORY CONDITIONS

Contractor : S.C.K./C.E.N., Mol, Belgium
Contract No : FI 1W-0033-B
Duration of contract : May 1986 - December 1989
Project Leader : W. Debruyn

A. OBJECTIVES AND SCOPE

Objective of the programme is to determine corrosion rates of selected candidate materials under realistic repository conditions over long exposure periods, to determine the in-situ clay agressivity and its evolution after introduction of waste containers, to evaluate the effect of gamma radiation on corrosion rates in a clay environment and finally, based on the combined results of these experiments, to estimate long term corrosion damage. This approach will enable to qualify materials for use as a barrier between vitrified high level waste and clay as a host medium, and between the underground facilities and clay.

B. WORK PROGRAMME

1. Installation and exploitation of corrosion tubes in the underground laboratory.
   1.1. Interaction of metal alloys with solid clay.
   1.2. Corrosion in a humid clay atmosphere.
2. Instantaneous and integrated corrosion measurements in the underground laboratory.
3. Characterization of the clay environment (solid clay and humid clay atmosphere) by means of pH- and Eh-measurements.
4. Assessment of the influence of an external gamma radiation field on corrosion rate and mechanism.
5. Electrochemical laboratory experiments in a range of conditions resulting from previous actions.
6. Estimation of long term corrosion damage accumulation.

C. PROCESS OF WORK AND OBTAINED RESULTS

State of advancement

The main effort during the contractual period covered in this report is situated in the programme segments of in-situ experiments B1 and B3, and in the segments of laboratory experiments B4 and B5.
All in-situ corrosion test tubes (B1) have been installed. The tubes designed for testing corrosion of materials in contact with humid clay atmosphere are still liable to excessive clay water ingress.
Electrochemical sensors (pH and Eh) (B3) in the direct contact with clay configuration are generating on-line information on the chemical characteristics of the clay environment.

C-steel, Hastelloy C4 and Ti/0.2 Pd-specimens have been irradiated (B4) for exposure times up to 1000 hours under a gamma radiation field of 10^3 gray/hour. The test medium was synthetic interstitial clay water under different conditions at 90°C.

Equipment to perform electrochemical corrosion experiments (B5) has been purchased and installed. Different experimental techniques have been evaluated and selected.

Corrosometer probes (B2) will be emplaced in the near future; action point B6 has not been started yet.

Progress and results

In the underground laboratory at SCK/CEN experimental work has been undertaken to maintain the corrosion test tubes and to characterize the clay environment. The corrosion test tubes in direct contact with clay already reached their target temperatures of 170°C, 90°C (two tubes) and ambient temperature by the end of 1986. The tubes in contact with humid clay atmosphere show, upon heating, a high water penetration rate across the porous stainless steel filters. The permeability increase of the clay/claywater system as a function of temperature (the target temperatures of the experiments are the same as in the direct contact with clay configuration), can explain only partially the observed flux increase. To be able to proceed the corrosion testing as planned, i.e. in contact with a humid clay atmosphere, different pumping and purging concepts have been tested. The purging equipment selected will be implemented in the underground experimental room.

The clay environment can be characterized in term of pH and Eh in the direct contact configuration. The redox measurements obtained at ambient temperature show a stable value of -235 mV to -335 mV versus SHE after an emplacement period of one month. This quick restoration of the reductive nature of the medium, indicates that the clay has a high capacity to recover from disturbances sich as drilling operations. This finding is in accordance with the pH-evolution reported in 1986. Throughout this year data points were collected and stored in the IBM host computer; on-line measurement for both pH and Eh is possible at this point in time. To obtain reliable electrochemical characterisation measurements with the (non-retrievable) electrodes, graphical and mathematical calibration methods have been evaluated. As a results of this, the graphical method was selected.

Apart from the in-situ experiments, overground laboratory experiments have been performed, which can be classified as conventional, electrochemical and gamma irradiation experiments. As to the first type of experiments, the conventional corrosion study, post corrosion analyses have been performed on U-bends exposed to interstitial clay water for stress corrosion cracking studies. Alloys evaluated were AISI 316, UHB 904L, Hastelloy C4 and IMI 115. These materials have been tested for five years in a corrosion chamber at 49°C and in flasks at 96°C. Two main conclusions can be drawn :

1. The AISI-316 material is liable to cracking. Since this material is typical for canister construction, this results is an argument for the canister/overpack concept.
2. All materials, except IMI 115, degrade by pitting and crevice corrosion to some extent. This means that if localised corrosion is to be avoided at any expense, only titanium alloys are left as possible corrosion resistant overpack materials. The alternative of corrosion allowance material (C-steel) of course remains a valid possibility.

Equipment to perform electrochemical corrosion experiments, has been purchased, installed and tested. The heart of this equipment is a Princeton Applied Research type 273 potentiostat. Different experimental techniques have been evaluated; these are : linear

polarisation resistance, Tafel-analysis, anodic polarisation and cyclic polarisation. Linear polarisation resistance (eventually combined with Tafel analysis) will be used for corrosion rate evolution of C-steel, Hastelloy C4 and Ti/0.2 Pd in different argillaceous environments. Anodic polarisation is suited for determining the passivation ability of these materials and cyclic polarisation is a means to estimate the susceptibility for localised corrosion. The strength of these electrochemical techniques is that the test environments are not confined to ordinary prevailing conditions, such as existing in the in-situ test configuration, but it is possible to simulate any other situation (gamma-irradiation, acidification,...). To evaluate the effect of gamma radiation on corrosion, the RITA facility of the BR2 reactor has been loaded with samples of C-steel, Hastelloy C4 and Ti/0.2 Pd under different conditions in synthetic interstitial claywater at 90°C. A radiation field of 10^3 gray/hour has been applied for exposure times up to 1000 hours.
Chemical characterisation of the claywater revealed no significant radiation effect; only a slight acidification of the oxidized water could be demonstrated.
The corrosion rates observed with and without irradiation were comparable. Irradiation enhances corrosion of carbon steel in oxic claywater; the effect under anoxic conditions remains within the experimental scatter. This difference effect might be due to the acidification occurring under oxic condition, as mentioned before. Radiation does not seem to affect extent or nature of the pitting effect.

List of publications :

1. Debruyn W., Dresselaers J., Tas H., NIRAS/ONDRAF, R & D programme on radioactive waste disposal, semi-annual report, first semester 1987.
2. Debruyn W., Dresselaers J., Tas H., NIRAS/ONDRAF, R & D programme on radioactive waste disposal, semi-annual report, second semester 1987.
3. Tas H., Debruyn W., Dresselaers J., Compatibility of candidate overpack materials with deep argillaceous HLW disposal environments, IAEA - TECDOC, p 25, 1987.

Corrosion of Carbon Steel Overpacks for the Geological Disposal of Radioactive Waste

Contractor: UKAEA, Harwell, UK
Contract No: FI IW/0034
Working Period: January 1987 to December 1987
Project Leader: Dr G P Marsh

A. Objectives and Scope

The main objective of the programme is to complete the assessment of the long term corrosion of carbon steel overpacks in granite or clay-like formations. It is also intended to complete a mathematical model for localised corrosion and to test the validity of this model together with a previously developed model for general corrosion, through long term immersion tests.

The programme will yield generic models for general and localised corrosion which may be applied to evaluate overpack life, or the metal thickness needed to achieve a specific life, in granite or clay disposal sites.

B. Work Programme

B.1. Completion of long term tests to validate the mathematical model of general corrosion.

B.2. Continuation and extension of long term tests to evaluate the localised corrosion model.

B.3. Completion of the development of a mathematical model for localised corrosion.

C. Progress of Work and Obtained Results

State of Advancement

Long term tests to measure general and localised corrosion in carbon steel, and to evaluate the predictions of mathematical models which have been developed for both forms of corrosion, are continuing. Additional tests are in progress using specimens prepared from the reference 0.1% carbon steel supplied by the Commission. These include long term immersion tests, under granite and bentonite backfills in synthetic granitic groundwater, as well as pit growth rate measurements with small and large area specimens. The development of an improved mathematical model for localised corrosion is continuing.
B.1., B.2. and B.3. are progressing normally.

Progress and Results

1. Long Term Tests (B.1.)

Eighteen long term immersion tests to investigate the general corrosion of three different carbon steels in both plain and welded form have been in progress for about 4½ to 5 years. Coupon specimens are embedded in granite or bentonite backfill flooded with synthetic granitic groundwater and held at temperatures of 25, 50 and 90°C. Rest potentials of selected coupons are being measured continuously, and their corrosion rates monitored periodically by the polarisation resistance method. These tests are scheduled to be dismantled after 5 years' exposure, beginning in February 1988 with the ones held at 50°C. The corrosion that has occurred will be evaluated by visual examination and weight loss of the individual coupons, and by measuring the migration distance of corrosion products into the backfill. Changes in the composition and pH of the synthetic groundwater also will be analysed. These data will be applied to test the validity of the mathematical model for predicting long term general corrosion.

Identical tests are in progress with plain coupons prepared from the Commission's reference carbon steel and it is planned to dismantle these after 12 and 24 months exposure.

2. Pit Growth Measurements (B.2.)

Pit growth rate measurements made on disc specimens prepared from a $0.17^{w}/o$ carbon steel had attained test periods of 10,000 hours by the end of the 1980-84 programme. These tests have been extended to longer exposure periods to establish a more accurate empirical relationship between maximum pit depth and exposure time. One group has now been examined after 17,500 hours exposure. The maximum depth observed (3.05 mm) is less than would have been predicted (4.2 mm) from the empirical equation derived form the data obtained in the earlier programme. Another group is being continued to at least 26,000h exposure. Similar tests are underway with the Commission's reference steel using disc specimens with the same surface area as before (8 cm^2) and also with larger area (x30) plate specimens to test the validity of the extreme value statistical method for extrapolating the results of small specimen tests to much larger area containers. Pit growth measurements have been made on disc specimens after 1080 and 3017 hours exposure and on plates that had been exposed for 2000 hours.

Extreme value data from these and the earlier tests have been analysed using both unlimited and limited cumulative distribution functions. Although the unlimited distribution gives the best fit to the 1080h (disc) and 2000h (plate) data, the 3017h results give a significantly better correlation with the limited distribution as do the data from the 17,500h test. These latter observations lend support to the expectation that charge and mass transport eventually must impose an upper limit to the rate of propagation.

3. Localised Corrosion Model (B.3.)

An improved finite element method of modelling cavity propagation has been developed to overcome inadequacies of the previous models. These were mainly related to factors such as an incomplete description of the solution chemistry within a cavity, neglect of the blocking effect of solid precipitation products on ionic diffusion and migration and the effect of moving boundaries of the system. The new model now includes active corrosion on the cavity walls and is in process of being extended to determine how the pit shape changes with time. Predicted corrosion rates are now assuming more realistic values.

Title : Etude des propriétés physico-chimiques des éléments transuraniens nécessaires à la compréhension des processus de retardement de la migration en champ proche dans la géosphère.

Contractor : CEA-IRDI/DRDD/SESD/SCPCS - Fontenay-aux-Roses - FRANCE

Contrat n° : FI1W-0035 F (CD)

Working Period : June 1986 - January 1989   Project leader : A. BILLON

A. Objectives and Scope

The modelization of the transfer of the transuranian elements through the different barriers to the geosphère implies the knowledge of :

- the exact nature of the species which are able to migrate under the influence of the groundwater ; ions, molecules, colloïds.
- the equilibrium relationship between these species and the surrounding dominant other species either in a mineral or an organic form.

From this point of view it is admitted that carbonate (e.g. the different species CO_2, HCO_3^-, $CO_3^{=}$) due to his relatively high abundance in the geosphere play a major rôle in this sense that it forms complexes whith almost all the transuranian elements.

Therefore the present work is devoted toward the identification of the different carbonated complexes of the transuranian elements. The determination of their stability constant, their comportment in the geological medium in the vicinity of the source term and in the man-made barriers and finally the elaboration of a model which will describe the migration of these radioelements.

B WORK PROGRAMME

B1 - Basic chemistry :
Measurement of solubility and stability constant of the transuranian elements with the ligand carbonate. Identification of the different species.E_h - pH diagramms.

B2 - Migration ; Experiment of transfer through argileous material. Preliminary assays of diffusion cells whith Cs and Sr. Application to the migration of americium (III).

B3 - Modelization. A model wich take in account the chemical properties of the elements issued from the source term with be elaborated and tested.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of avancement

In Basic chemistry (B-1) we have achieved an extensive study of the americium (III) and plutonium (VI) solubility in carbonate media. This work is a part of the Ph.D thesis of one of us [1]. We have precised the nature of the existing species in solution in equilibrium with the solid phase as a function of the logarithm of the free CO_3^{2-} ion concentration.

Measurements of the standard potential of the couple U(VI)/U(V) in non complexing media have been extended to carbonate solutions. The redox system $UO_2(CO_3)_3^{4-}/UO_2(CO_3)_3^{5-}$ has been investigated by polarography (mercury droping electrode) and the modeling of the experimental results led to a value of E° = $- 0.810 \pm 0.020$ V/ENH. Incidentely the formation constant for the specie $UO_2(CO_3)_3^{5-}$ has been calculated.

As stated in the previous APS'report the measurements of the potentials of the (MO_2^{2+}/MO_2^{+}) and (M^{4+}/M^{3+}) couples (where M = Np or Pu) have been initiated and completed in ClO_4^- medium of varying ionic strength. Measurements were made mainly by cycling voltametry. The data have been interpreted by using the Brönsted - Guggenheim - Scatchard specific ionic interaction theory. The data consist in a set of thermodynamical values with the available corresponding correction factors permitting the extrapolation of the values at a given ionic strength.

Transfert experiments (B-2) :

- the diffusion of tritiated water has been studied on the french clay a-4, a potential material to be used as a constituent of an engineered barrier. The effective diffusion coefficient of HTO, is in the range 2.10^{-3}-2.10^{-1} cm^2d^{-1} depending of the density of the material.
- partial experimental results are available with Cs and Sr ; experiments are going on.
- conditions of study of Am(III) have been precised.

Modelling (B-3). The Condiment code which has been written previously and has been tested in the case of the migration of the single specie (without interaction with others components of the source-term) extends now to solve the case of two ions forming a precipitate. Analytical and numerical solutions for a given scenario have been compared and are good agreement.

Progress and results

Am(III) solubility. The determination of the Am(III) solubility has been conducted in $NaClO_4$ 3M, at different carbonate concentration adjusted by varying either the partial pressure of CO_2 or the total carbonate concentration (fig. 1). The nature of the species (soluble and insoluble) have been found and quantitative data such as formation constants and redox potentials are available [1]. Complexation of Am(III) occurs via the ligand CO_3^{2-}. Mixed complexes with HCO_3^- or OH^- seem unlikely in the range of the investigated concentrations. Reinterpretation on that basis of the experimental values of the literature, when available, is in good agreement with our own values.

Pu(VI) solubility. The solubility measurements of Pu(VI) in carbonate media (fig. 2) led to the following values of the formation constants (thermodynamical values)

PuO_2CO_3 (s)	pS	= - 14.2
$PuO_2CO_3^0$	$\log\beta_1$	= 9.2
$PuO_2(CO_3)_2^{2-}$	$\log\beta_2$	= 14.8
$PuO_2(CO_3)_3^{4-}$	$\log\beta_3$	= 17.4

More details are to be found in [2].

Standard potential of the couple U(VI)/U(V) in carbonate medium :
Experimentally, the study has been conducted at different ionic strengths (from 0.5 M to 3 M Na^+) ; carbonate concentration was 0.1 M. The limiting complex $UO_2(CO_3)_3^{4-}$ gives a unique reduction step (non-reversible). The study of the displacement of the half-wave potential has a function of the drop-time of the electrode permits the calcules of the formal potential of the couple U(VI)/U(V) which is then extrapolated by the appropriate method (SIT) at a zero ionic strength (E° = − 0.81 ± 0.02 V/NHE). Using this latter value and the constant $\log\beta_3 U(VI)$ given in the literature, it follows that the constant of formation of $UO_2(V)(CO_3)_3^{5-}$ is $\log\beta_3 U(V)$ = 6.1 ± 0.5.

Standard potential of the MO_2^{2+}/MO_2^{+} and M^{4+}/M^{3+} couples in non complexing medium. The following thermodynamical values have been obtained (given in V/NHE)

E° NpO_2^{2+}/NpO_2^{+}	1.162 ± 0.011
E° PuO_2^{2+}/PuO_2^{+}	0.954 ± 0.010
E° Np^{4+}/Np^{3+}	0.210 ± 0.010
E° Pu^{4+}/Pu^{3+}	1.015 ± 0.010

More details are to be found in [3]. This work will be extended in the future to the carbonate medium.

Transfert experiments (B-2)
The diffusion of tritiated water HTO in the french a-4 clay has been investigated as a function of the thickness, the degree of compaction and the percentage of additive (sand) in the material.
The apparent diffusion coefficient does not vary significantly with these parameters, but seems more affected by the apparent density of the material. Values are :

ρ_{app}	D_e ($cm^2 j^{-1}$)
1.98 - 2.33	2.7 10^{-3} - 23 10^{-3}
1.10	0.16 - 0.20

Some results are of interest for Sr, the diffusion of which has been studied as a function of thickness (diffusion cells of 0.1 to 0.6 cm). After one year, the cells'compartiments have been emptied, refill with pure water and the desorption of the Sr previously trapped in the material by diffusion was monitored by radioactive counting.
Preliminary conclusions are as follow :
Sr is trapped in clay by a fast process (1 to 2 months) and is slowly desorbed with an apparent diffusion coefficient of 10^{-7} $cm^2 j^{-1}$. Experiments will go on with that element and with Cs.

Modelling (B-3). The validation of Condiment II has been tested in various configurations ; cylindrical or spherical, with or without radioactivity decay and in the case of the formation of a precipitate.

[1] P. ROBOUCH. Contribution à la prévision du comportement de l'américium, du plutonium et du neptunium dans la géosphère ; données chimiques. Univ. Louis Pasteur (F). Novembre 1987.
[2] P. ROBOUCH and P. VITORGE. Inorg. Chim. Acta, 140 (1987), 239-242.
[3] Ch. RIGLET, P. VITORGE. Inorg. Chim. Acta, 133 (1987), 323-329.

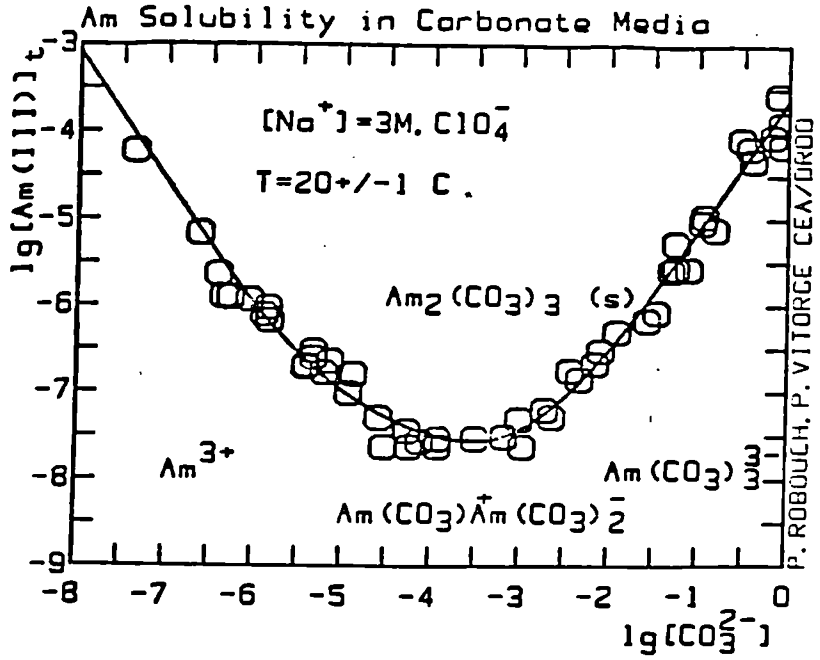


Fig. 1 : Solubility of americium (NaClO4 3M, t = 25°C)

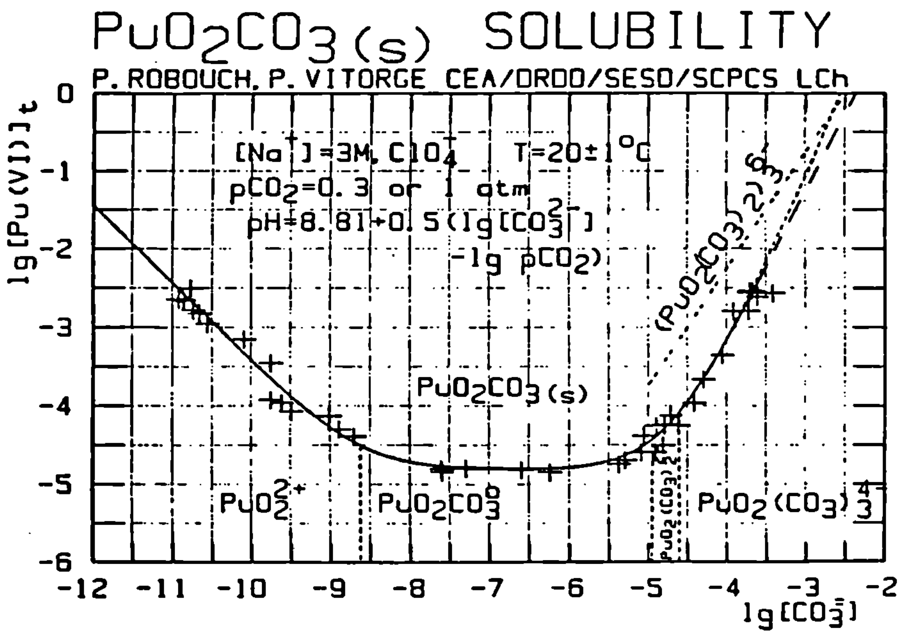


Fig. 2 : Solubility of plutonium (NaClO4 3M, t = 25°C) ; note the potential existence of a trimer specie at high free carbonate concentration (dashed line)

3.D. Development of tests for quality control and quality inspection purposes

Evaluation of non-destructive methods for quality-checking of vitrified HLW

Contractor: UKAEA - Harwell Laboratory
Contract No: FI1W/0036
Duration of contract: 2 years
Project Leader: J. Farren

A. OBJECTIVES AND SCOPE

The aim of the programme is to evaluate the use of on-line non-destructive methods, based on x-ray absorptiometry and γ-spectroscopy coupled with advanced data processing techniques, for the quality checking and/or characterisation of vitrified HLW. Particular emphasis will be placed on developing and demonstrating techniques that will be applicable to fully active glass samples. A cylindrical container of active vitrified waste produced by the Fingal process is available for this work.

Resulting from the proposed programme, we intend to demonstrate firstly the use of γ-emission measurements for determining the content and distribution of γ-emitting isotopes within a highly active sample container and secondly the use of X-ray absorptiometry for measuring the loading of active glass. On completion we aim to have sufficient information to enable the design of a plant instrument to be undertaken.

Harwell is collaborating with BAM in the exchange of data processing expertise and hardware developments, particularly with respect to detection systems.

B. WORK PROGRAMME

Task 1 Construction of the facility to enable γ-emission and x-ray absorption measurements to be carried out on highly radioactive samples, particularly the Fingal glass container.

Task 2 Adaption and improvement of computer algorithms required for the application of γ-emission tomography to the sample.

Task 3 Construction of an inactive simulant sample containing cavities to permit the introduction of sealed γ-sources.

Task 4 Use the inactive simulant sample to test the mechanical handling aspects of the equipment.

Task 5 With the inactive sample loaded with sealed sources; test the measurement and data processing parts of the γ-emission system.

Task 6 Carry out x-ray absorptiometry on the inactive sample.

Tasks 7/8 Repeat the emission and absorption measurements, respectively, on the active glass.

Task 9 Apply the equipment development for Fingal glass sample to small (1 litre) samples of cemented intermediate level waste available at Harwell.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Statement of advancement

The main development this year has been the design, construction and delivery of the sample changer mechanism. The equipment is described and illustrated in more detail in /1/.

Task 1 is therefore still in progress. Task 2 is largely complete. Task 3 is complete as far as it apppropriate at the present time. No further work has been undertaken on Task 8 and all other tasks await the completion of Task 1.

The 160kV X-ray system that will be used for the absorptiometry studies has been commissioned and a safety system based on key interlocks has been designed to ensure that the system is safely operated under all conditions.

Dr. Kettschau from BAM spent 4 months at Harwell this year. He has established a means of transferring images and data between Harwell and BAM. After this was complete, he spent some time revising the format of the Harwell reconstruction programs to provide a more integrated environment which is more suited to the interchange of software between the two groups. Dr. Kettschau implemented Chang's method of attenuation correction which is complementary to software existing at Harwell. He has supplied a report to the Commission.

Progress and results

Task 1 - Construction of facility

The equipment was finally delivered to Harwell and assembled in the last days of December and commissioning trials will take place in early January, after which the main work programme will commence.

Task 2 - Computer algorithms

As a consequence of work undertaken at Harwell and of Dr. Kettschau, mentioned above, three main methods of attenuation correction have been implemented. These are Kim's method, the RCM method, and Chang's method. The theory of these methods and others is discussed in /2/. In addition, in preparation for the experimental programme, a considerable amount of effort has been undertaken in computer simulations of the examination of the glass specimen. This has permitted the estimation of what shape and size of defect are likely to be measured in the actual sample.

Task 3 - Inactive glass simulant

This sample has now been modified to allow it to be handled in the same manner as the active specimen. It will be used in the commissioning trials, and also for transmission and emission tests using radioisotope sources.

/1/ HUDDLESTON, J. and TAYLOR, B.L., Harwell Laboratory Report AERE R 12549.

/2/ HUDDLESTON, J., HUTCHINSON, I.G., BURCH, S.F., PERRING, J.K., and DAVIES, G., Harwell Laboratory Report AERE R 12319.

Quality Assurance of Radioactive Waste Packages by Computerized Tomography

Contractor: BAM, Berlin Germany
Contract NO: FI 1W1-0037
Working Period: August 1986 - July 1988
Project Leader: P. Reimers

A. Objectives and scope

According to task 3 "Testing and Evaluation of Conditioned Waste and Technical Barriers" quality assurance is a main scope of research concerned with the handling of radioactive waste. It is provided to characterize medium and high active waste by standard test methods which are to be developed and experienced in this contract. Quality evaluation of radioactive waste packages is preferentially done by nondestructive testing methods.

Our proposal is mainly concerned with the elaboration of specific testing methods for ready conditioned waste packages as well as the matrix materials themthelves (e.g. bitumen, concrete, ceramics and glass). CT with X-rays is one of the best methods for the comprehensive nondestructive characterization of the physical and technical properties of the above described test objects. The method is especially suitable for the nondestructive evaluation of the absolute density value, of the density distribution, of the gamma activity distribution, of the localization of voids, cracks and inclusions, of the visiualization of swelling, shrinking and phase precipitations, as well as the detection of liquid phases in bentonite and cemented waste. Until now the objectives of the contract have not been subject of any variation.

B. Work programme

B.1 Literature survey for high energy radiography and CT applications for waste assay.
B.2 Specification of suitable detector system for Linac radiation.
B.3 Development, construction and test of a single detector.
B.4 Acquisition and test of a multidetector system.
B.5 Simulation program for ECT.
B.6 Choice and collection of real waste packages.
B.7 Preliminary investigations on those packages.

C. Progress of work and obtained results

Summary

Literature survey and visits in laboratories in UK and USA have shown that quality assurance of radioactive waste is considered to be very important in many countries. As quality evaluation of radioactive waste packages is preferentially done nondestructively digital radiography and computed tomography are invaluable tools.

Preliminary investigations were performed on real and simulated waste packages with the existing CT-Scanner using Co-60 radiation.

Digital radiography and CT has been carried out on a 50 l drum containing bituminized MAW with a total (beta, gamma) activity of 37 GBq (10 Ci) inside a standard 200 l barrel. A low viscosity of the bitumen matrix was discovered. 80 l containers filled with HAW simulate glass have been investigated by CT in order to find out the best cooling procedure producing a glass block free of cracks and voids.

For high attenuating packages like cemented 200 l-drums a higher energy radiation source is inevitable. At present a 17 years old radiographic linear accelerator with a maximum dose rate of 8 Gy/min/m is available.

Due to the fact that the Linac works with very short pulses of 2.3 µsec the main efforts were devoted to the specification and the development of a suitable detector system for Linac radiation.

A new Linac with a 20-fold higher pulse dose will be delivered at the end of 1988.

A single detector set up was installed and tested. This was done by measuring the intensity of the Linac radiation after penetrating through high density concrete of various thickness. For 60 cm of high density concrete the intensity is attenuated by a factor of 500. Further improvements are expected by using different detector crystals to decrease the percentage of lost radiation. The multidetector set up will consist of nine detectors with 1° angular spacing. The detector-source distance is sized to 2700 mm. The collimator system is ordered.

Preliminary HECT (high energy CT) measurements were performed on a sample 200 l-drum filled with concrete and artificial voids. Liquids with slightly variing density (0,7 - 1,3 g/cm³) could be visualized.

D. Progress and results

1. Development of CT-System (B.2, B.3, B.4)

The claims of a detector system for high energy computed tomography (HECT) are determined by the used radiation source, the required spatial and density resolution and the objects to be investigated. The existing radiation source is an electron linear accelerator with the following parameters:

LINAC Vickers Super X	
Beam energy (maximum):	9 MeV
Focal spot diameter:	2 mm
X-ray output:	8 Gy/min at 1 meter (800 R/min/m)
Pulse length:	2,3 µsec
Repetition rate:	50 or 250 pps

The dynamic range of the detectors must be at least 1:1000 for measuring drums filled with normal concrete up to a thickness of 100 cm. The electronic circuit of the detector has to work with the short linac pulses. The choice of scintillators depends on the efficiency and the afterglow of these materials.

The requirements of the detector collimator are the following:

- shielding to scattered radiation from the object
- shielding between the detectors
- variable slice thickness
- slit width should be suitable to focal spot diameter, magnification of the system source-object-detector and scan conditions (e.g. sampling)

Due to literature studies, we decided to use single crystal scintillating material, photo diode light detection, and low voltage amplifier circuit with fast, low noise operational amplifiers.

Because we want to use the same mechanical scanner as for our ^{60}Co and X-ray - CT the detector - source distance is sized to 2700 mm. The collimator aperture will be 0,8 x 1 to 15 mm² (variable by a tungstenblind).

As radiation penetration measurements have shown the collimator length must be increased to 300 mm. The intensity of the radiation emitted by the linac is highly anisotropic. Therefore only nine detectors with 1° angular spacing will be used. The collimator-system has been ordered. As central part of the detector electronics the fast low noise amplifier AD 380 Kh was chosen and has been procured with all other electronic parts.

2. Attenuation correction for ECT (B.5)

The spatial distribution of the gamma-emitting radioactive inventory of a waste package can be measured with emission computed tomography (ECT). However, the attenuation correction, inevitable with ECT, must be calculated much more accurately than with traditional medical applications. The diameter of a cemented 200 l-drum corresponds for most gamma-ray energies to several half layer values. Therefore, the radiation emitted in the central part of the package is strongly attenuated and attributes only a small percentage to the external signal. Additionally, inhomogeneities of the matrix material, voids, and cracks have a strom influence onto the external signal. This again is in contrast to the medical ECT where the matrix material (human brain) has nearly constant attenuation and nearly constant shape for any patient.

A simple method for the attenuation correction is the calculation of the average attenuation factor for each pixel following to Chang /1/. The resulting matrix can be obtained from a measured transmission tomogram (TCT) or from a reasonable model of the waste package. We wrote a program for either method of attenuation correction.

3. Experimental CT-investigations on different waste packages (B.6, B.7)

Bituminized waste in 50 l-barrel.
The 50 l-drum containing bituminized MAW with a total (,) activity of ca. 0,37 TBq (10 Ci) is housed in a standard 200 l barrel. As can be seen from the digital radiographs the small drum is in an oblique position inside the big barrel. Also, the concave surface of the bitumen is clearly imaged. The tomograms reveil a lot of voids which indicate a low viscosity of the bitumen matrix. Also this drum gives an example of corrosion attack.

80 l steel container filled with HAW-simulate.
For KFZ Karlsruhe a series of 80 l containers (outer diameter 32 cm) filled with HAW simulate glass wàs investigated by CT. It was intended to find out the best cooling procedure producing a glass block free of cracks and voids. For this purpose the container was equipped with 3 series of 5 thermocouples in 3 different heights. Each of the 5 thermocouples of one series was adjusted to monitor the temperature at a different radius. There were found very few voids and practically no cracks over the rtotal height of the container.

Sample 200 l-iron hoop drums for the simulation of defects, liquids, hidden shieldings and active sources.

With the first single detector system for HECT as described above some preliminary tomographic measurements were performed. The test object was a 200 l-iron hoop drum filled with normal concrete. In the lower part there are some plastic tubes with different diameters imbedded in the concrete filling. So it is possible to insert liquids or variing density and other test objects into these artificial voids.

References

/1/ CHANG, L.T., IEEE Trans.Nucl.Sci. vol NS-25, 638-643 (1978)

STUDY OF A NON DESTRUCTIVE TESTING METHOD FOR PACKED RADIOACTIVE WASTE CONTAINERS

Contractor : CEA, CEN Cadarache, France
Contract n° FI 1W-0038
Duration of contract : from 1 May, 1986 to 30 April, 1988
Project leader : J.F. MONTIGON

A. Objectives and scope

A computerized tomograph is developed in order to test the physical homogeneity of radwaste packages, that will be 200 l drums filled either with polymer or bitumized radwaste, and also inactive glass packages.

Special studies are required to design such a machine; in 1985, a feasibility study gave the preliminary design of a high-energy tomodensitometer, the realization of which must have been cancelled because of its cost.

The design and realization of a simplified tomograph (drum-scanner) has then been undertaken.

The objective of this programme is to start operation on this drum scanner by the end of 1988.

B. Work programme

B.1. Dedicated feasibility study for the drum-scanner, aiming at defining a low-cost, easy-to-build tomograph.
B.2. Design and realization of mechanical and electrical hardware.
B.3. Design and realization of measurement electronics.
B.4. Design and realization of the computer system.
B.5. Design and realization of the shielding.
B.6. Assembly of the components and tests on the machine.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The feasibility study (B.1) has been achieved and has given the preliminary design of the drum-scanner.

The detailed design of the components remains to be completed before their realization and the assembly of the system (B.2 to B.6). The work is progressing as scheduled.

Progress and results

The preliminary design of the drum scanner shows the following main features :

1. Source

The gamma source will be isotopic : 10 curies of Co-60.

2. Detectors

Multi-detector system using NaI scintillators (10 channels).

3. Type of scanning

Fan-beam projection (250 points); image computing by filtered backprojection.

4. Movements

41 During one projection, the drum is rotated continuously around a vertical axis, perpendicular to the projection plane and passing through the source.

42 Between two projections, the drum is rotated around a vertical axis, perpendicular to the projection plane and passing through the centre of the drum.

43 The positioning of the slice investigated is made by vertical translation of the drum.

5. Capacity

The maximum outer dimensions of the drums will be 0.6 m in diameter and 1.35 m in height.

6. Examination time

The image will be issued a few hours after starting the examination.

7. Transportability

This machine is designed to be transportable.

Development of Test Methods for Quality Control of LLW and MLW in Cement or Polymers

Contractor: ENEA, C.R.E. Casaccia, Rome, ITALY
Contract N°: FI1W-0101-I(A)
Working Period: January-December 1987
Project Leader: G. De Angelis

A. Objectives and Scope

Purpose of the R & D programme is the investigation of the industrial operation of a MObile WAste Conditioning Plant (MOWA) with regard to quality control.

The application of the proposed controls is evaluated by comparing the product qualities from inactive simulated full scale tests and labo. scale preparation.

Expected results are the realization of the proposed quality assurance procedures and the technical improvements of process control.

The MOWA plant operation can be outlined as follows: the simulated waste, as it is or pretreated, is pumped from a storage tank into a metering tank inside the MOWA and checked for temperature, density and volume by means of the external control panel. After stirring it is transferred to the conditioning station, where a 200 or 400 lt steel drum with a non-recoverable stirrer, previously filled with the correct amount of incorporation matrix (cement or polymer), is ready to receive it. At last the drum is transported away by a fork lift and the final waste form is left to cure and harden.

B. Work Programme

B.1. Optimization of recipes for the cementation with MOWA of bead ion-exchange resins, filter sludges, BWR evaporator concentrates
B.2. Labo. scale tests in the frame of a quality assurance programme
B.3. MOWA plant operation and collection of process data to be compared with standard process parameters fixed before.
B.4. Full scale tests.

C. Progress of work and obtained results

Summary

According to the formulations reported in Table I full scale samples (400 lt drums) have been prepared by the MOWA plant concerning the following waste forms:

425 Pozzolanic cement/mixed bead ion-exchange resins
425 Portland cement/filter sludges
425 Portland cement/BWR evaporator conc. + decon. solutions.

A characterization programme has been initiated according to the requirements imposed by the Italian Regulatory Body, which include:

a) Compressive strength: not less than 500 N/cm2; for viscoelastic materials the compressive load corresponding to a deformation of 5% has to be reported.

b) Freezing-and-thawing cycles: no cracks after at least 30 cycles (24 hours each) from -40 to +40 C (RH > 90%); compressive strength not less than the above mentioned limit.

c) Radiation stability: after exposure at 10E6 Gy of radiation, compressive strength must not be less than 500 N/cm2.

d) Fire resistance: solidified wastes must behave as non-burning or at least self-extinguishing materials, according to ASTM D635-81.

e) Leachability: conditioned waste must display high leaching resistance, evaluated by using long-term test methods.

f) Free standing liquids: absent, according to ANSI:ANS 55-1.

g) Biodegradability: mechanical strength not less than the above limit after bacterial attack.

h) Water resistance: no cracks after immersion in tap water for 90 days; compressive strength over the above mentioned limit.

The general work progress status is as follows:

.B.1. and B.3 are completed,
.B.2. is progressing normally,
.B.4. is delayed.

Progress and results

1. Characterization of cemented waste forms (B.1, B.2, B.3)

400 lt samples were checked for free standing water, heat evolution and internal cracks:

• no free standing water was observed on the surface of the mixes after the preparation;
• temperature recorded by iron-constantan thermocouples embedded in the middle centre of the samples ranged from 84°C (bead resins and filter sludges) to 124°C (evaporator concentrates);
• crack formation after sawing was shown only by filter sludges.

- Mechanical properties

  Crush strength was determined after normal curing, freezing-and-thawing cycles, water immersion and bacterial attack (usually with very good results) (Table II). Correlation between crush strength and other mechanical properties, such as tensile and flexural strength, ultrasonic pulse velocity, elasticity modulus and Poisson's ratio, was also made.

- Thermal properties

  Freezing-and-thawing cycles and fire test were performed. The former (24 hrs cycles between -40 and +40°C (RH>90%), proved quite severe for the specimens tested. Deep cracks appeared quite early in cemented filter sludges (5 cycles); bead resins showed evident crumbling after 10 cycles; more resistent proved the evaporator concentrates, which cracked after 15 cycles.

  As to the fire test the only effects concerned shallow cracks for bead resin samples.

- Behaviour versus water

  No damage to the specimens (like cracks or swelling) was caused by immersion in tap water for 90 days.

  Leach tests using deionized water as leachant were conducted at 40°C. The results obtained with chemical tracers ($CsCl$ and $SrCl_2$) are reported in Table III.

- Biodegradability

  No bacterial growth of Pseudomonas aeruginosa was noticed after incubation at 37°C and RH>90% for three weeks. At the same way no growth of fungi occured after incubation at 30°C (RH>90%) for the same time length.

2. Full scale tests (B.4)

Tests on the whole package, including drop test onto a target, water test and stackability, are scheduled for the next year.

TABLE I

Composition of waste/cement mixes (recipes for 1 Kg)

A - Pozzolanic/bead ion-exchange resins, PZ/IER

Cement	599.30 g
Water	171.00 g
Amberlite IR120*	114.85 g
Amberlite IRA400*	114.85 g

* Both types of resin containing about 50% w. of water

B - Portland/filter sludges, PC/FS

Cement	617.90 g
Water	307.30 g
Diatomaceous earths	74.80 g

C - Portland/ evaporator concentrates (Sulphates) + decontamination solutions, PC/S

Cement	654.68 g
Water	264.00 g
Sodium sulphate	70.94 g
Potassium chloride	1.60 g
Decon-solution (6% of Turco Decon)	8.78 g

TABLE II

Compressive strength (MPa) of cemented wastes (average of three values)

Cement/waste	Normal curing	Freeze-thaw cycles	Water immersion	Bacterial attack	
				Pseudomonas aeruginosa	Fungi
PZ/IER	25.0	cracked	23.5	20.5	23.5
PC/FS	42.5	28.5	52.0	46.0	41.0
PC/S	35.5	22.0	46.5	44.5	40.0

TABLE III

Leaching of Cs and Sr from cemented samples (105 days of leaching)

(average of two values)

cement/waste	PZ/IER		PC/FS		PC/S	
chemical tracer	Cs	Sr	Cs	Sr	Cs	Sr
leaching rate (Kg/m2.s)	$8.0\ 10^{-8}$	$1.1\ 10^{-8}$	$9.0\ 10^{-8}$	$1.0\ 10^{-8}$	$4.9\ 10^{-7}$	$1.9\ 10^{-8}$
leaching factor (m/s)	$4.6\ 10^{-11}$	$6.3\ 10^{-12}$	$4.8\ 10^{-11}$	$5.3\ 10^{-12}$	$2.4\ 10^{-10}$	$9.3\ 10^{-12}$
cumulative leached fraction % (m)	0.15	0.02	0.16	0.02	0.55	0.04
% release	18.7	2.5	19.7	2.3	67.4	4.6

RADIOACTIVE WASTE PACKAGE ASSAY FACILITY

Contractor:	Taylor Woodrow Construction Ltd, Southall, UK
Contract No:	FI.IW.0102 UK (H)
Duration of Contract:	January 1987 to July 1990
Period Covered:	January 1987 to December 1987
Project Leader:	Mr. I.Ll. Davies

A. Objectives and Scope

Neutron and gamma interrogation of drums of radioactive waste may be used to determine actinide content. A linac, with appropriate targets, provides powerful gamma and neutron sources yielding the potential for a very sensitive technique for actinide determination.

The objective of the work is to provide information which will enable an integrated assay facility, incorporating a number of examination techniques, to be designed. The present programme is directed at research to determine the feasibility and sensitivity of a linac driven interrogation system in the assay of the contents of 500 litre drums of cemented wastes and the development of methods by which signals generated in the experiments may be processed.

The programme is led by TWC supported by the Harwell Laboratory, Fisher Controls Ltd. and Ray Technology.

B. Work Programme

Stage 1 (Feasibility Study)

B.1.1 Investigate suitability of linac and neutron target for active neutron interrogation.

B.1.2 Determine and evaluate the performance and limitations of combined active neutron and active gamma interrogation chamber, and compare with separate chambers. Consider compatibility of chamber with passive neutron examination.

B.1.3 Establish data processing model and test against available calculated and experimental information.

Stage 2 (Main Experimental programme)

B.2.1 Provide suitable components for an experimental assay system.

B.2.2 Commission experimental system.

B.2.3 Operate system in neutron and gamma interrogation modes and measure initial responses.

B.2.4 Make preliminary evaluation of system and modify accordingly.

B.2.5 Operate system in neutron and gamma interrogation modes and measure responses under different conditions.

B.2.6 Evaluate characteristics of common neutron and gamma interrogation system and identify development needed for use in an integrated assay facility.

B.2.7 Develop data processing model and check agianast test results.

Stage 3 (Application to practical assay facility)

B.3.1 Evaluate performance of integrated assay facility

B.3.2 Consider engineering and systems developments required for an integrated assay facility.

C. Progress of Work and Obtained Results

Summary

Start of the work programme was delayed until July 1987 following a thorough re-appraisal of the project. A revised technical statement was published /1/ in which the original five stages were reduced to three. Increased research was identified to enhance confidence in assay capability, and whereas this will be paid for by increased UK contributions, a shortfall of budgets was exposed requiring a request to the CEC for increased support. At the end of Stage 1 a major independent review of results has been requested by the major UK sponsor to justify continuance of the programme. Although invaluable to the project, this will have no financial implications.

The intermediate progress report /2/ described the planning and programming of the work and the use of Task Analysis Sheets for the initiation and control of programme activities. The overall work programme, especially for Stage 1, was revised and refined, as shown in Section B.

A suitable calculation method has been developed and validated for establishing the neutron output from a LINAC - target assembly. Experimental confirmation was used in the case of photo-production of neutrons from a beryllium target, where previous experimental results were found to be in disagreement with theoretical calculations. It was found that the varying energy neutrons from targets, at least down to about 3 MeV, gave responses per source neutron, and radial spatial variations similar to monoenergetic 14 MeV neutrons.

Calculation of the effects of interrogating neutron energy for a beryllium target and position of actinide within a hypothetical cemented waste drum showed that radial spatial variation at mid-plane is about 3 and overall variation about 6.

As a target material, beryllium was found to give slightly better results than heavy water (ie lower spatial variation, higher neutron yield). The optimum target size has been provisionally established. Comparison of a linac plus target neutron source with a D-T neutron tube has confirmed the superiority of the former in terms of neutron yield per pulse and pulse repetition frequency.

B.1.1, is completed

B.1.2 is started

Other activies are expected to start in accordance with the revised programme.

Progress and Results

Neutron energy spectra (B.1.1)

Neutron outputs were calculated for heavy water and beryllium targets illuminated by bremsstrahlung generated from a tantalum radiator itself bombarded with electrons from a linear accelerator (LINAC). Comparison with published experimental data revealed good agreement for heavy water but a discrepancy of about factor 50 in the case of beryllium, for neutron energies greater than 2 MeV. It was suspected that the experimental results were unreliable, and experimental validation of the theoretical calculations was sought.

Measurement of outputs from beryllium and heavy water targets (B.1.1)

Measurements were made of the energy spectra of neutrons photoproduced from 50 x 50 x 100mm beryllium and heavy water photoneutron targets illuminated by bremsstrahlung from a radiator consisting of 1mm tantalum and 40mm aluminium. This unit was installed in the low energy cell of the HELIOS linear accelerator at Harwell.

Preliminary analysis indicates that neutron yield ratio for beryllium/heavy water at 90° to the incident 15 MeV electron beam agreed with calculations to within factor 2 overall and within about 50 per cent above 2 MeV. Neutron energies were measured between about 0.5 and 5 MeV. These results validated the calculations and confirmed that the previous beryllium experimental data were in error. Further analysis of these data is in progress including examination of indium foil activation measurement.

Neutron output and target design parameters (B.1.1)

Calculations of neutron yield were made for heavy water and beryllium, these materials being the most efficient photoneutron producers for electron energies up to about 15-20 MeV. A plot of neutron yield versus electron energy indicated that an electron energy of about 15 MeV would be a reasonable value, conditioned by the cost and efficiency of the LINAC.

A plot of neutron yield versus bremsstrahlung radiator thickness showed that an optimum radiator thickness should be less than the mean electron range. Use of a low Z material to stop the residual electron beam would be beneficial since it would reduce the gamma flash without significantly affecting neutron output.

A plot of neutron yield versus target thickness (the dimension parallel to the electron beam), indicated a levelling off at thickness above about 300mm, which represents a maximum practical value. A plot of neutron yield versus target width (the dimension at right angles to the electron beam and parallel to the generated interrogating neutron flux) also indicated a levelling off above about 300mm (for beryllium). However, the generated photo-neutrons have a mean free path of about 30mm and a much greater thickness than this would simply prevent some neutrons from ever escaping from the target. Thus a practical maximum thickness is about 100mm. Provisional photoneutron target dimensions are 300 x 300 x 100mm with the electron beam direction normal to a 300 x 100mm face and tangential to the drum.

The Monte Carlo neutron transport program MCNP was used to determine the effects of certain subsequent neutron interactions, within the target itself, namely elastic scattering and neutron multiplication due to n, 2n reactions. The main effect of the former is a shift in neutron energy from above to below about 1 MeV.

Approximately 15 per cent neutron multiplication was obtained with the beryllium target, whereas for heavy water multiplication was negligible.

Neutronics of neutron interrogation system (B.1.1)

The interrogation responses were obtained using the MCNP program, for a 750mm diameter 500 litre drum filled with a homogeneous mix of cement grout plus iron representing CAGR waste hulls. The neutron transport code MORSE was used to calculate detection efficiencies.

Initially, the effect of changing the interrogating neutron energy was determined, obtaining the response per gramme of fissile material located in each of three zones at the horizontal mid-plane of the drum. It was found that spatial variation did not worsen at energies above about 1-2 MeV. This indicated that a neutron source with a spectrum of energies greater than 1 MeV should give results similar to those from monoenergetic 14 MeV neutrons. Thus a linac plus target interrogation system was seen as probably viable.

The next calculations assumed the drum to be within an interrogation chamber surrounded at the sides and bottom by 300mm of concrete and borated resin shielding. A neutron target as described in the preceeding section was centred 200mm from the drum surface on mid-plane, within a cutout in the shielding. Neutrons were counted by a single ^{3}He counter located outside the drum shielding on the opposite side of the drum to the target. The neutron counter was surrounded by 50mm polyethylene moderator itself surrounded by cadmium, shielded from the drum by 50mm of lead.

Responses were calculated for one gramme of fissile material located in each of three zones as before, and in each of five horizontal slices. Detection efficiency was assumed to be the same at all heights, although it is actually about 30 per cent smaller at the bottom, and this effect will need to be included later. Neutron counting was thus assumed to start 200 μs after each interrogating pulse. Results for both heavy water and beryllium targets were obtained and are shown in Table I.

The results indicate that the beryllium target seems to perform almost as well as a 14 MeV monoenergetic source, which gave a mid plane spatial variation of 1.5 and an outer response of 8.3 counts. g^{-1}. $(10^{10}$ source neutrons$)^{-1}$. The heavy water target seems to be inferior both in absolute yield and positional variation.

Comparison of LINAC and neutron tube (B.1.1)

The results obtained from the previous work showed that a LINAC plus target and a D-T neutron tube are broadly comparable, as regards variation of response and absolute neutron count. Other factors influencing the choice are:

- capital and operating cost
- neutrons per pulse
- pulses per second

These data are shown in Table II which indicates that a linac plus target assembly can produce from 3 to 100 times as many neutrons per pulse, and at least 30 times as many pulses per second. Thus, a LINAC based assay facility should be able to detect considerably smaller amounts of actinides than would be possible using a neutron tube, in a shorter time, and with greater accuracy. Although a LINAC has a much higher capital cost, this is likely to be outweighed by the high cost of frequent replacement of neutron tubes.

References

(1) Radioactive Waste Package Assay Facility. Proposed Research Programme Un-numbered Report (April 1987).

(2) Findlay. D.J.S, Sene, M.R, Swinhoe. M.T, Molesworth. T.V. Radioactive Waste Package Assay Facility. Taylor Woodrow Intermediate Progress Report. 8250/RDD/0001A (September 1987)

Table I

Calculated rotation averaged response per gramme of fissile material as a function of height within drum

(a) Heavy Water Target

height from mid-plane mm	response counts g^{-1} (10^{10} source neutrons)$^{-1}$ centre	intermediate	outer
460	0.2	0.4	1.9
230	1.3	1.1	4.6
0	2.1	1.5	7.2
-230	1.3	0.9	5.0
-460	1.2	1.7	4.9

The two top heights are not representative of a real facility because of the absence of a roof to the model, and can therefore be neglected. The mid-plane variation is a factor of 5 and the overall variation is a factor of 8.

b) Beryllium target

height from mid-plane mm	response counts g^{-1} (10^{10} source neutrons)$^{-1}$ centre	intermediate	outer
460	0.9	1.3	3.0
230	2.5	2.0	5.4
0	4.0	2.7	8.1
-230	2.3	2.3	6.0
-460	1.4	2.2	4.6

The mid-plane variation is a factor of 3 and the overall variation ia a factor of 6

<u>Table II</u>

<u>Comparison of linacs and neutron tubes for interrogating 500 litre drums</u>

	principle of operation	neutron output	neutrons $pulse^{-1}$ for current application	capital cost (buildings excluded)	maintenance costs (excluding electricity + operators salaries)
<u>Linac</u> <u>Small</u> ~ 10 MeV ~1 Kw S Band	accelerated e^-'s produce brems. in high Z radiators; brems. produces n's from beryllium or heavy water	$\sim 8 \times 10^8 \mu C^{-1}$ $\sim 2 \times 10^8 \mu C^{-1} \geqslant 2$ MeV	$\sim 2 \times 10^8$ $\sim 4 \times 10^7 \geqslant 2$ MeV (2 μs, 100 mA pulse (~ 500 pps max.)	~ £350k (including neutron target)	~ £30K $year^{-1}$
larger ~15 MeV L - band		$\sim 2 \times 10^9 \mu C^{-1}$ $\sim 7 \times 10^8 \mu C^{-1} \geqslant 2$ MeV	$\sim 10^{10}$ $\sim 3 \times 10^9 \geqslant 2$ MeV (~ 1A, 5μs pulse) (~ 300 pps max.)	~ £800k (including neutron target)	~ £60k $year^{-1}$
<u>Neutron</u> <u>tube</u> GEC Avionics (UK)	~ 125 kV deuterons on tritiated target	4×10^8 s^{-1} mean max.	4×10^7 (14 MeV) (15 μs pulse, 10 pps max.)	~ £50k	~ £7k to replace tube after ~ 3×10^5 pulses
Sodern (France)	~ 125 kV mixed beam on mixed target	2×10^8 s^{-1} mean max. 2×10^{11} s^{-1} peak max.	$\sim 2 \times 10^7$ (14 MeV) (100 μs pulse)	~ £100k	~ £30-£40 to replace tube after 1000 hours

CHAPTER 4

TASK No 4

Research in support of the development of disposal facilities; shallow burial and geological disposal studies

CHAPTER 4

TASK No. 4 : RESEARCH IN SUPPORT OF THE DEVELOPMENT OF DISPOSAL FACILITIES; SHALLOW LAND BURIAL AND GEOLOGICAL DISPOSAL STUDIES

A. Objective

Evaluation and modelling of the long-term behaviour of the geological barrier

Development of disposal facilities.

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

a) Work related to sites and their characterization

- General survey of geological formations and development of measuring techniques with a view to develop large scale in-situ characterization of the geological formations by direct or indirect methods

- Geoprospective studies : development of an operational method for the prospective analysis of the characteristics of geological containment

- Rock mechanics studies.

b) Work related to geological repositories and barriers

- Improvement of the designs and technologies required for the setting up of repositories in geological formations (salt, granite, clay)

- Development of long-lived containers for vitrified waste and of methods for the backfilling sealing of openings in geological repositories.

c) Work on radionuclide migration in the geosphere

- The work mainly comprised integral experiments on migration simulation, laboratory studies concerning the properties of materials from specific sites, hydrogeological investigations, research on natural geological migration systems and the role of micro-organisms, and, finally, the development of calculation tools and the intercomparison of codes regarding transport and geochemistry.

d) Shallow land burial

- Studies dealt with migration phenomena, improvement of barriers and radiological assessments.

C. 1985-1989 programme

The work will be mainly a continuation of the research started during the 1980-1984 programme; however, special emphasis will be put on calculation tools and their intercomparison, on investigations attached to specific sites as opposed to laboratory work of general nature, on the role of colloïds and complexes in radionuclide migration, on studies of natural analogues, and on the development and assessment of various backfilling materials and concepts.
Co-ordination is ensured by a structure of projects or working groups :

GEOPROS	:	Geoprospective Studies
ROCMEC	:	Rock Mechanics
COSA	:	Comparison of Rock Mechanics Codes for Salt
B & S	:	Backfilling and Sealing
MIRAGE	:	Migration of Radionuclides in the Geosphere
COCO	:	Colloïds and Complexes
CHEMVAL	:	Geochemical Benchmark for Mirage
NAWG	:	Natural Analogue Working Group

D. Programme implementation

56 contracts have been signed and the available information is listed thereafter. However information has not been received as far as contracts no. FI1W/0145 and FI1W/0083 are concerned.

4.1 RESEARCH RELATING TO SITES AND THEIR CHARACTERIZATION

4.1.A. General survey of geological formations and development of measuring techniques

The 600 m borehole project:
"Development of a surveillance method during dry-drilling of a 600 m deep borehole in salt and performance of geotechnical measurements in the 600 m hole"

Contractor: Netherlands Energy Research Foundation (ECN)
Petten, The Netherlands
Contract No.: FI-1W1/0084
Working Period: January 1987 - December 1987
Project Leader: J.R. van Seuren

A. OBJECTIVES AND SCOPE

During the dry-drilling experiment performed under contract with the Commission of the European Communities in the framework of its previous R&D programme (1980-1984), it was obvious that the applied techniques were limited with respect to the maximum diameter and depth. In fact, a hole with a diameter of 30 cm and a depth of 300 m was succesfully drilled. Since then, a dry-drilling technique was developed for larger diameters and depths.

This technique will be tested by drilling a borehole with a diameter of 60 cm, typical for a disposal hole, and a depth of 600 m. As there is a need for an alternative for the reconnaissance drilling of each individual borehole in a HLW repository, a surveillance method during the dry-drilling will be developed in cooperation with GSF. In the 300 m hole of the previous programme, several experiments concerning the creep behaviour of the salt were performed at ambient and elevated temperatures. The convergence measurements of the diameter as a function of the depth of the hole gave insufficient results, i.e. the convergence as a function of the lithostatic pressure could not be checked. As this parameter is important, lithostatic pressure tests will be performed (see figure 1).

The project is funded by the Ministry of Economic Affairs, ECN, GSF and CEC and carried out in close cooperation with GSF-Institut für Tieflagerung Braunschweig, FRG. In a first phase, free convergence measurements over the length of the hole and a non-isothermal lithostatic measurement will be carried out. In a subsequent phase of the current five year programme, additional non-isothermal lithostatic measurements at two other levels and isothermal lithostatic measurements will be performed; all these results will be used for the validation of analytical techniques and computer codes such as GOLIA.

B. WORKING PROGRAMME

B.1. Design, construction and testing of a surveillance method.
B.2. Exploration and experiments.
B.2.1. Geochemical exploration.
B.2.2. Isothermal convergence measurement.
B.2.3. Non-isothermal lithostatic pressure measurements.
B.2.4. Isothermal lithostatic measurements.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The present concept of the licensing authorities is to have a reconnaissance drilling for boreholes with large diameters. With a working surveillance method these reconnaissance drillings may be reduced. Therefore there is a need to develop a surveillance method during dry-drilling.

The present database for thermo-mechanical computer code validation, consisting of the ECN 300 borehole experimental data, needs to be complemented with free convergence and lithostatic pressure data from a 600 m deep bore hole to be drilled in a relative undisturbed environment.

1. Development of a surveillance method (N. Jockwer, GSF)

Laboratory and in-situ investigations have shown that rock salt contains different gas components trapped within small inclusions and pores or adsorbed to the crystal boundaries. Calculations on the liberation of these gases indicated that it is possible to determine them within the flushing air and to determine layers with higher porosity and gas content. Technical concepts have been developed and analytical systems for the gas determination are selected. Components necessary for system construction have been ordered.

2. Exploration and experiments

The previous APR, issued under this contract, reported analytical work, which predicted the isothermal radial free convergence of rock salt at different depth up to 600 m, based on extrapolation of the measured convergence in the 300 m borehole. These analytical results are necessary as basis for designing of equipment for performing actual measurements. The analytical work has continued during the period of the APR-87. In this period an analogous method has been used in order to compare four different convergence measurements, which were performed in the Asse Salt mine. The four sets of considered convergence measurement locations were:

- Temperature Test Field (TTF 4);
- Brine Migration Test Field;
- Convergence measurement at the bottom of the ECN 300 m hole;
- Prototype cavern.

Some geometrical characteristics of the measurements are given in table 1.

CHARACTERISTIC ASPECT	CONVERGENCE MEASUREMENT			
	TTF4	BMTF	ECN conv.	cavern
Level in Asse (m)	750	800	1042	978.2
Measured quantity	horiz. room conv.	horiz. room conv.	borehole conv.	diam. cav. conv.
Dimension of cavity (m)	6*6*300	10*7.5*55	Φ0.31*300	Φ24.1 H36.4
Length of meas. (days)	640	485	834	365

Table 1. Summary of characteristical aspects of the four convergence measurements

The comparison of the four convergence experiments with each other and with predictions based on several constitutive relations leads to the following important conclusions.

- The convergence can be described accurately with a constitutive law, based on elastic strains and a secondary creep law. The transient character of the convergence is not necessarily caused by transient material behaviour but can be explained by the transient state stress in the material around the openings.
- A secondary creep law and elastic parameters based on laboratory experiments do not describe the in-situ convergence experiments. The reason for this discrepancy might be the transient primary creep and the time independent plasticity which are not taken into account with this constitutive equations.
- As demonstrated, the experiments can be described reasonably well with a secondary creep law, based on laboratory experiments and a reduced modulus of a elasticity (by a factor 12). The same good description however can be found with the elastic constants from the laboratorium but with a higher creep constant A.
- The convergence measurements cannot be used to derive both the elastic constants and the secondary creep constants.
- For the thermo-mechanical analysis the constitutive relations should be able to describe the in-situ behaviour. This means that a combination of elastic behaviour and secondary creep strain both determined in a laboratorium can lead to completely wrong results.
- For the near field analysis the constitute relations derived from the ECN 300 m borehole experiments can be used.

The theoretical work is based on the concept of small displacements and an infinitely extended salt formation. Further work has to be done to investigate the influence of these assumptions. The work planned in the 600 m hole in the Asse can be used for this purpose. The results however can be used for the near field analyses as the time period of concern and the maximum strain to be expected do not deviate substantially from the experimental ones.

2.1. Design of experiments

During the detailed design considerations of the experiments, it became obvious that the design of isothermal lithostatic experiments, which measurements will be carried out at 600 m in the borehole, excerted a big strain on the time schedule of the design of all other experiments. More so because of the useful additions of experiments which were added after safety studies of stored radioactive waste in boreholes. To alleviate this problem, it was decided to use two boreholes of 60 cm diameter and a depth of 600 m. One will be used to perform the isothermal lithostatic measurements, while in the second hole the free convergence measurements along the length of the hole and a non-isothermal lithostatic measurements will be carried out. The detailed design of the experiments is now underway, based on the above-mentioned basis.

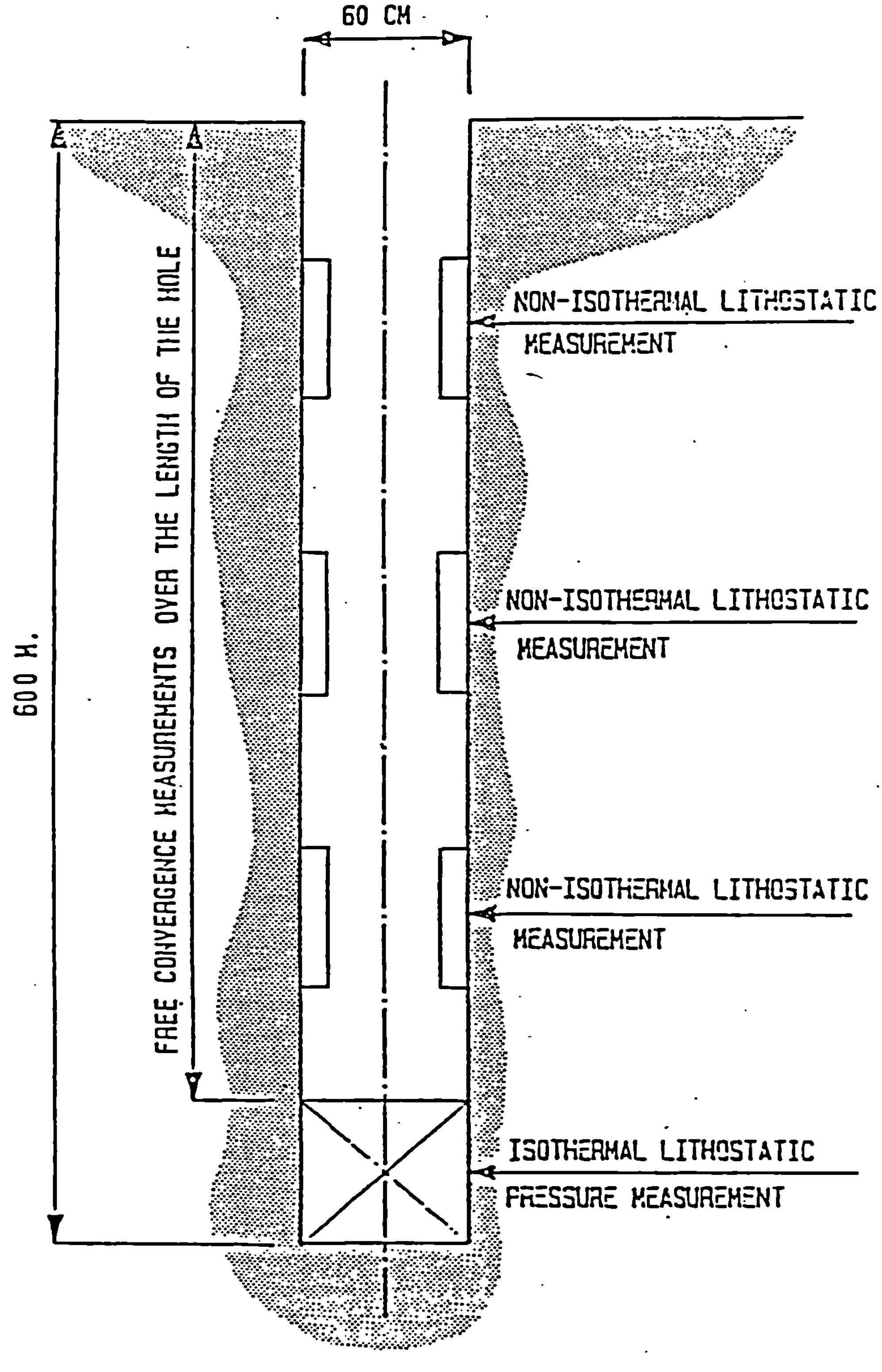


Fig. 1 : Sketch of the 600 m bore hole measurement set up.

Faults in clays: their detection and properties

Contractor: BGS, Keyworth, Nottingham, UK

Contract No.: FI1W/0085/UK

Contract Period: October 1986-October 1989

Project Leader: N.A.Chapman

A. Objectives and Scope

Faults occur in most mixed sedimentary environments but their effects on regional groundwater flow patterns are poorly understood. The hydrogeological significance of faulted clay layers is of particular relevance where mudrocks are potential host formations for radioactive waste repositories.

In cooperation with ISMES of Italy two faults through clay layers will be studied (one site in the UK and one in Italy). The project has three objectives :-

1. To develop suitable geophysical techniques to detect water bearing faults in clays. These techniques will aim to differentiate between hydraulically active faults and those which are either sealed or non-water bearing.
2. To measure the hydrogeological properties of faults in sequences of mudrocks and aquifers. This will be achieved by measuring the hydraulic and chemical properties of the fault directly and by measuring the effect of the fault on the underlying aquifers.
3. To define suitable techniques for use in site investigations and methods for assimilating faulted boundaries into flow and transport models in clays and mixed sediments.

B. Work Programme

B.1. Desk study to evaluate a number of potential UK study sites; selection of two preliminary sites.

B.2. Initial geological and geophysical investigations of the preliminary UK sites; selection of the final study site.

B.3. Development of geophysical techniques for fault identification.

B.4. Detailed geophysical survey of the study site.

B.5. Borehole drilling.

B.6. Wireline geophysical logging of the boreholes.

B.7. Hydrogeological testing of the boreholes.

B.8. Synthesis of the results to evaluate the significance of the fault.

C. Progress of work and obtained results

State of advance

Reconnaissance geophysical surveys have been performed at both initial U.K. field sites. A more detailed geophysical survey has been performed and some shallow boreholes have been drilled at the Down Ampney site. These investigations accurately located a fault running approximately East-West across the site. Down Ampney has been preliminarily selected as the U.K. field site for detailed study.

B.2. has been completed.

B.3., B.4. and B.5 are progressing.

Progress and results

1. Preliminary geophysical investigations (B.2.)

Preliminary reconnaissance geophysical surveys were performed at two initial field sites, Down Ampney and Wombleton, with the aim of proving the existence, location and geometry of any faults at these sites. The chief geophysical technique employed during the preliminary surveys of the two sites was electrical resistivity traversing. A Schlumberger array was chosen in preference to a Wenner array because it provides higher resolution data during traversing due to its shorter potential dipole and because gradient array profiles can be made with current electrodes fixed if lateral effects are disturbing the survey. Seismic refraction and EM ground conductivity surveys were also performed to support the resistivity traverses.

Two resistivity lines (Lines A and B, Figure 1) were run from SW to NE at Down Ampney. The resistivity along Line A showed a 30m displacement between 800-1000m (Fig. 2). An EM profile along Line A showed a near surface resistivity anomoly at the same location. Two seismic refraction lines were run either side of the displacement which indicated that the Cornbrash was 31m below ground level on the southern side and at least 50m deep on the northern side.The resistivity survey along Line B produced very variable results, most probably caused by near surface debris. There was therefore no corroboration of the apparent fault seen along Line A. The conclusion from this work was that there was a fault at Down Ampney of unknown orientation with a displacement of at least 20m but with limited Oxford Clay - Oxford Clay contact which could be as little as 10m.

Three resistivity lines (A,B, & C) were run from NW to SE at Wombleton. The resistivity values from Lines A and C were very variable, most probably as a result of interference with debris from the old airfield constructions, and these lines showed no obvious faults. The resistivity profile along Line B showed a step profile (Fig. 3) which can be interpreted as a fault. However if the sequence is one of clay overlying limestone then the throw of the fault is in the opposite direction to that predicted by the regional seismic survey. An alternative explanation is that the resistivities of the clay either side of this "supposed fault" are different (i.e. this is a phenomenon within the clay itself). These hypotheses were examined using a number of resistivity soundings either side of the fault, the aim being to identify the likely vertical resistivity distribution. They suggest that the resistivity of the Kimmeridge Clay is different either side of the fault within the topmost 100m, being 17 and 50 ohm-m.

The aim of the intial reconnaissance geophysical surveys was to allow the selection of a single site where detailed field studies would be performed. The reconnaissance survey at the Down Ampney site clearly defined a potential fault whereas the interpretation of the survey at Wombleton is open to some discussion. However the limited clay to clay contact at Down Ampney gave rise to doubts as to the likely hydrogeological significance of the fault, particularly as this interval of clay contact may lie within the zone of weathering. A second phase of investigations was therefore initiated to enable the confident selection of a suitable single site for detailed geophysical and hydrogeological study.

2. Secondary site investigations (B.3.,B.4.,B.5.)

A further eight electrical resistivity traverses (lines D-J, Figures 1 and 2) were performed at Down Ampney. Lines A,E,G,H,J and K all crossed the fault line and showed a consistent distinctive response to the fault. This takes the form of a large resistivity peak separating the two sections of differing resistivity (see for example line E, Figure 2). This has allowed the line of the fault at the surface to be accurately mapped across the site and it trends broadly East-West (Figure 1). Line C which runs approximately sub-parallel to the fault line shows a trend of resistivity decreasing to the East indicating an increasing thickness of Oxford Clay in that direction. It was not possible to make accurate estimates of the strata thicknesses by one dimensional resistivity modelling due to the lack of data describing the resistivity profile of the Oxford Clay, Kellaways Beds, and Cornbrash sequence at the site. The extent of the clay to clay contact at the fault plane therefore remained unknown. Two dimensional finite element resistivity modelling indicated the peak resistivity value observed at the fault was a feature of resistivity variations within the fault itself. An array of three very shallow boreholes, 7-12m deep, was drilled on each side of the fault (Figure 1). Core samples were subjected to detailed palaeontological examination which allowed the stratigraphic zone of the samples to be determined. By estimating the thicknesses of the underlying stratigraphical zones the Oxford Clay was predicted to be 19m thick on the upthrow side and 51m on the down throw side which implies a fault throw of 32m and a clay to clay contact of 19m at the fault plane. The Down Ampney site was however preliminarily chosen as the UK site for detailed study on the basis of these investigations and further work at the Wombleton site was suspended.

Seismic reflection measurements using sources both at the surface and in the shallow borehole arrays have been performed. The data is currently being interpreted. The drilling of two boreholes, one on either side of the fault, is currently being planned. These will be fully cored and penetrate the Cornbrash allowing an accurate measurement of the clay to clay contact at the fault and determination of the depth of weathering of the Oxford Clay. Wireline resistivity logs will provide accurate resistivity profiles allowing more detailed interpretation of the resistivity traverses.

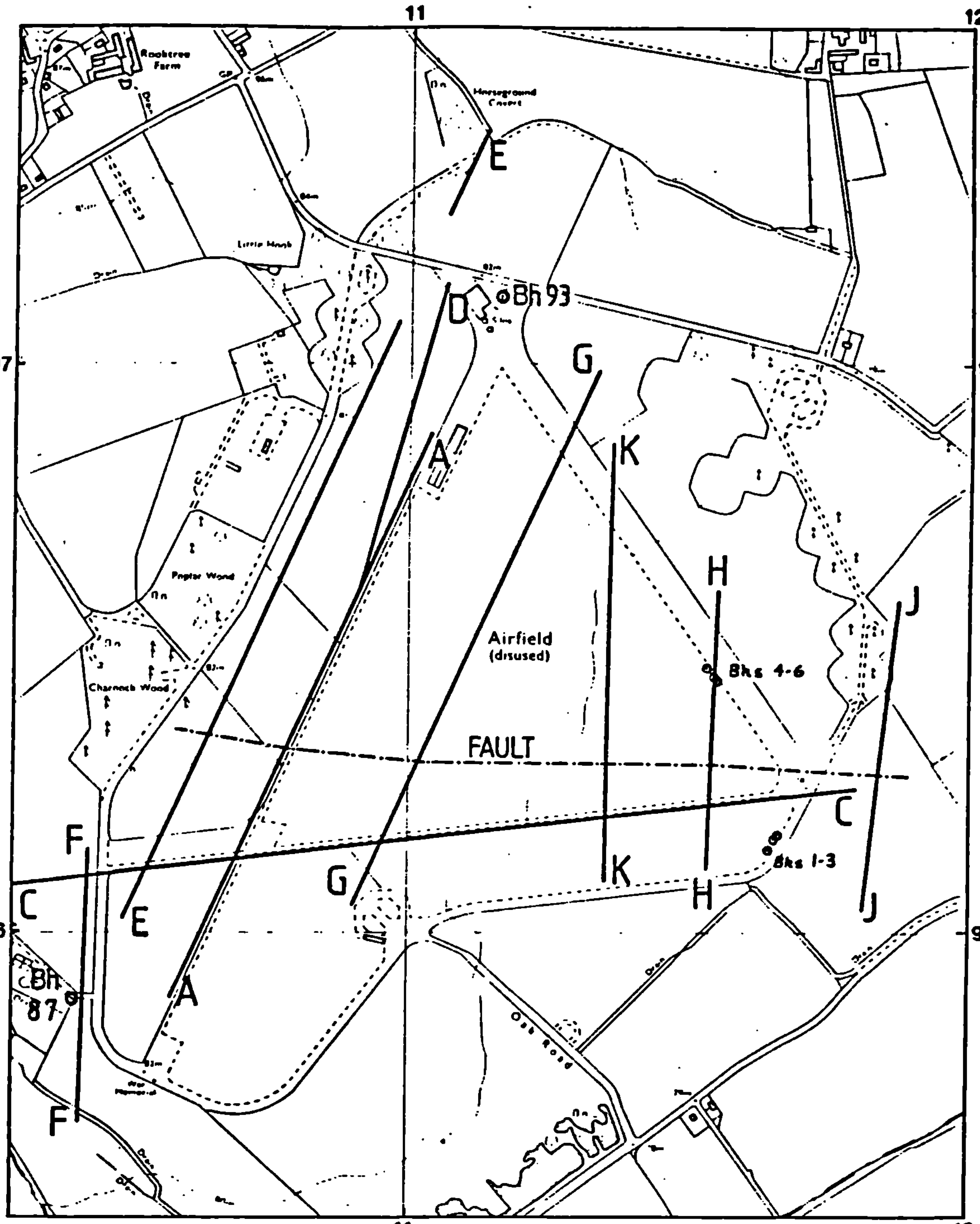


Figure 1. The airfield, boreholes, resistivity traverse lines and the position of the interpreted fault at the Down Ampney site

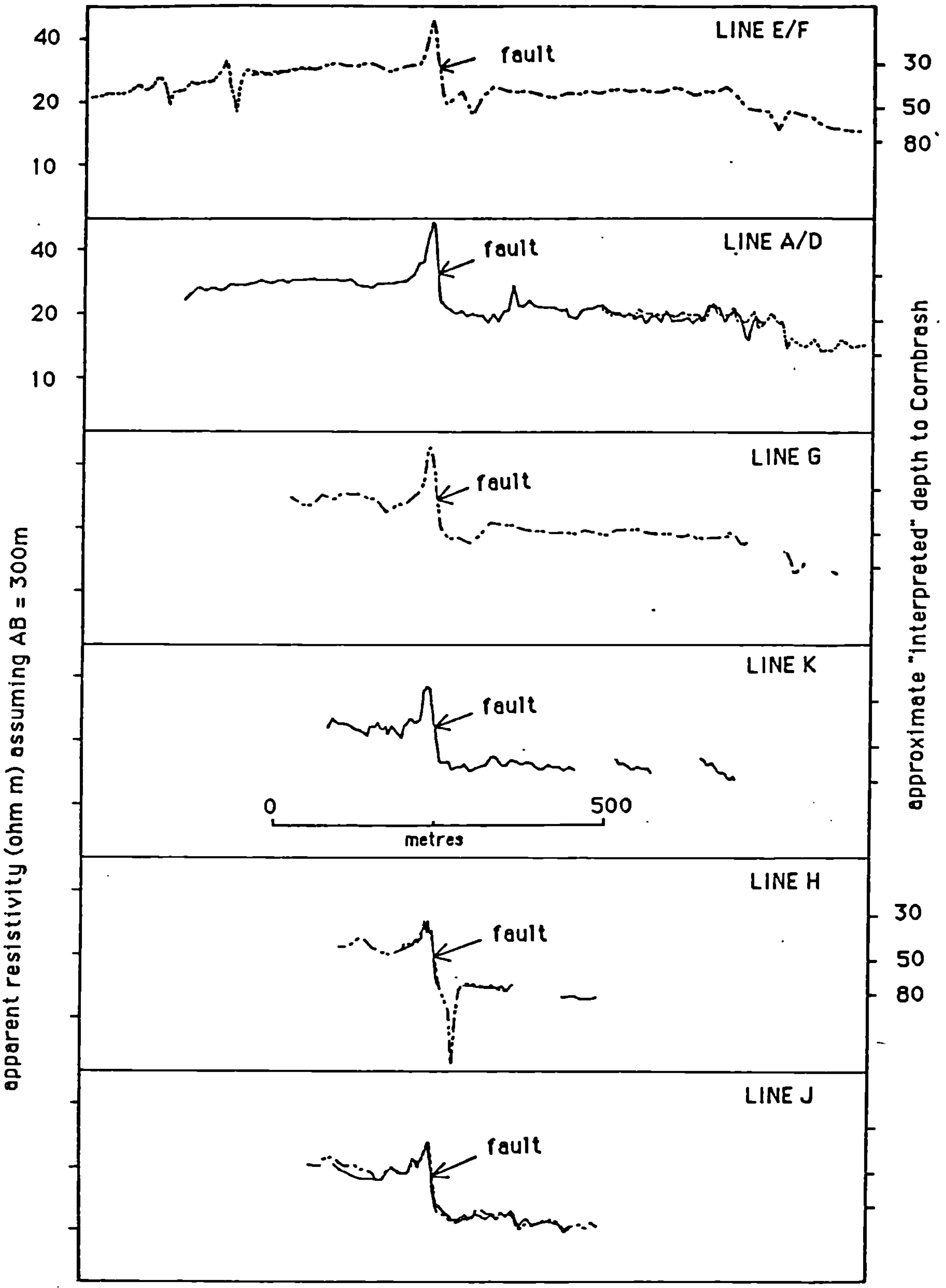


Figure 2. Resistivity profiles across the presumed fault

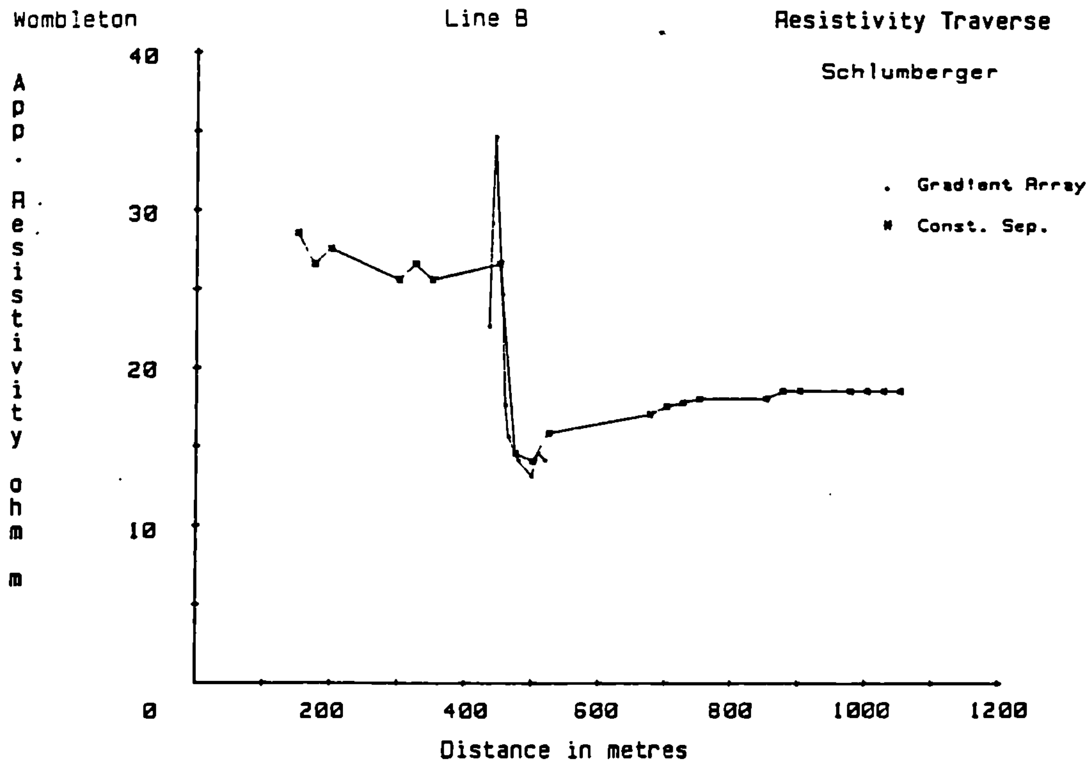


Figure 3 Resistivity traverse along Line B.

METHODOLOGY FOR APPLICATION OF ELECTRIC AND ELECTROMAGNETIC BOREHOLE TECHNIQUES FOR DETAILED EXPLORATION OF FRACTURED ROCKS

Contractor : BRGM, Geophysics department, Orléans, France.
Contract n° : FI1W/0086/F.
Duration of contract : July 1986 - June 1989.
Project leaders : G. POTTECHER, P. VALLA.

A. OBJECTIVES AND SCOPE

The aim of the research work is first to complete the technical developments of three borehole geophysical methods for which prototypes have been built, and second to develop a methodology for these tools applied to detailed investigation of fractures.

These tools are :

- ELIAS, an electrical imaging technique to investigate the borehole wall and determine the depth, strike and dip of conductive or resistive fractures,
- ROMULUS-ERIC, a set of induction transmitter-receiver probes to point out conductive fractures and measure their conductance with a one to a ten meters radius of investigation,
- ARLETT, a three axis induction receiver used together with a surface electromagnetic transmitter, to help assess the geometry of the more conductive fractures in a ten to one hundred meters range.

The first and third systems are still in the technical development stage while the second is now operational. Numerical modelling of the methods is needed to fully assess their capabilities.

B. WORK PROGRAMME

1. Technical and theoretical development of electric and electromagnetic probes.
1.1. ELIAS
1.1.1. Final step of prototype development
1.1.2. Design of data acquisition and processing software
1.2. ROMULUS-ERIC
1.2.1. Design of modelling software for thin sheet conductors
1.2.2. Set up of a catalog of theoretical response curves
1.2.3. Study of complex geometry of thin conductors
1.3. ARLETT
1.3.1. Study of improvements to be made in the probe design
1.3.2. Development of a new prototype
1.3.3. Numerical modelling

2. Field tests and methodological studies
2.1. Technical field tests of ELIAS and ARLETT
2.2. Methodology for detailed exploration of fractured rocks
2.2.1. Data acquisition on available test sites
2.2.2. Data processing and interpretation
2.2.3. Analysis of results and methodology assessment

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The technical developments done this year include the completion and field test of the orientation module, part of the ELIAS and ARLETT probes (2.1). The former is being built and will be field tested in a few months (1.1.1). The work on ARLETT deals with the sensors (1.3.1).

Data has been acquired on two sites with ROMULUS, ERIC and an axial-only ARLETT (2.2.1). It has been interpreted with the help of 3D modelling (plates and discs) and showed the interest of working at higher frequencies. The modelling results obtained so far build a comprehensive set of master curves (2.2.2 and 2.2.3).

Progress and results

1.1.1 . Orientation module for the ELIAS and ARLETT probes

The orientation module (two servo-accelerometers and three fluxgate magnetometers) has been mounted in a probe for field testing. At normal logging speeds, it has a 1 degree accuracy on the dip and 4° on the azimuths. These performances wil be somewhat improved in the definitive version.

. ELIAS probe development

After some measurements on rock samples, the measuring pads mechanics and a part of the acquisition electronics have been revised. The prototype is now under construction.

1.3.2 ARLETT probe development.

Three kinds of electromagnetic sensors have been studied. Low resistance air coils proved to be too voluminous and are abondonned. Work is going on with high impedance air or ferrite coils, trying to solve the noise-sensitivity problem and the coupling problem. The objective is to cover the 10 Hz-10 kHz range of frequencies. Meanwhile, measurements are carried out with a probe limited to an axial sensor and operating in the 10 Hz-1 kHz range.

1.2.2, 1.3.3 Numerical modelling

Models have been computed for ROMULUS and ERIC using conductive plates and discs in free space, good approximations for fractures in hard rock. In the case of ARLETT, layered earth models have been examined in addition. The curve catalogue enables quantitative interpretation for bodies cut by the hole at a high angle : lateral extension, strike direction, conductance. "Near miss" signatures have also been studied.

These model data indicate that the interpretation is quite easy in the case of strong and distinct anomalies but that the signal level will be low in most hard rock cases.

As a consequence, the working frequencies should be choosen as high as possible : several kiloherz with ARLETT and 10 kHz for ERIC, in order to remain in the low induction range.

2.2 Field data acquisition and interpretation

A survey done at Chassole (France) in orthogneiss yield a low signal level but some features could be interpreted quantitatively, showing distinct responses for the various tools. The signal-to-noise ratio is insufficient, corroborating the need for higher frequencies in hard rock.

Another survey in sedimentary rocks enabled quantitative interpretation, validating the multispacing tool concept. Information could be obtained on structures of dimensions 0.3 to 7 m and larger, crossed by the borehole or not. The model catalogue seems to be an efficient approach to data interpretation.

DEVELOPMENT OF A SELF-CONTAINED DRILL-HOLE CHROMATOGRAPHIC PROBE

Contractor : CEA - CEN CADARACHE
F 13108 St. Paul-lez-Durance

Contract No. : FI1W/0087

Working period : 36 months

Project Leader : J.M. VINSON

A. OBJECTIVES AND SCOPES

The study of the transuranian nuclide migration from radioactive waste storage places is based on the knowledge of the natural environment and, in particular, of the chemical composition of the water : the transfer vector.

In addition to major elements, the water also contains trace elements which play a prominent part not only on the general equilibrium, but also on the radionuclide migration possibility.

This is in particular the case of the Lanthanides, present in the granitic and argillaceous environments, whose role of sorption competitors with respect to the Actinides has been exhibited throughout numerous experiments.

The scope of this contract is to manufacture and operate a chromatographic probe to be used in a deep drill-hole, so designed as to acquire a representative sample under conditions of equilibrium of the natural environment, to preconcentrate it by elimination of the saline content and to store it for ulterior analysis at the surface.

B. WORK PROGRAM

B1. Process Development

B11. Principle laying-down and delineation. In-laboratory model.

B12. Definition of final probe design after study on model. Realization and adjustment on CADARACHE site.

B2. Probe Qualification in the Deep Drill-hole of AURIAT.

B3. Application to 3 reference sites.

C. STATE OF ADVANCEMENT

Summary - The study of the methods of salt charge concentration and separation and of lanthanide separation has been complemented. A new gradient has been defined and is now being implemented in the laboratory-made model. The probe design has been revised in consideration of the technical requisites. The pump system is completed and the probe fabrication is progressing.

Work progress and results obtained

1. Laboratory model

The first stage consists in implementing, in the laboratory, all the processes required for the realization of the experiment.

1.1. Preconcentration

A preconcentration is necessary because of the feeble concentrations existing in the natural environment and of the analytical dead ends of the conventional methods. The preconcentration, however, must be limited because of the perturbation it is likely to create during the following elution, but also because of the dimensions of the storage reservoirs inside the probe. A concentration factor of 10^3 has been obtained together with correct yield values. The latter have been improved by some modifications of the elution system. A 10^4 factor would correspond -in the probe- to the percolation of 200 ml water for each column.

The analytical performances are being improved with the implementation of the laser spectrofluorimetry in order to limit this preconcentration stage, if possible.

1.2. Elimination of the salt charge

The elimination of the salt charge and, in particular, of the monovalent alkaline ions, is necessary in order to avoid any risk of column saturation by ions highly concentrated in comparison to the elements and whose analysis may be performed elsewhere.

To achieve that elimination without affecting the fixation of the valuable elements, an acid is added to the drill water in order to create an environment with a $pH < 2$.

After rinsing, the column may be reused for the separation and analysis of the lanthanides.

1.3. Lanthanide separation

The salt charge concentration and elimination stages somewhat modify the conditions of the lanthanide fixation. A new gradient has been studied to preclude that inconvenience :

Phase A is made up of distilled water and phase B is made up of hydroxyisobutyric acid 0.2 M at pH 4.6. The new linear gradient is :

0 at 100 % B in 45 min.

Figure 1 shows an example of separation.

1.4. Analysis

The lanthanides are analyzed after complexation by ARSENAZO I using spectrophotometry at 585 nm.

The sensitivity limits have been improved by the use of a post-column reactor, high quality elution water (18 MΩ) and strict circuit rinsing procedure. They are in the order of $4 \cdot 12^{-12}$ Mole per element and per sample.

2. Study and realization of the probe

2.1. Design

Other modifications have been made ; they consisted in limiting the number of stages while keeping the modular aspect. Thus, the upper outlet in the drill-hole has been cancelled and a rinsing circuit connected to the effluent tank. The dual liquid connection interfaces have been eliminated by grouping up the corresponding stages. The gain over the whole length of the tool may be evaluated at 1.5 meters. Such a gain is not negligible knowing that the length (estimated at about 11 m) of such a system is an impairing factor in the implementation procedure ; it is then a plus for the success of the experiment.

Figure 2 illustrates schematically the modified design.

2.2. Pump system

The pumps with their associated electronic circuits are now realized. Functional and flow rate tests are being made in shop.

3. Work continuation

The work is being pursued by the study of the "column" stage and the study of the general electronic design of the probe.

Similarly, the laboratory processes are being improved and adapted for their implementation on the site.

In-situ qualification tests are contemplated for the second half-year 88.

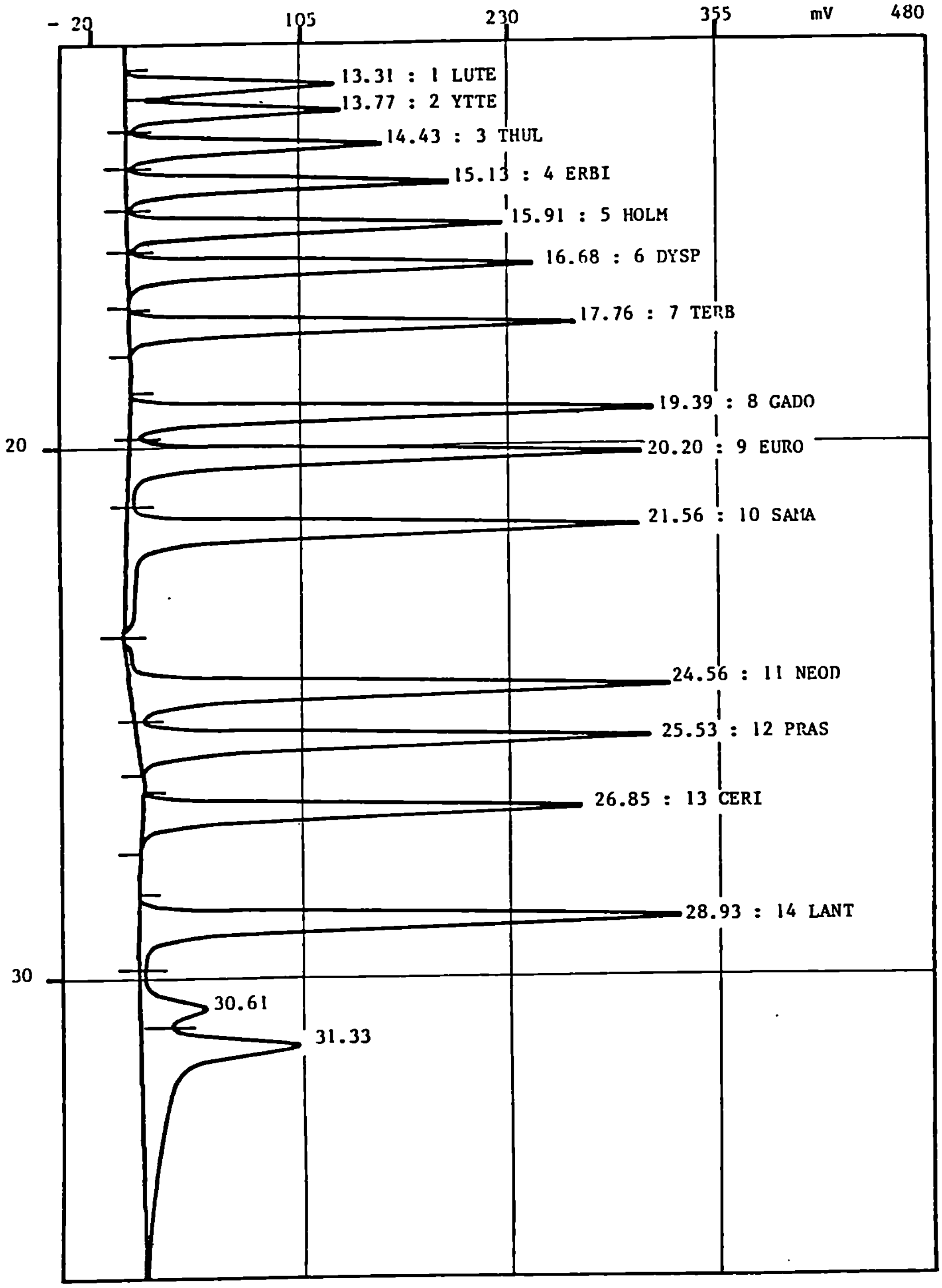


Figure 1 : Diagramme HPLC Lanthanides

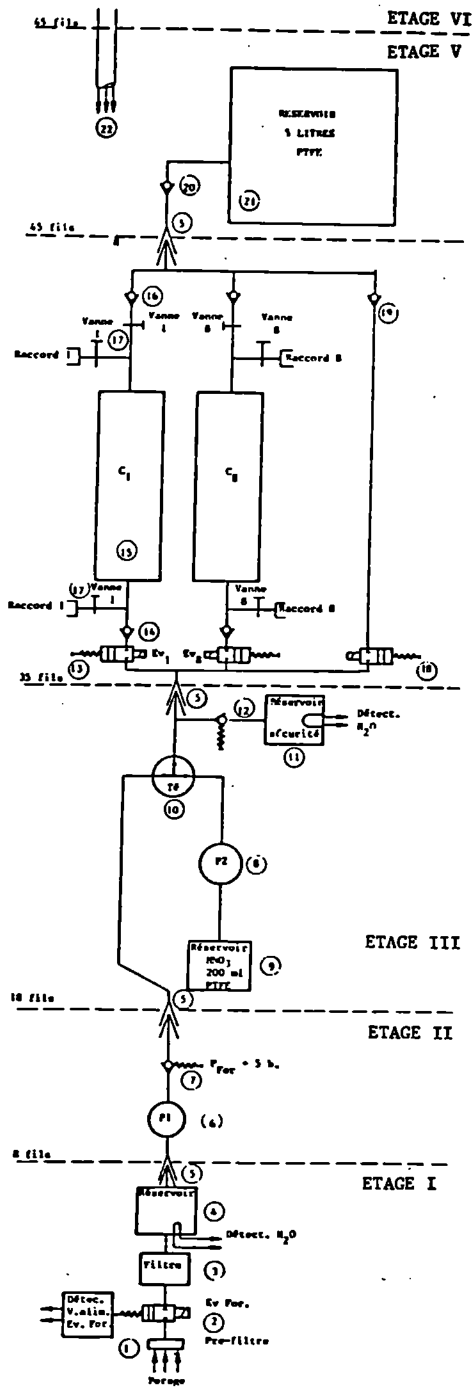


Figure 2 : Schéma de principe de la sonde

Fracture mapping in clays

Contractor: University of Exeter, Exeter, UK.

Contract No: FI1W/0088/UK

Duration of Contract: September 1986 - August 1989

Period covered: January 1987 - December 1987

Project leader: Dr. E.M. Durrance

A. OBJECTIVES AND SCOPE

If faults occur in the rock mass surrounding a nuclear waste repository, there is a risk that the return of hazardous radionuclides to the biosphere will take place by migration along these zones of higher permeability. However, the detection and characterisation of faults is difficult, especially in soft rocks such as clay, and little development of techniques has taken place. The objective of this programme is to develop techniques that will be suitable for routine use in both the preliminary and detailed stages of site investigation. The approach used is based on the observation that faults act as zones of preferential migration in the natural degassing of the Earth. Soil gas exploration methods are applied to detect zones of anomalous gas geochemistry. The procedure followed is based upon samples obtained from a depth of about 0.5m along a series of traverse lines. Once a fault has been located, spiking of the high permeability zone, from a borehole drilled to intersect the fault plane, will take place with specific gases of different compositions. The ground will then be resurveyed to determine the migration characteristics of the gas within the fault. Test sites in the UK and Italy are to be investigated in co-operation with BGS (Keyworth) and ISMES (Rome). BGS and ISMES are responsible for site selection and the drilling programme, but some trials will be conducted at sites near Exeter.

B. WORK PROGRAMME

B.1. Equipment development.

B.2. Site selection.

B.3. Soil gas geochemistry.

B.3.1. Reconnaissance soil gas surveys measuring ^{4}He, ^{220}Rn, ^{222}Rn, O_2, CO_2 and some organic gases.

B.3.2. Detailed soil gas surveys of anomalous zones identified in the reconnaissance surveys.

B.3.3. Spiking of vertical boreholes and resurvey of soil gases.

B.3.4. Spiking of inclined boreholes and resurvey of soil gases.

B.4. Modelling and interpretation of results.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The construction of a mobile laboratory, for the analysis of soil gases at remote sites, has been completed. The equipment has been thoroughly evaluated at sites near to Exeter to prove the viability of the techniques before visiting the BGS survey site (Down Ampney). A total of 35 man days at Down Ampney survey site has completed the initial soil gas background survey, and identified 6 major fractures. Site selection for our own purposes has been completed, and computer modelling programs prepared. The programme is on schedule as far as can be achieved by co-operation with the BGS and ISMES projects. In terms of programme items,

B.1. has been completed.
B.2. has been completed.
B.3. is in progress:
B.3.1. and B.3.2. have been carried out at one survey site (Down Ampney). These programme items will continue at ISMES' survey site and our own sites in Dorset, to best accommodate progress by BGS and ISMES.
B.3.3. and B.3.4. await drilling of exploration and test boreholes by both BGS and ISMES.
B.4. is in progress.

Progress and Results

1. Equipment development

Much of the first year was directed at the construction and thorough testing of a mobile gas geochemistry laboratory /1/. The design includes mains power wiring throughout, to support a Dupont 120SSA leak detector mass-spectrometer installed in the vehicle (for ^{4}He analysis) and with the potential for powering other equipment.

Other gases which can be routinely analysed are CO_2, O_2, CH_4, ^{220}Rn and ^{222}Rn. The portable equipment used comprises an EDA RD-200 scintillation counter (for Rn), Servomex PA404 infra-red analyser (for CO_2), and Servomex 570A paramagnetic gas analyser (for O_2). Analysis of CH_4 is carried out at Exeter using a Pye Unicam 104 gas chromatograph fitted with an OV101/chromabsorb column and flame ionisation detector.

Local trials of the newly devised equipment were carried out prior to surveying at the specified contract sites to prove the capabilities of the equipment /1/. These surveys were carried out over fractures at Exmouth (Rn), Chudleigh (CO_2, O_2, He, Rn, CH_4) and Buckfastleigh (CO_2, O_2, CH_4). For comparison, trials were carried out over fractures and mineralisation at Gooseford (CO_2, O_2, He, Rn, CH_4). In addition, evaluation and comparison of soil gas signatures over coal mining districts was carried out at Rhos-wen Colliery (CO_2, O_2, He, Rn, CH_4). Identification of fractures is possible using the equipment and sampling techniques devised. Typical anomaly threshold/background ratios are in the order of 1.5 - >2.0.

2. Site selection

Survey sites in southern England have been assessed for their potential viability as additional test sites /1/ to complement those selected by BGS and ISMES. Those most suitable are in the Sherborne area of Dorset. Sites on the Bishops Caundle Fault, Crouch Hill Fault and Westrow - Goat Hill Fault are targeted for investigation. Sites on the Stalbridge Fault and Hatherly Fault are considered as secondary possibilities. Sites in the Oxford Clay appear to be the most promising, and site investigation visits have already been made to the three primary test sites.

In the Westrow and Crouch Hill survey areas, mapping of poor surface drainage areas and a study of early topographic maps has shown that roughly N-S trending features appear to be present throughout the survey areas. These approximate with the positions of the faults as marked on geological maps, but deviate in their trend direction by a few degrees to the north. It is likely that the surface features represent the fracture pattern for the area, and that the faults have a network of major sub-parallel fracture planes associated with them, constituting fracture zones of higher permeability.

In accordance with BGS site selection criteria /2/ the Wombleton test site has been abandoned, at the present time, in favour of Down Ampney. Site selection in Italy is now limited to two quarry sites /3/. The availability of suitable field conditions for soil gas sampling at these sites, as specified at the commencement of the contract /4/ is still unclear. Soil gas sampling within the quarry sites at Orte or Narni does not appear feasible. Information from ISMES is awaited regarding the nature of the surrounding terrane, and available access.

3.1, 3.2 Soil gas surveying

Following the evaluation trials, fieldwork was carried out at the main BGS test site, Down Ampney aerodrome, in Gloucestershire. The geology comprises a faulted sequence of Oxford Clay underlain by the Cornbrash (limestone). The whole area is overlain by about 5m of gravel and 1m of soil. Soil gas samples for He, Rn, CO_2 and O_2 were taken on 9 traverses perpendicular to the suspected trend of the fault-line. The timing of the surveys was such that programme items 3.1 and 3.2 were combined at this site. Six close-spaced traverses were concentrated at the eastern end of the survey area, where BGS intend to site their boreholes. Three more widely spaced traverses completed the soil gas survey scheme. In addition, dissolved gas samples were collected from groundwaters in the BGS 10m deep boreholes to the north and south of the suspected fault.

The results of the groundwater sampling shows effectively no difference in the ^{222}Rn activity of each sample site. The dissolved ^{4}He content is significantly greater than that previously observed from fractured ground in southwest England /5/, indicating that on site-specific grounds, gas retention is high.

The results of the soil gas survey are excellent /6/. They show that E-W trending linear structures can be traced for the whole length of the survey area. These features are both faults and fractures. Identification of displacements along these features is not directly possible by gas measurement alone. However, the precise location of the fracture planes using gas geochemistry is at least as accurate as can be achieved by geophysical methods. By combination with seismic or borehole data, an accurate representation of the underlying structure may be established. The fractures show soil gas signatures comparable with those seen over fractures in older metasediments /7/, and therefore may be classified similarly. Four fracture types are recognised, differing in respect to their overall permeability to gases and their ability to act as channelways for groundwater movement. This information should be used specifically to select suitable faults and fractures for detailed study. One of these fractures coincides directly with the fault identified by BGS electrical resistivity surveying /2/. The others were not detected by BGS survey methods and are assumed to be fractures with no measurable displacement on them. Their behaviour with respect to gas migration is comparable with the fault.

4. Modelling and interpretation

The development of computer programs has been documented in the first progress report /1/. The suite of programs have not been utilised in the Down Ampney surveys for the reason that the main computer program relies on an evenly scattered data set with rectangular boundaries for optimum results. Thus, for a wide spaced survey of the type carried out, the density distribution is far from optimal. The programs will be more useful when close-spaced samples from a regular grid are taken in the planned gas-spiking tests (programme items 3.3, 3.4).

References

/1/ GREGORY, R.G., CEC Progress report, September 1986 to July 1987 (1987)

/2/ BRIGHTMAN, M.A. and BLACK, J.H., Proceedings of a CEC contractors' meeting, Brussels, 10th December 1987, CEC Report RWD 87/20 (1987)

/3/ CHIANTORE, V., Proceedings of a CEC contractors' meeting, Brussels, 10th December 1987, CEC Report RWD 87/20 (1987)

/4/ GREGORY, R.G., Faults in clays joint meeting of BGS, ISMES and Exeter University, Keyworth, 5th September 1986. Unpublished Report, Annex 5 (1986).

/5/ GREGORY, R.G., Unpublished Ph.D. thesis, University of Exeter (1987)

/6/ GREGORY, R.G., Proceedings of a CEC contractors' meeting, Brussels, 10th December 1987, CEC Report RWD 87/20 (1987)

/7/ GREGORY, R.G., DURRANCE, E.M. and MITCHELL, C.R., Proc. Ussher Soc. 6, 389-397 (1986)

FAULTS IN CLAY: THEIR DETECTION AND PROPERTIES

Contractor: ISMES S.p.A., Bergamo, Italy
Contract No.: FI1W/0103
Duration of contract: November 1986 - May 1990
Period covered: January 1987 - December 1987
Project leader: Ferruccio Gera

A. OBJECTIVES AND SCOPE

The contract has to be coordinated with a companion contract to BGS to perform similar work in UK clays (Contract FI1W/0085).

Faults and fractures are known to intersect argillaceous formations that might be considered suitable as host rocks for a radioactive waste repository. In some cases these structural discontinuities have been observed to enhance the hydraulic conductivity of mudrocks. Consequently any argillaceous formation considered for the location of a waste repository should be characterized thoroughly from the points of view of occurrence of fractures and their hydraulic significance.

Available geophysical techniques are not adequate for identifying faults and fractures in argillaceous materials. If geophysical techniques with the capability of revealing the existence of structural discontinuities in mudrocks, particularly water-bearing ones, could be developed, then site investigation studies would rely more on geophysics and less on drilling with significant advantages from different points of view.

The objectives of the contract are:

- to develop suitable geophysical techniques to detect water-bearing faults in mudrocks. The main intended application is for surface investigations, but possible application in tunnels and boreholes should be considered;
- to carry out hydraulic testing across deep faults to determine their hydraulic conductivity and the hydraulic conditions of any measurable water flow;
- to define suitable techniques for use in site investigation campaigns.

B. WORK PROGRAMME

The project consists of the following activities:

1) a survey within the country to identify sites where faults intersect mudrocks;
2) chosing the most suitable sites for carrying out field work;
3) drilling at least two boreholes in such a way that the fault plane will be intersected at a suitable depth;

4) performing geophysical investigations of the fault zone both from the surface and down hole;
5) hydraulic testing of the fault zone;
6) geophysical logging of the boreholes;
7) geotechnical measurements of samples obtained from the cores;
8) hydraulic modeling of groundwater flow in the fault zone.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

1) The search for suitable sites for performing field work has consisted of three parts:
   a) a bibliographic study, b) a careful analysis of geological maps and c) site visits.
   The bibliographic and cartographic analyses have been completed. A certain number of site visits have been performed allowing to select a few potential sites.
2) A currently disused clay quarry, nearby Orte, a small town located about 80 km north of Rome, has been selected as the first study site.

Progress and results

1.a, 1.b BIBLIOGRAPHIC AND CARTOGRAPHIC SURVEY

The starting point of the activities related to the "faults in clay" project was a bibliographic and cartographic survey based on available documents and new acquisitions.

A critical review of new data and information published in geological and engineering-geological literature did not provide useful information regarding major faults in argillaceous formations in Italy. However, some information on tunnelling works in clays was collected and in few cases it was possible to visit tunnels under construction.

A careful exam of information contained in the official topographic and geologic maps regarding railway tunnels in argillaceous formations was carried out. This part of the work provided a tool for the selection of some sites; for some of them additional field verifications were necessary.

1.c SITE VISITS

As far as site visits are concerned some valleys and many quarries in argillaceous formations have been visited in the last years for various purposes (site selection for field tests, underground laboratory; site selection for landfills, etc.). On the whole, six quarries were selected as possible sites for field testing: one in northern Italy, three in the center and two in the south of the country. All of them have been excavated in clays of plio-pleistocenic age.

Several tunnels excavated in clay formations all around central and southern Italy have been surveyed to find out if there were signs of intersecting faults. In fact a fault plane crossed underground would provide an ideal situation for field testing. Most of the tunnels are abandoned railway galleries in central and southern Italy; some of them have been constructed at the beginning of the century and have been abandoned for decades so that now they are usually in bad conditions.

Only one of the visited tunnels was under construction but no significant tectonic feature has been recognized along the excavation.

However, finding a good site for field testing in a tunnel is difficult in old galleries for the ubiquitous presence of the lining, in new ones for the difficulty of performing tests during excavation work.

The surveyed tunnels cross various kinds of clay formations and, with the exception of the galleries near Civitavecchia, about 70 km north of Rome, they are all located in southern Italy.

2. THE CHOICE OF THE ORTE QUARRY

The result of the above mentioned activities is that the best sites for in-situ tests are those quarries in argillaceous formations in which faults were clearly recognized. They are located in central Italy near Orte (northern Lazio, about 80 km from Rome) and near Narni scalo (southern Umbria, about 110 km from Rome) but the final choice was Orte, for the ease of access due to its abandoned state. Moreover at Narni a landslide on the quarry face obliterated the fault plane so it would be difficult to localize the points for in situ tests (drilling, geophysics, etc.).

At Orte a fault plane is visible in the upper part of the quarry face where the clay formation is interested by sand levels; the estimated displacement of the fault is about 2 m, the direction is the so-called "antiappenninica" (NE-SW, consistent with the second main regional system of faulting), and the dip is about 60°NW.

At the beginning of February 1988, after a detailed topographic survey to localize precisely the drilling points, field operations will start with the realization of two reconnaissance boreholes to intersect the fault plane, collect samples and perform in-situ hydraulic tests; a preliminary geophysical survey will be carried out at the same dates to obtain more details on the stratigraphy of the area.

A figure showing the localization of the surveyed sites and two tables summarizing data on quarries and tunnels are attached.

TABLE I: SUMMARY OF CLAY QUARRIES DATA

	LOCALITY	DISTRICT (REGION)	GEOGRAPHIC SECTOR	CLAY TYPE AND AGE	MAIN SEDIMENTOLOGICAL FEATURES	MAIN TECTONIC FEATURES	NOTES
Q1	Fiorano modenese	Modena (Emilia Romagna)	north	plio-pleistocenic blue clays	rich in fossils	nothing visible	quarry hasn't been in operation for more than two years: surface processes may have obliterated existing features
Q2	Narni scalo	Terni (Umbria)	center	plio-pleistocenic blue clays	lignite level; sands on top	fault 4 m displacement	quarry is waiting for new operating licence in larger area
Q3	Orte	Viterbo (Lazio)	center	plio-pleistocenic blue clays	thin sandy layers; sands on top	fault 2 m displacement; fractures	unused quarry since 1983; oxidation bands along the fractures but not along the fault
Q4	Guidonia	Rome (Lazio)	center	plio-pleistocenic blue clays	sand lenses; oxidized bands	2 faults; fractures	oxidized bands can originate either from sedimentological or surface processes; calcite in fractures
Q5	Cosenza	Cosenza (Calabria)	south	plio-pleistocenic blue clays	nothing visible	fracture systems; slickensided surfaces (faults?)	5 quarries with similar features
Q6	Milazzo	Messina (Sicily)	south	plio-pleistocenic blue clays	(see text)	fracture systems (subvertical)	site visit was carried out in 1986 for other purposes; new visit could provide additional information

TABLE II: SUMMARY OF TUNNELS DATA

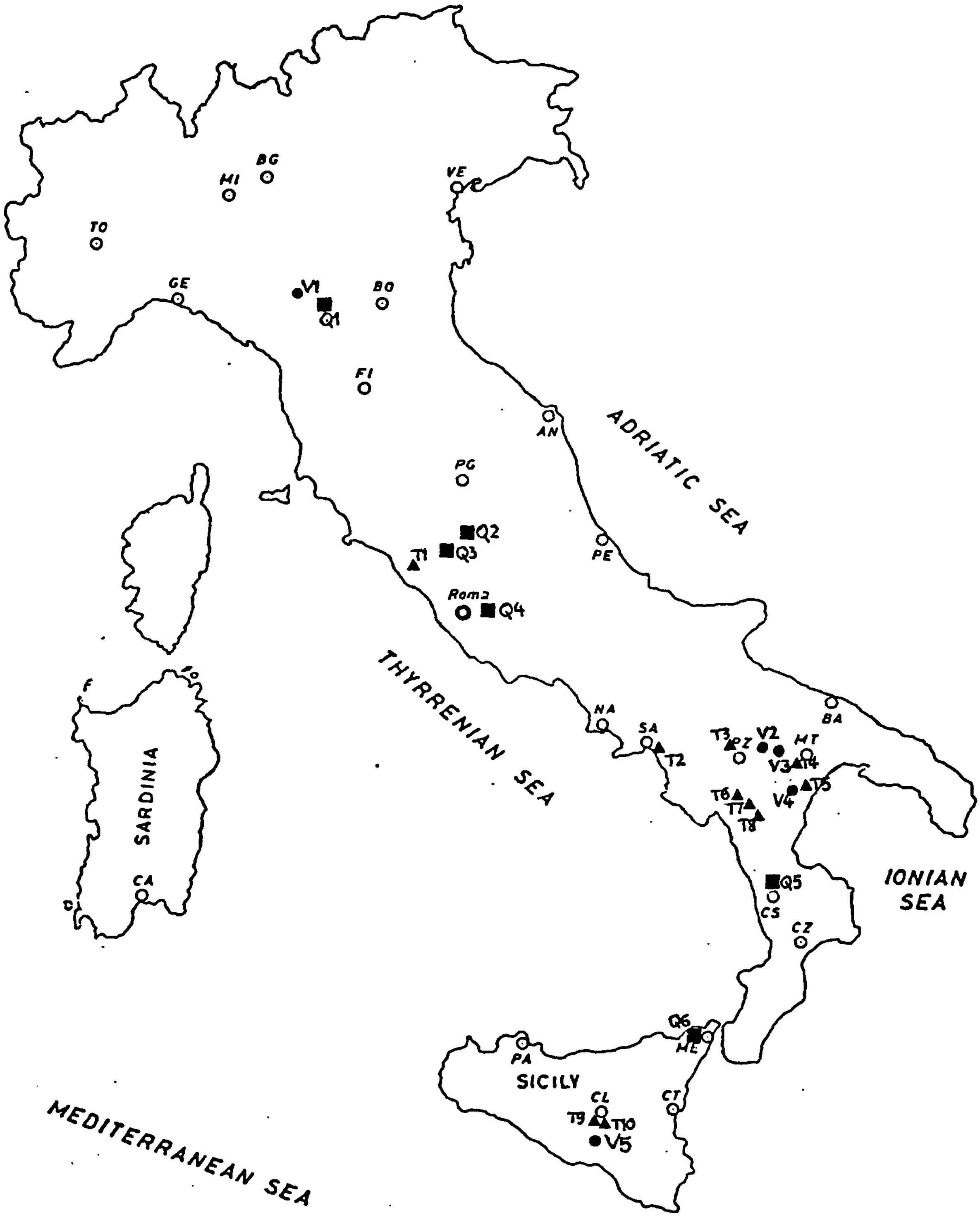
*	LOCALITY	DISTRICT (REGION)	GEOGRAPHIC SECTOR	CLAY TYPE AND AGE	MAXIMUM OVERBURDEN (THICKNESS OF CLAY) in m	EXTERNAL MORPHOLOGIC OR TECTONIC SIGNS	INTERNAL MORPHOLOGIC OR TECTONIC SIGNS
T1 a/b/c	Civitavecchia Allumiere	Rome (Lazio)	center	blue-gray clays (Pliocene)	var. max 30	nothing particular; few landslides in the area	the tunnels are under restoration; holes crossing the lining didn't show any sign of tectonics or seepages; water inflows near the entrances
T2	Salerno	Salerno (Campania)	south	blue-gray marly clays (Tortonian)	150 (70)	none	rock is divided in small prisms by latent, tight fractures; no sign of faulting has been recognized; no water inflows, nor humidity was present
T3	Avigliano	Potenza (Basilicata)	south	scaly clays ("argille sca-gliose" - Tertiary)	150 (150)	none	seepages near the two exits (low overburden) and around a section damaged by 1981 earthquake
T4	Miglionico	Matera (Basilicata)	south	pliocenic blue clays	300 (200)	landslides on the southern slope of the hill; surface alteration	water inflows of various entity almost all along the tunnel; spots: white with abundant salts, and black aligned with the strata (sub-horizontal); no signs of faulting
T5	Pisticci	Matera (Basilicata)	south	pliocenic blue clays	30 (30)	surface alteration and heavy erosion; see text	absolutely nothing; a fault plane could pass near the bottom of the tunnel (see text)
T6 ▲	Lagonegro	Potenza (Basilicata)	south	scaly clays (Tertiary)	80 (80)	rock movements at southern exit	heavily stressed rock (and tunnel) near southern exit; seepages at various points
T7 a/b ▲	"Flysch galestrino" formation	Potenza (Basilicata)	south	argillite (up. Giurassic - lo. Cretaceous)	75 var.	heavily tectonized rock; little springs	abundant water inside the longest tunnel; less water inside the shortest (and shallowest) one; no signs of faulting
T8 ▲	Serra Rotonda near Lauria	Potenza (Basilicata)	south	complex formation in marly-clayey matrix (lo. Paleocene-Eocene)	40 (?)	fault surface on the slope of the mountain in competent rock	some localized water inflows but apparently not related to faulting
T9	Rocca di Messana near Sommatino	Caltanissetta (Sicily)	south	scaly clays (Tertiary)	130 (?)	landslides	roof collapse in corrispondence of a tectonic contact between clay and limestone aboet 200 m from eastern entrance
T10	Cammarera near Riesi	Caltanissetta (Sicily)	south	scaly clays (Tertiary)	80 (?)	landslides; fault on geological map	water inflows (togheter with plastic clay) on the floor of the gallery about ½ km from northern entrance

* All tunnels are abandoned with the exception of T1 (under restoration) T2 (under construction) and T3 (railway in exercise)

▲ All these tunnels are on the abandoned FCL railway Lagonegro-Lauria-Castrovillari

FIGURE 1: MAP SHOWING THE LOCALIZATION OF VISITED SITES

● VALLEYS
■ QUARRIES
▲ TUNNELS



EVALUATION AND DEVELOPMENT OF GEOHYDROLOGICAL SURVEYING METHODS IN AREAS WITH SALINE GROUNDWATER

Contractor : RIVM, Bilthoven, The Netherlands
Contract no. : FI1W-0160-NL
Duration of contract : November 1987 - April 1989
Period covered : November 1987 - December 1987
Project leader : P. Glasbergen

A. OBJECTIVES AND SCOPE

In order to set-up a network of boreholes for geohydrological research in the next phase of the Dutch research programme on radioactive waste disposal, a careful consideration of the scientific requirements for such boreholes is necessary.

Boreholes in deep sedimentary rocks were drilled in the past to explore groundwater or sometimes hydrocarbons. However experience with unconsolidated rock sampling at depths during the performance of a drilling without disturbing the natural structure is limited. In particular techniques to set-up observation wells in aquifers where high density brines occur, need improvement. Such aquifers occur above salt domes in The Netherlands and Germany. Moreover, an overview of methods for obtaining geohydrological data from deep boreholes does not exist.

Aims of the project are:

- To inventorize, evaluate and indicate necessary developments of in-situ measurements of geohydrological parameters.
- To give recommendations for the set-up of deep geohydrological boreholes near salt structures in phase 2 of the Dutch disposal research programme.
- To test in-situ measurement techniques in several existing deep boreholes.
- To determine the value of natural isotopes analyses and specific microparameters of the interpretation of deep groundwater flow.

Analyses of groundwater are being carried out in cooperation with the Netherlands Energy Research Foundation (ECN). Natural isotopes will be studied in cooperation with the Laboratory of Hydrology and Isotope-geochemistry of the University of Paris-Sud

B. WORK PROGRAMME

1.1 Techniques to be studied and evaluated
- possibilities of borehole measurements (gamma, logs, etc.);
- possibility and reliability of in-situ measurements of temperatures, pH, Eh;
- methods for carrying out pumping tests in low permeable aquifers at large depth;
- possibilities of isotope techniques for dating;
- sampling methods of undisturbed unconsolidated rock.

1.2 Boreholes requirements, which follow from section 1.

1.3 Evaluation of section 1 and 2 in order to give recommendations for an optimized programme of geohydrological boreholes near a proposed radioactive waste repository in a salt formation.

2.1, 2.6 Selection of existing deep boreholes in The Netherlands accessible for well-tests.

2.2, 2.3 Performance and evaluation of well-tests methodologies as a function of the aquifertype.

2.4, 2.5 Sampling of water from deep aquifers applying different methods and analyses of macro and micro parameters as well as natural isotopes.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The review of literature on well tests is in progress. Therefore results presented here are preliminary and incomplete. For the determination of permeability of aquifers several methods are available. One possible subdivision of these methods can be based on interpretation of data obtained from well tests, methods based on sample testing, and methods based on description of grainsize. Some preliminary laboratory experiments on samples are carried out so far. Interpretation of the permeability in relation to the chemical composition and porosity is underway. Some field experiments are carried out in order to evaluate the differences between the interpretation methods.

PROGRESS AND RESULTS

1.1 Geohydrological techniques for parameter determination

For the relation between permeability and porosity several formulae are available in the literature. Well-known is the Kozeny-Carman equation. This equation is not valid for sand containing clay or silt. Because this is usually the case in deep permeable aquifers, this method seems hardly applicable. Sample tests on their turn are to be preferred over grain size methods, because the structure of the soil element is not disturbed.

The advantage of well tests compared with other methods is the fact that the area of influence is much larger. Pumping tests provide data on horizontal permeability, and if an observation well is available, storativity may also be measured. Standard pumping test assumptions include complete aquifer penetration, radial flow, and homogeneity and isotropy of the aquifer. With a length of test zone of e.g. 50 m a pumping test is suitable for conductivities higher than 10^{-8} m/s (= $8{,}6.10^{-4}$ m/d).

The wellbore storage effect in low transmissivity formations is significant, and renders much of the early part of the drawdown data unusable for determination of conductivity. Analytical solutions which take account of the wellbore storage effect have been described in literature and are further elaborated. One of the most important premises of this method is the assumption of an instantaneous transport of a water volume in the well. Furthermore it is assumed that the aquifer is homogeneous and isotropic and is fully penetrated. After the time period during which wellbore storage effects are of influence the solution of Theis for confined aquifers gives the most reliable results. In low permeable aquifers the time required to overcome storage effects might be several days upto several tens of days. For a good interpretation of the field data the pumping time should amount at least 500 r_c^2/T. The meaning of r_c is the radius of the well-casing.

2.2 WELL-TESTS

Some field experiments are carried out in order to evaluate the differences between the interpretation methods. Pressure changes were introduced by injecting a deep well with an amount of water. On the same well also a one day lasting pumping test has been carried out. Interpretation of the results is underway. It looks like the results do not lead to significant differences.

At another location, where artesian conditions occur, the pressure build-up was recorded after opening of a valve. For this aquifer the transmissivity proved to be 0.18 m^2/d (fig. 1). For calculation the formula $T = \frac{2.30}{4\Pi\Delta\phi}$ was used, where

Q = rate of water flow (m^3/s)

$\Delta\phi$ = difference in head per logarithmic cycle (m)

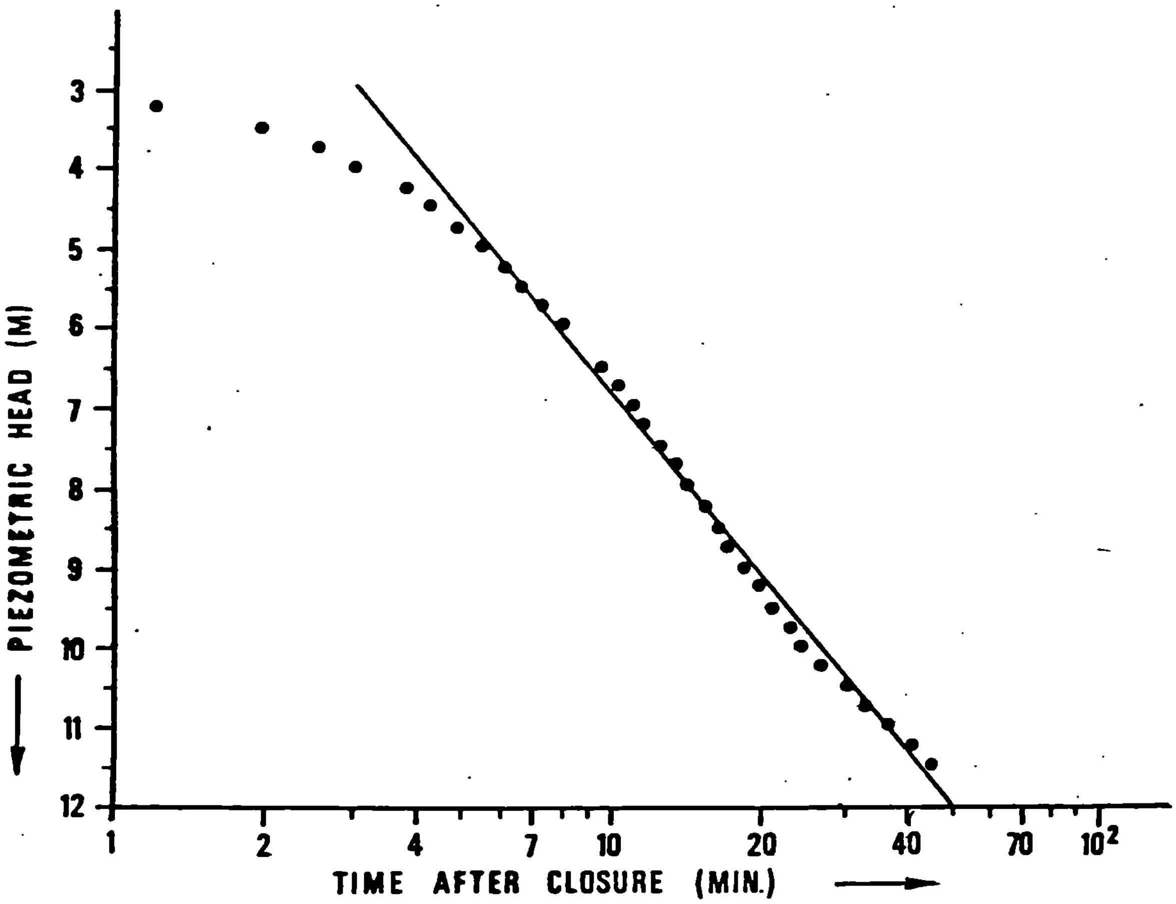
2.7 LABORATORY TESTS

Some preliminary laboratory experiments on samples are carried out so far. A permeability test is performed on small cylinders (ϕ 0,02 m, length 0,03 m) drilled out of sandstone cores from the Brussels Marl formation. This formation extends from surface in Belgium, under The Netherlands, till under the North Sea. The permeability proved to be lower than 1.7 mD at a porosity of 2-6%. The $CaCO_3$ content was about 50% (weight).

To demonstrate the variation also permeameter tests were performed on unconsolidated samples taken in the outcrop area. The permeability ranges from 3-20 D, at a $CaCO_3$ content <17%.

Because the $CaCO_3$ content proves to be an important parameter in characterization of an aquifer in terms of permeability, the Chalk formation is also the subject of research. In the literature, the data on permeability of deep-lying chalk are available. These can be compared with laboratory experiments performed on samples from quarries, where the same geological formation outcrops. Permeameter tests were performed on cylinders taken out large blocks of rock. The permeability ranges from <1 mD till 23 D. Interpretation in relation to chemical composition and porosity is underway.

Figure I. Results of a recovery test on an artesian well.



4.1.B. Geo-forecasting studies

Geoprospective modelling
Contractor : BRGM - Orléans (F)
Contract n° : FI 1W/0048
Contract period : 01.07.86 - 30.06.88
Project Leaders : P. PEAUDECERF - J. FOURNIGUET

A - Objective and Scope

Since 1981, the BRGM has been working on the development of a method aiming at the study of all the factors that might influence the evolution of a waste storage site, and their interactions. One of the work phases consisted in a quantifying of the links between the factors and in modelling them in order to complete realistic scenarios of natural evolution of sites. These operations are carried out with a simulator called CASTOR (Automatic Design of scenarios evolution of a radionucleide storage site).

The first phases of the work showed that only a few mechanisms among all those theoratically consistents with the evolution, should be the major ones and need to be represented more realistically. They are mainly those concerning climate variations, weathering and erosion processes and relationships between stress and hydraulic parameters. The simulation programme will have to be modified inorderto take these mechanisms and their relationships into account simultaneously. These enhancements should make the CASTOR simulator operational for most of the possible sites contexts.

B - Work programme

Work programme will revolve around two main aspects :

1- increasing knowledge and modelling of mechanisms which appeared essential in previous phases.

   a. climatology : as well mathematical expression of fluctuations in the near past and future according astronomical data, as search for present climatic equivalents to past climates.

   b. weathering erosion:better or quantifying of rates according to lithology, slopes, vegetal cover, rainfall, temperature, and a tentative modelling of erosion processes.

   c. relationships between stress and hydraulic parameters mainly in the case of the occurence of an ice-cap covering the site area.

2- improving the modelling of the phenomena and the representation of the results obtained.

C - Progress of work and obtained results

1- State of advancement

Items 1-a and 1-b had been launched during the second part of 1986, with only preliminary results obtained by the end of that year (cf annual progress report 1986). 1987 has been devoted to the completion of these items and to a large part of item 2. Item 1-c has begun late in 1987 due to an overload of work of the project-team. 1988 will see the completion of the work with mainly :

- end of the different modelling improvements
- attempts on some selected targets
- presentation of the final report

2- Progress and results

2.1. Climatology

. Up to now, climatic fluctuations had been taken into account using climatic curves established by various geological methods (palynology, bio-stratigraphy of foraminifera, oxygen isotops...). These curves do not allow and extrapolation towards the future. Other curves, derived from astronomical parameters (formerly by MILANKOVITCH and recently by A. BERGER) make this possible. Some of the computed curves have been used and integrated in the CASTOR so that :

- former (Quaternary) climatic variations have been corelated with calculated ones
- future variations forecasts are now possible

This showed that at least 1 or may be 2 "cold periods" more or less equivalent to the Würm period, will necessarely take place within the next 100 000 years (very roughly around + 10 000 and + 50 000 AP*).

. The search for "present equivalent to past climate" aimed at finding quantitative data (rainfalls, temperatures...) of worldwide examples in order to propose relevant values for past and future "cold periods". The most usefull and widespread method is palynology. The first part of the work thus consisted in the characterization of the vegetation and the quantifying of the pertinent climatic parameters. A special Phytoclimatic Index has been derived from an already existing one. It takes into account the annual rainfalls, extrem temperatures, and aridity by the mean of the driest quarter of the year. A Diagram called "climagramme" has been developped, plotting the Phytoclimatic Index against the mean of annual temperatures. It allows to localize any vegetal associations of the northern hemisphere between semi-arid to glacial climates. Thus, the past climates defined by typical vegetal associations (derived from palynological records) are now known by their quantitative climatic characteristics... As future climates had been calibrated on past ones, one can now propose quantitative values for the climates of the next 100 000 years.

* After Present

. A bibliographical analysis has rapidly demonstrated that erosion processes in temperate conditions are for more rapid than weathering. Only during periglacial and glacial periods, can specific processes (such as cryoclasty) produce a relevant amount of erodible sediments.

The main results are as follow :

- weathering profiles progress at 0.3 to 3 cm per 1 000 years in European zone, with maxima of 4 to 7 cm in tropical zone.
- chemical erosion induces a denudation rate of roughly 5 to 8 cm per 1 000 years.
- in european conditions, including various conditions of relief, denudation rates range from 6 to 400 mm per 1 000 years.
- vegetal cover is a major factor for denudation control; rates may change from 1 to 10 between sporadic vegetation and forest for a similar lithology.
- denudation rates vary according to lithology from 10 to 200 mm/1 000 years in limestones, from 30 to 70 mm/ 1 000 years in granites (for european present climatic conditions including northern Europe).

The data-base compiled on denudation rates is being used with a global erosion model to be complete by the beginning of 1988.

3- List of publications

Results concerning Geoforcasting studies, and more precisely those of the present contract have been presented (or will be in a next future) in several circumstances.

- 12th International INQUA Congres in Ottawa (August 1987): Modelling of Quaternay parameters and the choice of nuclear waste disposal sites by J. FOURNIGUET.
- International Association of Hydrogeologists - International Symposium, to be held in Orleans (France) in June 1988 :
  Prévision quantitative de l'évolution à long terme des caractéristiques hydrogéologiques des sites de stockage profond by Ch. FILIPPI & al.
- ISPRA courses : Advanced Seminar on Risk analysis in Nuclear waste Management : May - June 1988.
  Predictive geology in the analysis of the repository evolution :
  Description of the relevant natural phenomena by J. FOURNIGUET.
  Modelling combined effects and making scenarios by Ch. FILIPPI.

4.1.C. Rock mechanics

Studies of disposal possibilities in geological formations : investigations in granite media

Contractor: Commissariat à l'Energie Atomique, Fontenay-aux-Roses, France
Contract N° : 127.80.7 WASF
Working period: 01/01/1985 - 31/12/1987
Project Leader: S. DERLICH

A. Objectives and Scope

The Thermo-Hydro-Mechanical (THM) experiment consists into heating a granite volume 10 meters, by 12 meters with a thickness of 3 meters between the free surface and the heat source.
In an uranium mine, a room 10 meters by 13 meters horizontally and 5 m in heigth has been excavated, and a heat source made of 5 cylindrical radiators has been placed in horizontal boreholes, drilled from an auxiliary drift, below the centre of the room floor (see fig. 1 and 2).
The purpose of this experiment is to simulate a high level waste disposal, buried at a depth of 1000 m.
The similitude bears on time and on the distance between the heat source and the surface (and on the energy dissipated).
The duration of heating and of cooling are 50 days each.
The total thermal energy of the heaters is 1000 W.
The heating started by the end of september 1987 and lasted till mid november. The cooling period will end in January 1988 with the stop of the measurements.

B. Work Programme

The site was chosen after the thorough geological study of a mining work in a granitic pluton near Limoges (Mining Division of La Crouzille, COGEMA).

The selected site is at a depth of 100 m in a zone with a fracture density from 2 to 4 fractures per meter. The zone has been partially drained out by the mining drifts.

Two horizontal boreholes, 50 m long and 76 mm in diameter, have been cored all along, in order to specify the position of the experimental chamber.

Fracture studies have been conducted both during the selection phase, in the drifts and on the boreholes cores, and during the excavation phase, in the access drift and auxiliary drift, on the floor and walls of the chamber, and on the cores of the radiator boreholes and probe boreholes.

The aim of the experiment is to ascertain the mechanical and hydrogeological effects as a function of the temperature distribution in the medium.

So temperature measurements, mechanical measurements (surficial movements and volume movement in boreholes) hydrogeological measurements (permeability, measurements at regular intervals in small diameter boreholes) have been conducted.

The experimental array includes :

Temperature probes arranged in the following way :
33 in the rock mass in 46 mm diameter boreholes
12 on borehole extensometers
19 on surface extensometers
2 on the data processing system

Borehole extensometers
12 extensometers by groups of 3 in 4 vertical boreholes

Surface extensometers

Knobs for invar-wire distancemeter measurements

Laser interferometers and photoelectric cells :
during the instrumentation fitting period, laser interferometers have been added thus allowing to follow the movements of the sides of the main fissures on the floor. Photo electric cells allow the recording of the swelling of the floor with reference to an horizontally rotating laser bean.

Hydraulic measurements
Permanent flow measurements in 3 boreholes and permeability measurements every odd week in 5 boreholes aimed at assessing the permeability changes with regards to stresses due to the temperature variations.

Results

The rough results already allow the control of the predicting calculations done when the experiment was devised.

The measured deformations will be compared to those calculated from the temperature measurements : if differences are found they will have to be interpreted with reference to the fracture pattern.

In the final phase, which should come to an end in December 1988, several calculation codes writen at the CEA, at the BRGM and at the Ecole des Mines will be validated.

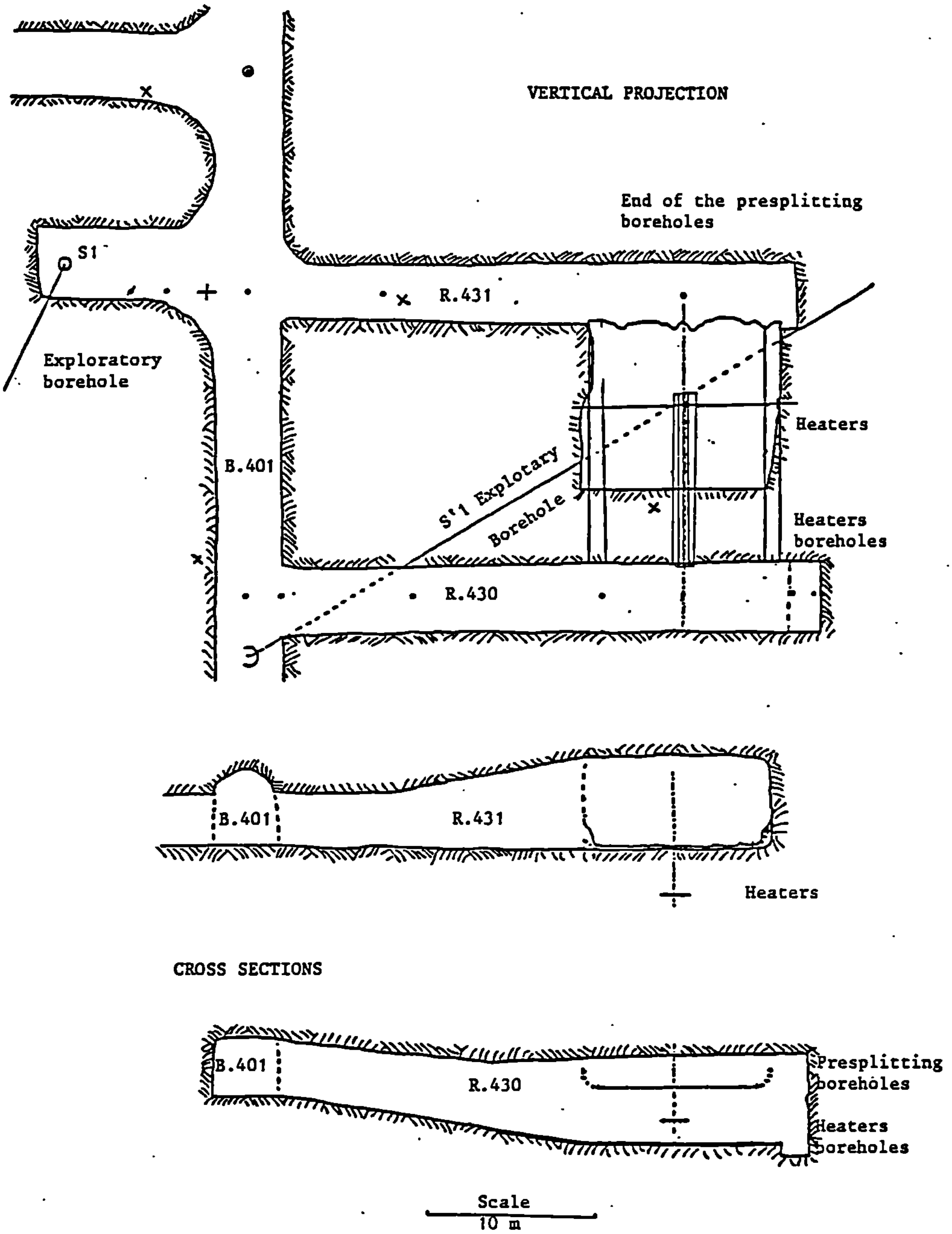


Figure 1
THERMO-HYDRO-MECHANICAL EXPERIMENT
Fanay-Augères - Tenelles

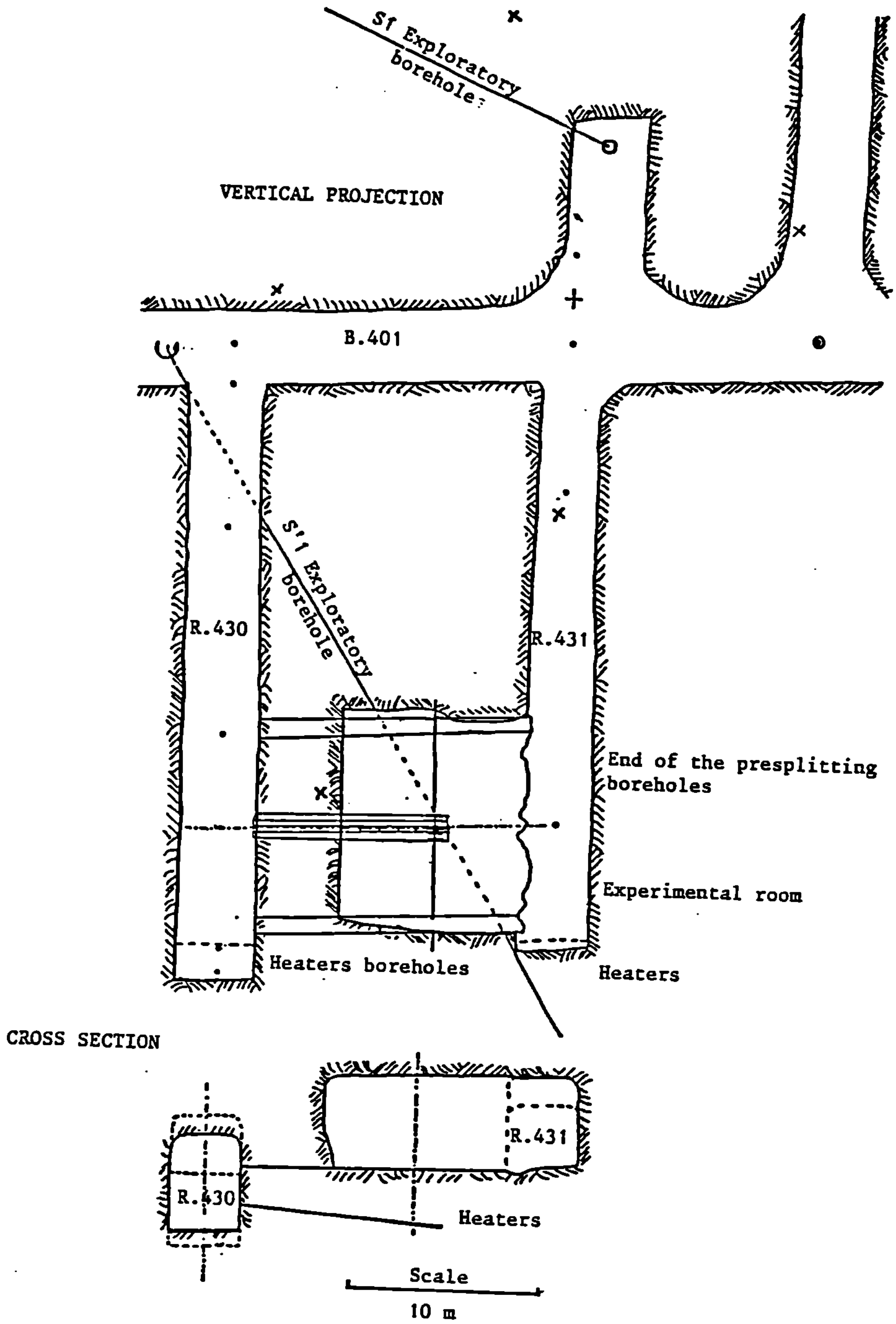


Figure 2

THERMO-HYDRO-MECHANICAL EXPERIMENT
Fanay-Augères - Tenelles

USE OF AN UNDERGROUND CAVITY AS A TEST FACILITY FOR RADIOACTIVE WASTE DISPOSAL IN CLAYS

Conctractor : ENEA.CRE CASACCIA , ROME (ITALY)
CONTRACT No. : 337-83-7 WASI
Duration of contract : January 1984 - December 1987
Period covered : January 1987 - December 1987
Project leader : E.Tassoni

A. OBJECTIVES AND SCOPE

The reliability of the geological disposal of radioactive wastes have to be verified both by laboratory and on site research, under both surface and underground conditions. The tunnel's availability should permit the development of the studies and researches that ENEA carries out in this field. The tests carried out under high lithostatic stress will allow extrapolations to be made having absolute value at the depths planned for the construction of the repository.

The main goals of the project are the following:

- Selection and technical evaluation of a deep experimental tunnel in a clay formation.
- Construction of an underground laboratory in the selected tunnel.
- Determination of the excavation effect on the clay formation.
- Design of the experimental tests (heating, permeability, convergence, backfilling and plugging).
- Design of experimental instrumentation.

B. WORK PROGRAMME

1. Detailed geologic survey at 1:5000 scale carried out on the area around the underground tunnel. Samples collection for laboratory analyses regarding sedimentological, mineralogical, geochemical, micropaleontological characters and interstitial water-content.
2. Establishment of the geotechnical and structural conditions of the clayey mass in both the static and dynamic phases (effect of the excavation on the tunnel walls).
3. Evaluation of the thermal behaviour and the self sealing capacity of deep clays. Heating experiments and convergency tests will be carried out by drilling holes at various depths from the floor of the tunnel.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

After the excavation of the tunnel and the installation of the geotechnical stations, the measurements have been carried on up to March 1987. At this date the work programme has beenunfortunately stopped by local authorities unfoundly suspecting Pasquasia mine would be used as waste repository. ENEA officially confirmed that mine was unsuitable as deposit for radioactive wastes in view of both its geological characteristics and the presence there of an economically important activity. The 37 cubic blocks, their sides measuring measurement 30 cm, along 72 samples collected during the excavation, have been analysed from different point of view (sedimentological, mineralogical, geochemical, thermal, etc).

PROGRESS AND RESULTS

1. On the area around the Pasquasia mine, a detailed geological mapping (1:5000 scale) has been carried out. The surveyed area is included in the Caltanissetta Basin (Enna-Centuripe Sector), neogenic in age and trending E-W. The geological investigations have individualized the following stratigraphic sequence from below :

- Sandy clay (Tortonian - Very low permeability)
- Tripoli (Rock composed by the rests of radiolaria and diatomeceous matter - Low permeability)
- Pasquasia Gypsum (two varieties such as selenitic and alabastrine gypsum - Messinian - Middle permeability with karstic phenomena)
- Clay interbedded with gypsum (Very low permeability)
- Trubi (Whitish clayey fine grained marls - Lower Pliocene Middle permeability
- Blue marly clay (Middle Pliocene - Very low permeability)
- Yellow sands and calcareous sandstone (Upper and Middle Pliocene - Middle permeability)
- Gray sands and sandy clay (Lower Pleistocene - Low-Middle permeability
- River conglomerates (Middle Pleistocene - High permeability)
- Alluvial fan, talus, recent alluvion, colluvium (Olocene Middle-High permeability)

The mineralogical analyses have been carried out by means of the diffraction of X-rays, with the powder method. "Tout venant" samples and the <2µ fractions, separated by means of sedimentation in distilled water, have been analysed; the results are shown in table I and II respectively. In table II some chemical crystallography parameters (Biscaye, Kubler and Esquevin) are pointed out. The main conclusions that can be drawn from these results are the following:

- the smectitic minerals are well crystallized
- the samples composition is between "biotitic" and "biotitic-muscovitic" type
- the clay formation shouldn't have been subjected to high lithostatic load.

The sedimentological analises have shown a good uniformity of granulometric composition (fig.1). The clay formation is constituted by silty clay and clayey silt. The sand fraction which is included between 2% and 12%, is higher in the terminal part of the experimental tunnel. The carbonate content measurement has been carried out by means of determination of CO_2 developed after etching clay sample with H_3PO_4. The average total quantity of carbonate is about 33%, with a standard deviation of ± 5%. The thermal conductivity and diffusivity have been measured in clay blocks by means of an automated laboratory method based on the use of needle and cylindrical probes, containing a heating resistance to supply the heat and a thermistor to measure the temperature rise of the probe. The probes are inserted into tiny holes bored into clay samples by a drill. The thermal conductivities and diffusivities measured on Pasquasia clay samples are shown in the table III and IV. The average thermal conductivity measured on the sedimentation plane is =1.7388 Watt $* m^{-1} * °C^{-1}$, with a little standard deviation (±0.0177); the thermal conductivity measured along the direction perpendicular to the sedimentation plane is lower (~ 9%) than the one measured on the sedimentation plane and the difference is due to the anisotropy of the clay layers. The average thermal diffusivity measured on the sedimentation plane is = 6.932 $* 10^{-7} m^2 * sec^{-1}$ with an higher standard deviation ($\pm 0.4007 * 10^{-7}$) 2. - 3. The geothecnical data collected up to march 1987 are being elaborated by Turin University.

TABLE I - *Semiquantitative analyses on the clay samples ''Tout Venant''*

Samples	0.0F1		0.0F2		0.2F1		0.3F1		0.5F1		0.0F1		1.3F1		1.3F2	
Minerals	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
C. M.	57	69	60	61	58	60	55	56	61	69	60	64	60	50	60	50
Qz	8	8	10	8	0	0	11	10	7	7	0	8	8	0	7	0
Fk	1	} 1	1	} 2	-	} 2	-	} 9	1	} 2	-	Tr	-	} 4	} 1	2
Foa	2		1		9		9		1		2	1	9			9
C	99	10	20	19	20	10	24	22	22	17	17	18	10	18	22	17
D	7	7	7	8	8	8	7	8	8	0	10	8	0	8	8	8
H. M.	9	1	1	1	1	2	1	Tr	1	1	2	1	1	1	1	2
Total	100	00	00	00	00	100	00	00	100	00	100	100	100	00	00	100

Samples	10.3F1		10.3F2		10.3F3		19.3F4		21.6F1		21.6F2		21.6F3		23.5F1	
Minerals	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
C. M.	56	50	58	60	50	64	62	50	62	64	65	65	66	64	58	69
Qz	11	10	8	0	0	10	10	0	0	8	8	0	8	0	11	8
Fk	2	2	1	} 2	-	} 1	-	} 1	-	-	1	} 1	1	2	-	-
Foa	2	2	6		9		1		1	1	1		-	-	2	2
C	20	17	18	17	10	17	10	21	10	10	18	10	18	17	18	10
D	7	8	7	0	8	7	7	7	7	7	5	8	6	6	8	7
H. M.	2	1	1	2	2	1	1	1	2	1	2	1	1	1	1	1
Total	100	00	00	00	100	100	100	00	100	100	100	100	100	00	00	100

Samples	4.0F1		4.1F1		5.6F1		5.6F2		5.6F3		5.6F4		8.5L1		8.5L1	
Minerals	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
C. M.	60	69	58	69	61	60	58	58	57	66	60	65	56	58	54	60
Qz	0	10	0	8	7	8	8	10	8	7	8	10	0	10	8	0
Fk	-	} 1	-	} 2	1	2	1	} 9	1	1	Tr	} 2	Tr	} 1	4	1
Foa	1		2		9	-	2		4	-	1		9		2	Tr
C	22	10	21	18	18	17	21	18	20	16	20	16	22	20	20	21
D	6	6	8	8	0	10	8	0	0	8	0	6	8	10	0	7
H. M.	1	1	1	1	1	2	1	1	1	2	1	1	1	1	2	1
Total	00	100	100	100	100	80	00	00	100	100	00	100	00	100	00	00

Samples	23.5F2		23.5F3		25.4F1		25.4F2		30.8F1		30.8F2		30.8F3		33.2F1	
Minerals	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
C. M.	61	62	69	64	60	65	56	61	56	56	50	62	58	60	59	50
Qz	8	7	8	8	8	7	8	0	10	10	8	0	0	8	10	11
Fk	1	} 1	1	1	-	} 2	-	Tr	-	2	-	} 1	Tr	1	2	2
Foa	2		2	2	9		9	2	9	2	9		2	9	1	1
C	20	20	17	17	20	17	20	20	21	21	20	19	22	17	22	10
D	7	7	7	7	7	7	10	7	7	8	8	8	7	0	10	7
H. M.	1	2	1	1	1	1	2	1	2	1	1	1	1	1	1	1
Total	100	00	00	100	00	00	90	100	00	100	00	100	00	00	00	09

Samples	8.5L2		10.1F1		10.1F2		10.1F3		10.1F4		10.7F1		12.0F1		12.8F1	
Minerals	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
C. M.	58	56	52	50	58	60	58	52	60	60	62	65	50	60	60	58
Qz	8	10	10	10	8	0	0	17	8	0	7	10	8	8	5	8
Fk	4	1	-	1	Tr	2	} 2	} 2	-	} 4	1	} 2	-	1	1	} 2
Foa	2	2	8	2	9	2			9		1		1	1	2	
C	21	20	24	22	20	18	22	18	21	18	20	18	29	20	21	20
D	0	10	0	5	8	8	8	9	6	6	7	8	7	0	0	10
H. M.	1	1	1	1	1	1	1	1	1	1	2	1	1	1	1	1
Total	00	100	00	100	00	100	100	00	00	100	100	100	00	100	00	00

Samples	35.4F1		37.5F1		41.0L1		42.5F1		44.8F1		44.8F2		44.8F3		44.8F4	
Minerals	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
C. M.	58	55	57	56	66	61	57	58	57	61	61	61	56	60	58	57
Qz	0	10	11	12	7	0	0	10	0	0	7	8	10	10	8	10
Fk	-	1	Tr	} 4	1	1	-	1	-	} 1	-	-	-	1	1	1
Foa	9	2	1		2	2	2	2	9		2	9	2	Tr	9	9
C	20	22	20	18	18	20	22	29	22	10	20	20	21	20	22	19
D	0	8	0	7	5	8	7	8	8	8	8	7	8	8	8	9
H. M.	1	1	1	2	1	1	2	1	1	1	2	1	2	1	1	1
Total	100	00	00	00	100	100	00	100	100	00	100	100	100	100	00	100

Samples	13.8F1		14.8F1		14.8F2		14.8F3		14.8F4		15.2L1		16.7F1		18.0F1	
Minerals	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
C. M.	59	61	58	60	57	56	62	65	69	58	54	60	58	67	60	62
Qz	9	8	9	8	0	11	7	8	7	7	11	8	8	6	8	8
Fk	-	2	1	} 2	1	} 2	-	} 2	1	1	-	} 1	2	} 2	-	Tr
Foa	8	2	1		1		2		2	2	2		1		2	1
C	21	17	29	18	20	21	18	18	17	20	21	21	20	16	20	20
D	7	7	7	7	10	7	8	7	8	0	10	8	0	7	8	7
H. M.	1	2	1	9	1	2	1	1	2	2	1	1	2	1	1	1
Total	100	100	100	00	00	00	00	00	100	00	00	00	100	00	00	100

Samples	47.8F1		50.0F1													
Minerals	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
C. M.	52	50	61	62												
Qz	10	0	10	8												
Fk	1	} 4	Tr	Tr												
Foa	2		2	9												
C	25	18	17	17												
D	8	8	0	0												
H. M.	1	1	1	1												
Total	00	00	100	100												

Semiquantitative analysis of the "clay fraction"

I= Illite K= Kaolinite Cl= Clorite V= Vermiculite SM= Mixed layers

Sample 0.3F1		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	87	Sm	32	30	v/p = 0.80
Qz	2	I	44	43	Kubler Value (Illite)
F	-	K	10	10	8
C	10	Cl	8	8	Esquevin Ratio (Illite)
D	Tr	V	Tr	Tr	$\frac{I(002)}{I(001)} = 0.20$
M.P.	1	S.M.	5	7	
Tot.	100	Tot.	100	98	

Sample 10.7F1		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	84	Sm	18		v/p = 1.10
Qz	2	I	55		Kubler Value (Illite)
F	-	K	10		8
C	12	Cl	8		Esquevin Ratio (Illite)
D	Tr	V	-		$\frac{I(002)}{I(001)} = 0.10$
M.P.	1	S.M.	9		
Tot.	99	Tot.	99		

Sample 1.3F2		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	89	Sm	29		v/p = 0.90
Qz	2	I	50		Kubler Value (Illite)
F	Tr	K	10		7
C	8	Cl	6		Esquevin Ratio (Illite)
D	Tr	V	Tr		$\frac{I(002)}{I(001)} = 0.10$
M.P.	1	S.M.	6		
Tot.	100	Tot.	99		

Sample 14.6F1		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	87	Sm	20		v/p = 1.10
Qz	2	I	55		Kubler Value (Illite)
F	-	K	8		8
C	10	Cl	8		Esquevin Ratio (Illite)
D	Tr	V	Tr		$\frac{I(002)}{I(001)} = 0.21$
M.P.	1	S.M.	8		
Tot.	100	Tot.	100		

Sample 5.6F3		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	83	Sm	25		v/p = 0.90
Qz	2	I	30		Kubler Value (Illite)
F	-	K	17		5.5
C	12	Cl	8		Esquevin Ratio (Illite)
D	Tr	V	-		$\frac{I(002)}{I(001)} = 0.11$
M.P.	2	S.M.	9		
Tot.	99	Tot.	100		

Sample 14.6F4		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	87	Sm	20		v/p = 0.84
Qz	2	I	50		Kubler Value (Illite)
F	Tr	K	12		7
C	8	Cl	8		Esquevin Ratio (Illite)
D	Tr	V	-		$\frac{I(002)}{I(001)} = 0.07$
M.P.	2	S.M.	10		
Tot.	100	Tot.	100		

Sample 8.5I.1		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	85	Sm	38	31	v/p = 0.98
Qz	2	I	40	44	Kubler Value (Illite)
F	-	K	11	13	7
C	12	Cl	8	8	Esquevin Ratio (Illite)
D	Tr	V	Tr	Tr	$\frac{I(002)}{I(001)} = 0.30$
M.P.	1	S.M.	5	8	
Tot.	100	Tot.	98	99	

Sample 19.3F1		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	88	Sm	20		v/p = 0.84
Qz	2	I	47		Kubler Value (Illite)
F	Tr	K	10		8
C	10	Cl	8		Esquevin Ratio (Illite)
D	Tr	V	-		$\frac{I(002)}{I(001)} = 0.10$
M.P.	1	S.M.	15		
Tot.	99	Tot.	100		

Sample 10.1F4		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	85	Sm	30	30	v/p = 0.88
Qz	2	I	40	43	Kubler Value (Illite)
F	-	K	12	10	7
C	10	Cl	8	8	Esquevin Ratio (Illite)
D	Tr	V	4	5	$\frac{I(002)}{I(001)} = 0.17$
M.P.	2	S.M.	6	4	
Tot.	99	Tot.	100	100	

Sample 21.6F2		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	85	Sm	21		v/p = 1.00
Qz	2	I	48		Kubler Value (Illite)
F	-	K	13		7
C	10	Cl	10		Esquevin Ratio (Illite)
D	Tr	V	Tr		$\frac{I(002)}{I(001)} = 0.10$
M.P.	2	S.M.	8		
Tot.	99	Tot.	100		

Semiquantitative analysis of the "clay fraction"

I= Illite K= Kaolinite Cl= Clorite V= Vermiculite SM= Mixed layers

Sample 23.5F1		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	86	Sm	32	30	v/p = 1.00
Qz	2	I	41	40	Kubler Value (Illite)
F	-	K	13	2	7
C	10	Cl	10	8	Esquevin Ratio (Illite)
D	Tr	V	Tr	2	$\frac{I(002)}{I(001)} = 0.13$
M.P.	1	S.M.	4	8	
Tot.	99	Tot.	100	100	

Sample 41.0I.1		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	89	Sm	30	30	v/p = 0.78
Qz	2	I	45	43	Kubler Value (Illite)
F	Tr	K	10	12	8
C	8	Cl	8	8	Esquevin Ratio (Illite)
D	-	V	-	Tr	$\frac{I(002)}{I(001)} = 0.11$
M.P.	1	S.M.	5	8	
Tot.	100	Tot.	98	100	

Sample 25.4F2		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	84	Sm	23		v/p = 0.98
Qz	3	I	40		Kubler Value (Illite)
F	-	K	10		8
C	11	Cl	8		Esquevin Ratio (Illite)
D	Tr	V	-		$\frac{I(002)}{I(001)} = 0.10$
M.P.	1	S.M.	10		
Tot.	99	Tot.	100		

Sample 44.8F3		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	85	Sm	20		v/p = 1.00
Qz	2	I	50		Kubler Value (Illite)
F	Tr	K	10		8
C	10	Cl	10		Esquevin Ratio (Illite)
D	Tr	V	-		$\frac{I(002)}{I(001)} = 0.20$
M.P.	1	S.M.	10		
Tot.	99	Tot.	100		

Sample 30.8F1		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	87	Sm	38	40	v/p = 1.20
Qz	2	I	45	37	Kubler Value (Illite)
F	Tr	K	6	9	7
C	10	Cl	6	9	Esquevin Ratio (Illite)
D	Tr	V	-	Tr	$\frac{I(002)}{I(001)} = 0.12$
M.P.	1	S.M.	4	5	
Tot.	100	Tot.	99	100	

Sample 47.8F1		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	89	Sm	38		v/p = 0.85
Qz	2	I	30		Kubler Value (Illite)
F	-	K	12		5
C	9	Cl	8		Esquevin Ratio (Illite)
D	Tr	V	4		$\frac{I(002)}{I(001)} = 0.18$
M.P.	Tr	S.M.	8		
Tot.	100	Tot.	100		

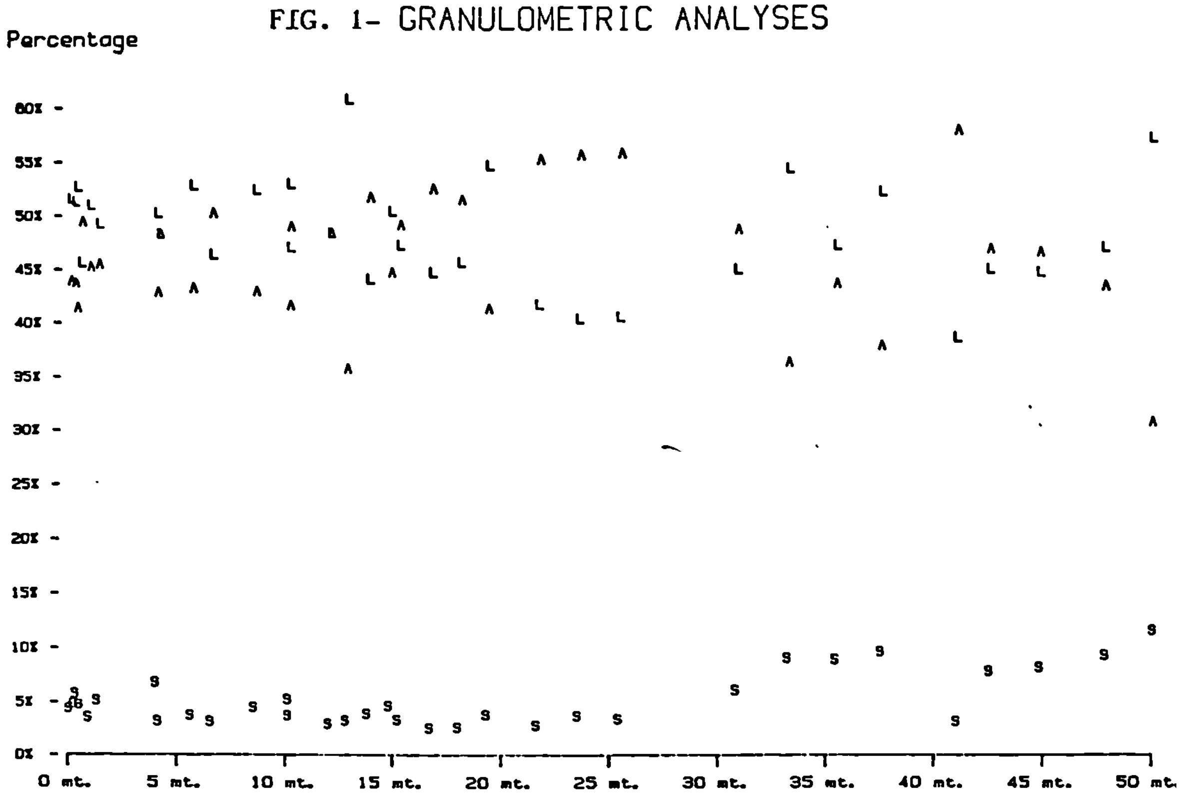
Sample 35.4F1		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	87	Sm	21		v/p = 1.20
Qz	2	I	31		Kubler Value (Illite)
F	-	K	8		8
C	9	Cl	9		Esquevin Ratio (Illite)
D	Tr	V	Tr		$\frac{I(002)}{I(001)} = 0.17$
M.P.	1	S.M.	11		
Tot.	99	Tot.	100		

Sample 50.0F2		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	89	Sm	40		v/p = 0.88
Qz	2	I	37		Kubler Value (Illite)
F	-	K	6		8
C	8	Cl	7		Esquevin Ratio (Illite)
D	Tr	V	Tr		$\frac{I(002)}{I(001)} = 0.28$
M.P.	1	S.M.	10		
Tot.	100	Tot.	100		

Sample 37.5F1		Clay Minerals			Crystallochem. parameters
			I	II	Biscaye Ratio (Smectite)
H.A.	88	Sm	35		v/p = 0.90
Qz	2	I	42		Kubler Value (Illite)
F	Tr	K	7		7
C	8	Cl	6		Esquevin Ratio (Illite)
D	Tr	V	-		$\frac{I(002)}{I(001)} = 0.10$
M.P.	1	S.M.	10		
Tot.	99	Tot.	100		

– TABLE. II –

FIG. 1- GRANULOMETRIC ANALYSES



S= Sand L= Silt A= Clay Station

TABLE III - Thermal conductivities measured in clay blocks coming from the underground laboratory (Pasquasia)

Sample	Test	Thermal drift (°C/sec *10^{-7})	Interpolation interval (sec)	Correlation value	Probe direction towards sedimentation plane	Thermal conductivity (W/m*°C)
B 10.1F4	ARG 44	7	80 - 420	.9999993	Perpendicular	1.7291
B 10.1F4	ARG 44A	10	120 - 420	.9999998	Perpendicular	1.7308
B 10.1F4	ARG 44B	3	40 - 480	.9999994	Perpendicular	1.7421
B 19.3F4	ARG 43	1	80 - 480	.9999994	Perpendicular	1.7331
B 10.1F4	ARG 44	7	80 - 420	.9999993	Perpendicular	1.7291
B 30.8F3	ARG 46	47	80 - 380	.9999992	Perpendicular	1.7238
B 30.8F3	ARG 46A	33	40 - 340	.9999917	Perpendicular	1.7300
B 30.8F3	ARG 46B	47	120 - 420	.9999998	Perpendicular	1.7280
B 44.8F4	ARG 47	12	40 - 380	.9999999	Perpendicular	1.7790
B 44.8F4	ARG 47A	63	120 - 620	.9999997	Perpendicular	1.7616
B 50.0F3	ARG 45	7	40 - 340	.9999967	Parallel	1.5887
B 50.0F3	ARG 45A	47	80 - 380	.9999978	Parallel	1.5855

TABLE IV - Thermal diffusivities measured in clay blocks coming from the underground laboratory (Pasquasia)

Sample	Test	Correlation value	Probe direction towards sedimentation plane	Thermal diffusivity (m^2*sec*10^{-7})	Thermal conductivity (W/m°C)
B 10.1F4	A-016A	.99993	Perpendicular	6.525	1.7538
B 10.1F4	A-016B	.99996	Perpendicular	6.496	1.7641
B 19.3F4	A-015A	.99998	Perpendicular	7.025	1.7574
B 19.3F4	A-015B	.99997	Perpendicular	6.663	1.7105
B 30.8F3	A-017A	.99999	Perpendicular	7.539	1.7478
B 30.8F3	A-017B	.99999	Perpendicular	7.499	1.7445
B 44.8F4	A-018A	.99993	Perpendicular	6.763	1.7302
B 44.8F4	A-018B	.99994	Perpendicular	6.739	1.7311

IN-SITU CHARACTERISATION OF THE BEHAVIOUR OF DEEP CLAY LAYERS

Contractor : ANDRA, PARIS, FRANCE
Contract n° : F I1W/0049
Duration of contract : August 86 - February 89
Period covered : August 86 - December 87
Project leader : R. ANDRE JEHAN

A - OBJECTIVES AND SCOPE

The objectives of this project are :

- to complete geomechanical investigations in the Boom deep clay formation, under natural conditions and after heating,
- to develop laboratory and in-situ methods to study deep clay layers, and to compare the results obtained by these two approachs.

This work forms a basis for dimensioning the storage facilities in deep clays. The interesting point is to study the time-lag behaviour of this material, at ambient and high temperature.

The sub-contractors of ANDRA for this project are :

- BRGM (Bureau de Recherches Géologiques et Minières) for the set up, execution and interpretation of in-situ test,
- LMS (Laboratoire de Mécanique des Solides de l'Ecole Polytechnique) for the laboratory thick tube test and for the conception of borehole probes in cooperation with Mazier and the BRGM,
- Mazier for the desing and fabrication of borehole probes.

B - WORK PROGRAM

1. Experiments at ambient temperature
1.1. Borehole dilatometer creep test
1.11. Design, realization and test of the apparatus
1.12. Set up a software for acquisition and automatic treatment of data
1.13. Boreholes drilling and dilatometers positionning
Three tests are considered, two in horizontal holes and one in a vertical hole.
1.14. Survey and measurement
1.15. Interpretation
1.2. Laboratory creep test on thick tube samples of clay
1.21. Design, fabrication and calibration of the apparatus
1.22. Experiments
1.23. Interpretation
2. Experiments at high temperature
2.1. Design and performance of the apparatus
2.2. Test and adjustement in laboratory
2.3. Borehole drilling and installation of devices
2.4. Survey and measurement
2.5. Interpretation

C - PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In-stitu sudies : one dilatometer was placed in horizontal borehole from the experimental drift in December 86. The applied pressure is maintained with decreasing stages. Duration of any of them was of the order of 3 months . A second dilatometer was set up in vertical borehole in June and a third one in Decembre 87. A heating dilatometer for the high temperature test (point 2 of the work program) is under conception and will be installed in mid 88.

Laboratory test : the experimental device is fabricated and the test procedure is defined. Several experiments were performed.

Progress and results

1.1. Borehole dilatometer creep test

1.11. Apparatus fabrication

The chosen apparatus is a dilatometer (Mazier type). It is modified in order to allow a local measurement of closure (with 4 displacement transducers) and a global measure of volume change. The experimental system includes also a pressure regulating device.

Three dilatometers has been made. The dilatometers n° 2 et 3 were calibrated in laboratory.

1.12. Data acquisition and treatment

The software of acquisition and treatment of data is implemented on a microcomputer joined to computer system of the CEN/SCK.

1.13. In-situ installation

The measuring boreholes are drilled from the experimental drift of the CEN/SCK. They are 17.9 m long, with a first cased portion 8 or 12 m long and a bare end of 123 mm in diameter (figure 1).

The dilatometer probes of 116 mm in diameter are oriented with inclinometer. They are placed with a maximum time lag of 2 hours after the end of drilling.

1.14. Measurement

The test principle is to observe the borehole strain when a constant pressure is applied to the hole wall, by decreasing stages of about 3 months.

The inflation pressure of the horizontal dilatometer was decreased first from 3.6 MPa to 3.0 MPa then to 2.4 MPa.

The initial pressure of the vertical dilatometer was 3.9 MPa. It has not changed yet.

1.15. Interpretation

Interpretation phase is in progress

1.2. Thick tube test

1.21. Apparatus fabrication

The experimental device was completed by spring 87 (figure 2). The clay sample is a cylinder of 20 cm high, with diameter of 10 cm, crossed by a coaxial hole of 2.6 cm of diameter. The tube geometry approaches the in-situ creep dilatometer test configuration. It can also be considered as a physical model for a gallery. Three independant hydraulic systems pilot inner radial pressure, outer radial pressure and axial pressure.

1.22. Experiments

Several experiments were performed on Boom formation samples taken during the excavation of experimental facilities at Mol in unfrozen clay.

The test procedure is defined to resemble the in-situ dilatometer one. The sample is initially loaded under isotropic condition to the value of lithostatic pressure. The internal pressure is then decreased by stages and kept constant until stabilisation of volume change.

Another type of test was carried out to investigate the pre-failure behaviour of material : the internal pressure is decreased with constant rate until perfect closure of the hole.

1.23. Interpretation

Interpretation will follow with the completion of more experiments. The test results will improve mechanical model developped with classical tests.

2. Experiments at high temperature

2.1. Apparatus fabrication

The apparatus will be a dilatometer modified to include a heating device, instead of the heating convergence probe initially planned.

The design and fabrication of a prototype are in progress. It will be tested in laboratory before realization and in-situ implementation of final probe.

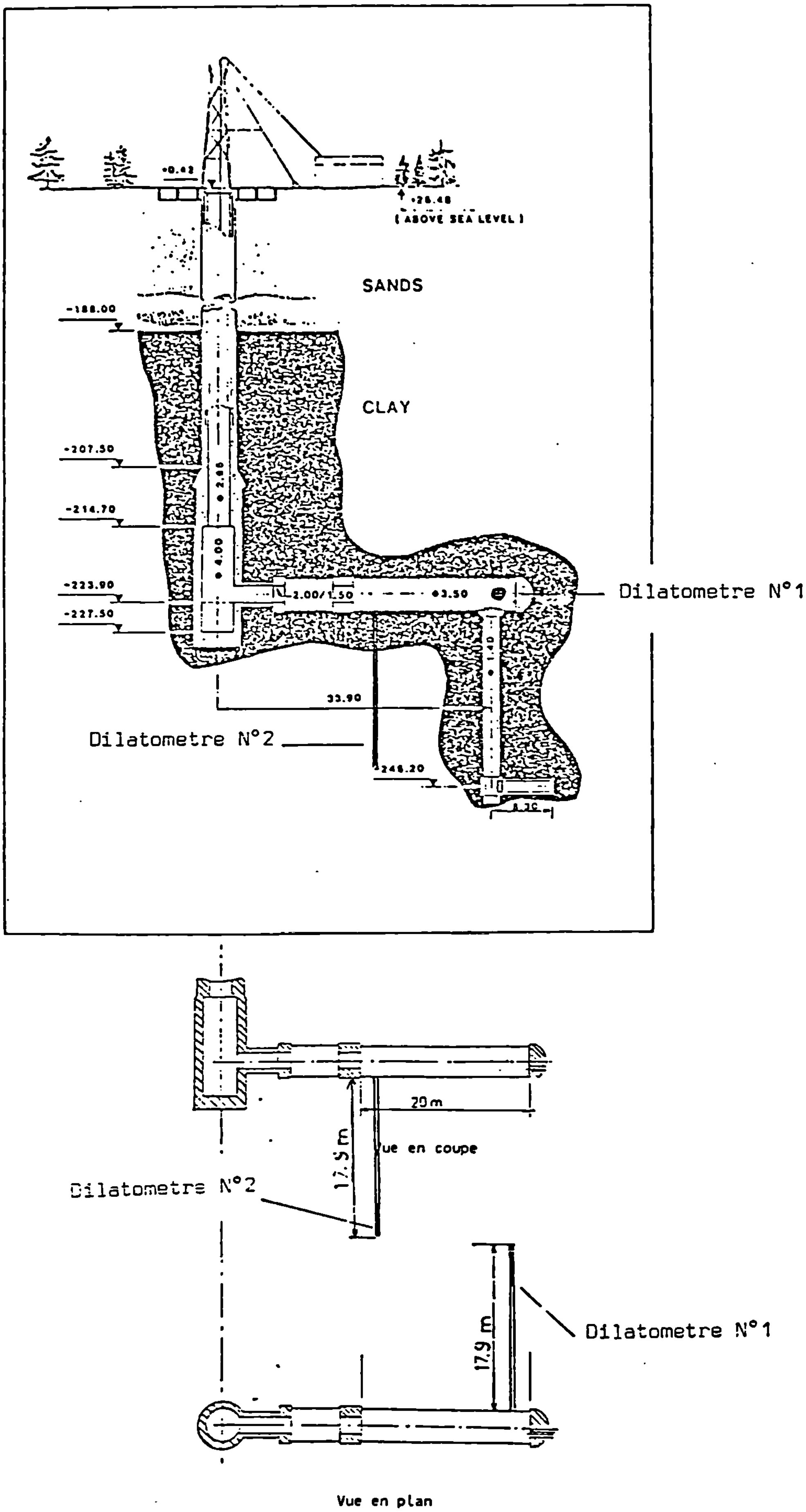


Fig. 1 : SITUATION OF THE DILATOMETER CREEP TEST

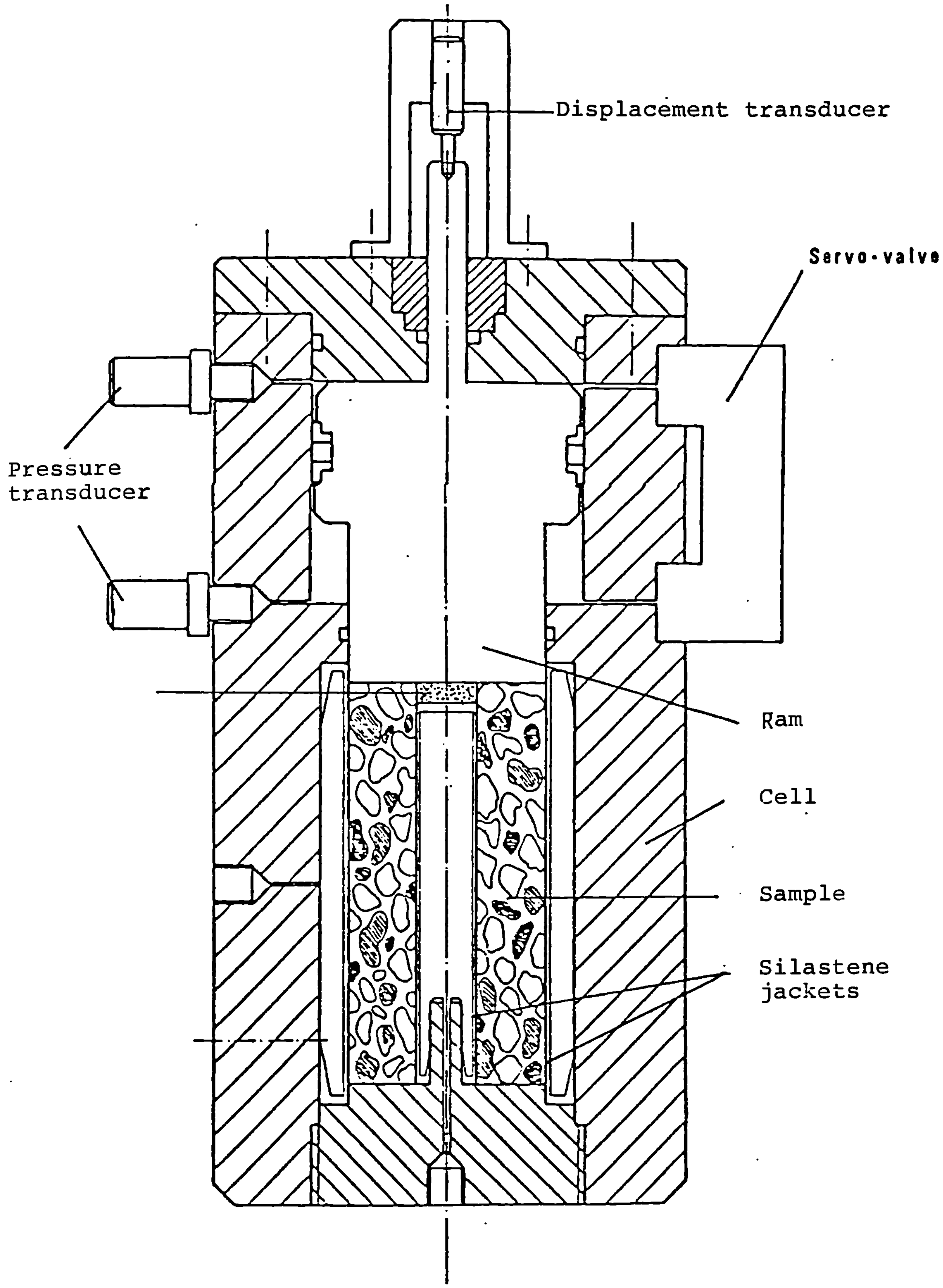


Fig. 2 : SCHEMATIC VIEW OF THE "THICK TUBE" CELL

CENTRIFUGE MODELING OF SALT DOMES

Contractor	: ANDRA, PARIS, FRANCE
Contract n°	: F I1W/0050
Duration of contract	: October 86 - September 88
Period covered	: October 86 - December 87
Project leader	: R. ANDRE JEHAN

A - OBJECTIVES AND SCOPE

The aim of the research is to study experimentally the different stages in the history of salt domes (or diapirs). It completes a prévious CEC contract which ended by autumn 85. The major part of the work is the inclusion of three dimensional models for comparison with two dimensional ones of the first period.

Tests are performed on equivalent materials on the large centrifuge of CESTA (in Bordeaux). Results can be applied to dome evolution though similitude transposition. By varying the artifical gravity acceleration the safety factors can be studied.

B - WORK PROGRAMME

1. Design, fabrication and tests in a cylindrical cell of 0.85 m net diameter
2. Improvement of visualisation and registering video systems
3. Continuation of two dimensional tests and set up of photoelasticity methods for direct measurement of stresses in the overburden

C - PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The installation for three dimensional tests is now operational. Two models were tested.

Two dimensional tests continued with ordinary clay models and new models for photoelasticity observation. They added information for the upper layer and for triggering.

Progress and results

1,2. Three dimensional tests

The basic problem is to be able to see what happens inside. This was accomplished by plomb pellets, fixed on cork ones, of different forms, for different vertical sections. A very heavy X-ray machine was used to photographe the model after each centrifugation period. When it was decided to stop the test, minute sections had to be carried out. This is normally impossible as the clay sticks to the cutting tool. Therefore a method based on electro-osmosis was developed. Thin copper rods were anodes, and flat metal plates (cathodes) cut the clay. The water which accumulated on the cathodes prevented any clay particles, and clean cuts were obtained.

Two tests were carried out (each taking two days of centrifugation), with an initial dome of 4 cm height and 20 cm diameter (as compared to 5 cm height and 20 cm with in the two dimensional case).

The rock was represented by a corundum loaded clay and the salt by ordinary clay ($\Delta\rho = 0.3$ g/cm^3 ; c ≅ 0.5 KPa ; μ ≅ 10.000 PaS). In the two dimensional case triggering was at 32 g's. In the first three dimensional test nothing was seen at 30 g's and the "salt" overlaid the rock after 30' at 40 g's. In the second one, slight motion was seen by X-rays from 32 g's to 38 g's, and inversion of the order of layers was almost complete after 15' at 40 g's. In these models the triggering for the two and three dimensional models was the same.

3. Two dimensional models

In order to study stresses in the "rock" it had to be represented by gelatine (g = 0.31 g/m^3) and a suitable material had to be found to represent the salt. The material had to have g ≅ 1. Glass micro-balls were mixed with clay and silicone oil. Two small models were tested which intended to show that the layer above the dome behaved as a beam.

In addition several clay models were tested in order to clarify the triggering mechanism.

LIST OF PUBLICATIONS

/1/ ZELIKSON A.
Large centrifuge simulation of diapiric growth and form (1987). 20' film, production - service audio-visuel de l'Ecole Polytechnique. (diffusion : Imagiciel 91/28 Palaiseau CEDEX FRANCE)

/2/ ZELIKSON A.
Large centrifuge models for video monitoring of diapiric growth, 28th US Sym. Rock Mechanics (Tucson 1987).

/3/ CHARO L., ZELIKSON A., BEREST P.
Risques de formation de dômes après stockage de déchets nucléaires dans une couche de sel - 6th congress, Int Soc. Rock Mechanics (Montréal 1987).

/4/ ZELIKSON A.
Anomalies géostatiques stables et instables dans le cas du sel, étude en centrifugeuse. Revue française de géotechnique n° 41 (1987).

LONG-TERM RHEOLOGICAL AND TRANSPORT PROPERTIES OF DRY AND WET SALT ROCK

Contractor: University of Utrecht, Netherlands
Contract No.: FI1W-0051-NL
Duration of contract: 01/07/86 - 31/12/87
Period covered: Jan. - Dec. 1987
Project leaders: C.J. Spiers, C.J. Peach (authors), H.J. Zwart

A. OBJECTIVES AND SCOPE

Prevous work at Utrecht has shown that small amounts of inherent or added brine can strongly influence the long-term rheological and transport properties of salt rock via processes such as fluid-assisted diffusional creep and recrystallization /1, 2/. Fluid-assisted recrystallization has also been shown to be capable of strongly reducing ("annealing out") radiation damage in salt /3/. The objectives of the present programme are as follows:

1) Characterisation of the long-term constitutive behaviour of salt rock, taking into account such parameters as fluid content, fluid pressure, grain size, and confining pressure.
2) Further characterisation of the dependence of creep-induced dilatancy and permeability in salt rock on parameters such as pressure, temperature, fluid pressure, and deviatoric stress.
3) Determination of the time-dependent compaction creep and permeability characteristics of dilated salt rock, granular salt (backfill), and anhydrite rock, under dry and wet conditions. Special attention will be given to the determination of an optimal (i.e. fast compaction/recrystallizing/sealing) "recipe" for granular salt backfill.
4) Preliminary determination of the rate of recrystallization (hence stored energy reduction) of γ-irradiated salt rock as a function of parameters such as specific stored energy, temperature, brine content, and brine impurity (Fe^{3+}) content.

B. WORK PROGRAMME

1. Rheological experiments (triaxial testing of coarse and fine-grained salt rock).
2. Creep-induced dilatancy/permeability tests.
3. Compaction creep/permeability tests.
4. Radiation damage/recrystallization studies.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

During 1987, investigations were directed at completing objectives 1-3 of the programme (see Section A), objective 4 having been largely completed in 1986. The compaction creep work on wet granular salt (objective 3) has proceded successfully, the experimental results showing excellent agreement with theory. Compaction creep laws have been developed for wet salt powder (pure NaCl) and for the backfill recipe proposed previously (see Table I). The permeability vs. porosity characteristics of the backfill recipe have also been investigated. So have the permeability vs. time characteristics of fractured anhydrite rock (objective 3). The deviatoric creep work (objective 1) has resulted in a "best estimate" constitutive law for creep of salt rock under in-situ conditions. Finally, the work on creep-induced dilatancy and permeability (objective 2) has shown that dilatancy is generally suppressed at hydrostatic stresses > 5 MPa. The overall status of the work programme can be summarised as follows:

.B1 - experimental programme completed satisfactorily, making use of inverted compaction data on fine-grained material.

.B2 - programme delayed, final results available 3/88.

.B3 - experimental programme complete.

.B4 - complete.

Separate final reports covering B1-B3 and B4 respectively are in preparation.

Progress and Results

1. Rheological Experiments on Salt Rock

Deviatoric creep experiments have been performed on natural Asse salt rock under conditions of constant strain rate and without added brine. These tests have confirmed that the results obtained from our previous stress relaxation tests /1, 2/, i.e. that fluid-assisted effects become important in natural salt when the confining pressure is sufficiently high to suppress dilatancy (i.e. > 5-10 MPa). Long-term creep experiments have also been performed on artificially prepared, fine-grained salt rock (∿ 1% brine), using the stress stepping technique Despite many complications, the results are broadly consistent with our earlier data /1, 2/ and confirm that the low-stress creep of brine-bearing salt occurs by fluid-assisted diffusional transfer (FADT). Analysis of our entire data set has yielded the following "best estimate" constitutive law for creep of brine-bearing salt by this mechanism

$$\text{Diffusional creep rate } \dot{\varepsilon}(DC) = (4.2 \times 10^{-10}) . \left[(8.25)T-2350\right] . \sigma/Td^3 (s^{-1})$$

where σ is the applied differential stress (MPa), T is absolute temperature (K), d is grainsize (mm), and where $\dot{\varepsilon}(DC)$ is thought to be insensitive to actual brine content provided trace brine is present. To a first approximation, this low stress creep law can be added to the well-known BGR creep law (high stress, dislocation mechanism) to obtain the general (upper-bound) constitutive equation $\dot{\varepsilon}(net) = \dot{\varepsilon}(BGR) + \dot{\varepsilon}(DC)$ for natural salt (non dilatant conditions). Note that the above diffusional creep law will be updated in our final report, taking into account grain boundary diffusivity data obtained from compaction creep tests.

2. Creep-Induced Dilatancy/Permeability Tests

Experimental data regarding the dependence of creep-induced dilatancy on pressure, temperature and deviatoric stress have been obtained during 1987 and combined with previously existing data (see /1, 2, 3/). Plotted in deviatoric vs. mean stress space, these data indicate that dilatancy should not occur in salt rock at hydrostatic stresses > 5 MPa under repository relevant conditions.

3. Compaction Creep/Permeability Work

Compaction creep experiments have been performed on brine-saturated NaCl powder to determine the constitutive compaction behaviour and to test theoretical models. The results show that under backfill/cement-relevant conditions, compaction creep occurs by diffusion-controlled FADT (see C.1) and is described by the constitutive law

$$\dot{\beta} = (46.27).P_e^{1.33}.(\emptyset_o - e_v)^{5.04}/e_v^{1.23}.d^{2.68} \qquad (2)$$

where $\dot{\beta}$ is the volumetric strain rate (s^{-1}), P_e is the applied effective pressure (MPa), $\emptyset_o$ is the initial porosity, e_v is volumetric strain, and d is the mean grainsize (µm). This law is thought to apply for $P_e \leq 2$ MPa, d < 2-3 mm, and for values of $\emptyset_o$ in the range 35-45%.

Compaction experiments on the backfill recipe given in Table I have shown that when the backfill is brine-saturated, the above law (eqn. 2) still applies to the matrix. When the brine content is reduced to 5 wt%, however, the "best fit" constitutive law for the bulk backfill mix (Table I) modifies to

$$\dot{\beta} \cong (13.88).P_e^{1.33}.(\emptyset_o - e_v)^{5.04}/e_v^{1.23}.d^{2.68} \qquad (3)$$

Permeability tests on the compacted mix have yielded the following relation between permeability (κ) and connected porosity ($\emptyset_c$)

$$\kappa = (2.55 \times 10^{-11}).\emptyset_c^{2.571}(m^2) \qquad (4)$$

This applies to backfill compacted both wet (5% brine) and dry. In the case of the wet-compacted samples, the relation between permeability and total porosity ($\emptyset_c$) is preliminary given

$$\kappa \cong (2.5 \times 10^{-12}).\emptyset_t^{2.6}(m^2) \qquad (5)$$

Finally, experiments have been performed to assess the time-dependent permeability characteristics of fractured anhydrite rock. Permeability measurements made on intact anhydrite (Switzerland) showed the material to have an initial permeability below $10^{-19}m^2$ at effective pressures in the range $P_e \leq 10$ MPa. "Faulting" in the laboratory increased this value to 10^{-15} - $10^{-14}m^2$. Long-term "annealing" in the presence of H_2O or brine at T = 20°C, a pressure of 20 MPa and a pore pressure of 10 MPa then led to reduction in permeability at an average rate equivalent to 1-2 orders of magnitude per year. This is thought to be due to mineral reactions within the "faulted" sample.

4. Radiation Damage/Recrystallization Studies

Hydrostatic annealing experiments have been performed on pre-irradiated salt rock samples (Dose = 1-10 Grad) at T = 70-120°C, P = 10-30 MPa using added brine contents in the range 0-0.5 wt%. Stored energies have been measured using solution calorimetry and DSC methods. Recrystallization rates have been determined by image analysis of sectioned material.

Most samples annealed with brine contents > 0.1% exhibit relatively rapid recrystallization and reduction of stored energy. However, the data show a wide scatter, making determination of the dependence of recrystallization rate on stored energy, temperature and brine content difficult. Nonetheless, it can be inferred that provided brine remains present (> 0.1%), recrystallization is a much more rapid annealing mechanism, under the conditions of interest, than purely solid state reactions. The results clearly demonstrate the need for in-situ irradiation experiments in connection with brine migration studies.

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/2/ URAI, J.L., SPIERS, C.J., ZWART, H.J. and LISTER, G.S., Nature, 324 (No. 6097), 554-557 (1986).

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Table I. Preliminary "fast compacting" salt backfill recipe (d = grain-size).

Material	Mass fraction (%)
Matrix of finely powdered salt (d < 0.5 mm)	∿ 75
Coarse-grained salt filter (1 ≦ d ≦ 5 cm)	15-20
Geochemical barriers:- anhydrite/Fe_2O_3 (d < 0.5 mm)	∿ 2
Brine	∿ 5

Study on fracturing and microfissuration of granite

Contractor: Commissariat à l'Energie Atomique, Fontenay-aux-Roses, France
Contract N°: FI1W/0053
Working Period: 01/12/1986 - 31/12/1987
Project Leader: S. DERLICH

A. Objectives and Scope

The digging of mine drifts is done by the blasting of explosives by which different shapes can be given to the galleries. It can also be achieved with tunnelling machines which give perfect circular sections in hard rocks.

The use of explosives brings on the formation of a fractured zone in a cylindrical volume around the drift. Its extent may be several meters in diameter, depending on the type of explosive and the array of the loads in the rock

Tunnelling machines and boreholes generally disturb the natural stress pattern in the walls of the excavations. The main disturbances extend as far as one to two hole diameters, from the wall.

When the natural stresses are high, bursting of the wall may happen either by slabling or spalling or by radial extensional fracturing.

In order to study these phenomena we sampled granite obtained from deep boreholes by coring or from drift walls bearing blast features.

Sampling methods and grinding and polishing of thin sections and polished surfaces induced also artificial fissures and we had to determine these artifices by using die injections at different stages of processing.

Work realised in 1987 bore on a choice of analytical methods to be used in this study.

The first method we intend to apply is the measurement of porosity by pressure injection of mercury in granite from the Auriat Borehole (cored to a depth of 1000 m). The sampling has been done at regular intervals, from a depth of 100 m to the bottom, so as to obtain tests-pieces having undergone increasing natural stresses, with depth.

The second method aims at visualizing the microfissures by pressure-impregnation of resin. The samples can then be studied by optical or electronical technics (microscopes and probes).

Porosity measurements

Before applying that method on a general basis to samples having undergone different stresses, we performed some tests on two of the granite type encountered in the borehole : the first being unweathered granite, the second having undergone hydrothermal weathering.

On each sample, several pore classes have been established, according to their diameter (following the Washburn cylindrical pore model).

Table 1 shows the volume and developed surface for each pore class (refering to 1 gramm of matter).

The smallest pore diameter is 60 Å, corresponding to a maximum pressure of 200 MPa.

To improve this method it will be necessary

1°) to increase the sensitiveness of the porosimeter, by constructing a penetrometer the same size as those commercially available, but with a smaller capillary tube.

With a 8 mm diameter capillary, the sensitiveness would be increased four-fold by comparison to the most sensitive penetrometer used in these tests.

2°) To do the same measurements on very weathered granite samples (such as in the 500 m Auriat borehole, at a depth of 100 m) so as to obtain a thorough relation between porosity (and its distribution) and the weathering of the rock.

Analysis of resin-injection visualized fissures

Preparation of samples

Granite samples, dehydrated in an oven at 80°C for 3 days, are degassed and then impregnated with a coloured resin under a pressure of 2 MPa. The samples are then placed in an oven till complete polymerizing of the resin is achieved. Thin slides, 30 microns thick, are then prepared and allow the transmitted light optical analysis of the fissures and of the adjacent minerals.

Instruments and use

Among several possibilities we have chosen a digitizing table as best suited to our purpose. The analyser's part is composed of a Benson 6440 Digitizing table with a 4 knobs cursor associated to a luminescent diode. The table is linked to an optical Olympus BH2 Microscope by use of a camera lucida. The displacement of the diode image along a fissure carries out the recording of its coordinates by a micro-computer.

Parameters studied

The presently used program allows the calculation of the following parameters : perimeter and cumulated surface of the observed fissures. Other characteristics such as orientation and shape coefficient will be obtained in 1988.

Studies of drifts

The drilling and overcoring program aiming at the study of the blasting-induced fractures and of the stress-release effects will start at the beginning of the second term of 1988.

Pore diameter (μm)	Unweathered granite (245 m)						Weathered granite (480 m)					
	Volume x 10^4 ($cm^3.g^{-1}$)			Surface x 10^4 ($cm^2.g^{-1}$)			Volume x 10^4 ($cm^3.g^{-1}$)			Surface x 10^4 ($cm^2.g^{-1}$)		
	Test number			Test number			Test number			Test number		
	1	2	Average	1	2	Average	1	2	Average	1	2	Average
18-8	0	1	0.5	0	1	0.5	1	1	1	0	0	0
8-1.2	1	0	0.5	2	1	1.5	1	0	0.5	2	1	1.5
1.2 - 0.11	7	7	7	81	81	81	3	6	4.5	55	102	78.5
0.11 - 0.03	2	1	1.5	107	94	100.5	5	6	5.5	367	454	410.5
0.03 - 0.009	0	0	0	31	0	15.5	5	7	6	1364	1686	1525
0.009 - 0.006	0	0	0	0	0	0	0	0	0	0	219	109.5
Total	10	9	9.5	221	177	199	15	20	17.5	1788	2462	2121

Table I

FURTHER BENCHMARK EXERCISES TO COMPARE GEOMECHANICAL COMPUTER CODES FOR SALT (COSA II)

Contractor: W.S. Atkins Engineering Sciences, Epsom, U.K.
Contract No: FI1W/0054
Duration of Contract: November 1986 - October 1988
Project Leader: N.C. Knowles

A. OBJECTIVES AND SCOPE

Research into geomechanical aspects of RAW repositories in salt formations has been active in the European Community for nearly two decades, with particular interest being placed on problems of heat producing waste. Central to this work is the prediction of stresses and deformations in the host strata, for which a number of computer codes have been developed /1/. A preliminary exercise ("COSA 1") to compare the ability of the different codes /2/ provided a limited "snapshot" of the European capability to predict the behaviour of rock-salt under well defined conditions. The purpose of the present contract is to extend the comparison to more complex but realistic situations.

Comparison problems in the first phase were relatively simple, and a number of difficulties to do with modelling of the in-situ behaviour of rock salt were deliberately avoided. The present exercise is directed at comparisons of realistic in-situ behaviour. Emphasis will be placed on the characterisation of material behaviour by individual participants. Other modelling topics to be addressed include the representation of 3-D behaviour by 2-D models, algorithms for treating the thermal and geomechanical discontinuity at the moment of encapsulation of the waste canister and the influence of far-field boundary conditions.

There are 9 participants in the exercise, each acting as a sub-contractor to the co-ordinator. In addition two independent experts provide advice as necessary on aspects of salt rheology (Table 1).

B. WORK PROGRAMME

B.1 To agree, at plenary meetings, suitable in-situ benchmark problems to be solved by participants.

B.2 Co-ordinator to prepare discussion documents and circulate to participants as necessary.

B.3 Co-ordinator to prepare and circulate detailed specifications of agreed problems.

B.4 Participants to solve agreed benchmark problems to the best of their ability using appropriate codes, according to the specifications produced by the co-ordinator.

B.5 Co-ordinator to collect and compile results and other data from participants.

B.6 Co-ordinator to prepare draft reports for discussion at plenary meetings to be held approximately every six months.

B.7 Co-ordinator to prepare and issue final reports taking account of participants' comments.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Three benchmark problems have been defined. These are based on the series of experiments performed by ECN in the 300m dry-drilled borehole at the ASSE research facility.

The first problem is the prediction of the isothermal free convergence (IFC) at the bottom of the borehole over a period of some 800 days. This stage is substantially complete and participants results have been compared and discussed in plenary meetings.

A second stage, to model the convergence onto a heated probe within the borehole during which pressures were monitored (HPP1) is currently in progress. This will be followed by a problem to model the free convergence during a heater test (HFC).

Progress and Results

1. IFC Benchmark

The modelling of the IFC benchmark was briefly discussed in a plenary meeting (November 1986) and a specification was subsequently drawn up and circulated by the co-ordinators. This highlighted the difficulty of obtaining definitive rheological data for such 'blind' predictions. Three sets of data were provided and participants selected from them on the basis of their experience and engineering judgement.

The results of the preliminary calculations of the IFC, as collated by the co-ordinators (3), not surprisingly contain wide variations. These can be attributed to the differing assumptions about the initial state of lithostatic stress and the materials constitutive law, since when 'normalised' with respect to stress and creep law constants, very good agreement was obtained (Fig. 1). This is in contrast to earlier benchmarks in which the initial results were substantially different due to analyst error and differing discretisation techniques.

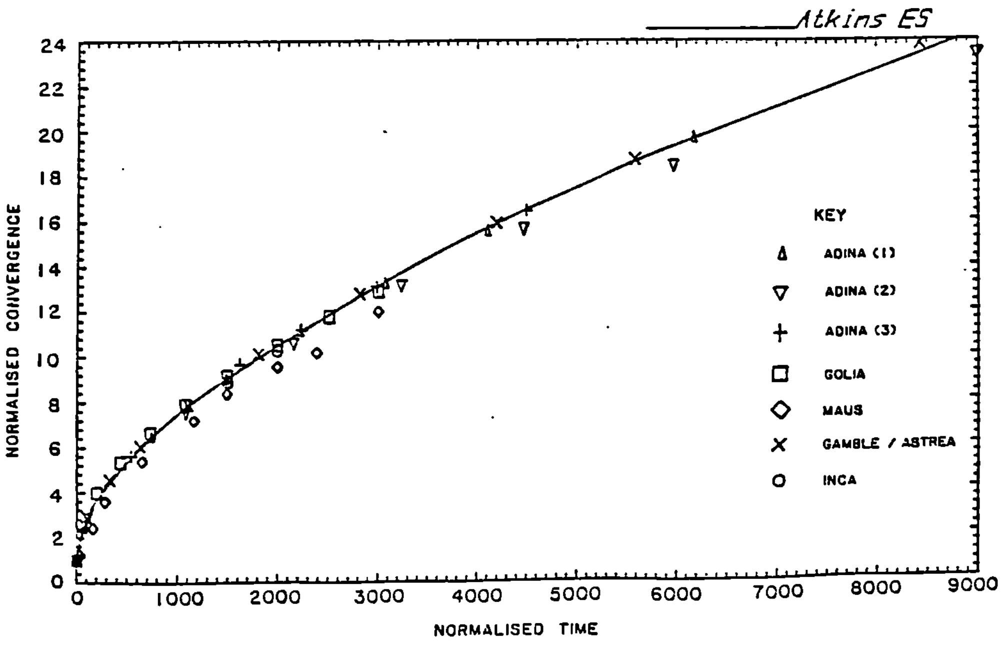

fig 1. RESULTS OF IFC AT 292m DEPTH

2. Plenary Meeting

A plenary meeting was convened at GSF (Braunschweig) on 30th June - 1st July 1987 and attended by 22 specialists from all participating organisations. In addition to reviewing progress on the project in general and reviewing the preliminary results of the IFC in particular, a number of other important topics were covered, including:

- o available materials data for the "Dutch' hole and subsequent modelling.
- o initial in-situ (lithostatic) state of stress at the start of the experiment.
- o modelling of the first heated pressure probe test (HPP1).

3. HPP1 Benchmark

The test on which this benchmark problem is based follows chronologically the IFC. It involves monitoring the temporal temperature and pressure variation on a heated probe fixed in the borehole at a depth of 262m. As with the IFC benchmark participants are free to exercise their own judgement in their choice of material data, constitutive law and initial state of stress. There has been some discussion about the initial state of contact (or otherwise) and the influence on short term behaviour of even small radial gaps between the probe and the borehole wall. Perfect contact has nevertheless been assumed in order to confine the model variations to reasonable bounds.

Results of the HPP1 test will be collated by 1.2.88. Thereafter participants will address the third phase i.e. the heated free convergence test (HFC1).

List of Publications

(1) Piper, D. & Knowles, N.C. "Project COSA - Addendum to Final Report" - W S. Atkins Engineering Sciences, AES Report 200487.

(2) Lowe, M.J.S. & Knowles, N.C. "Some experiences of Finite Element Calculations in a European Benchmark Exercise" - Proceedings of International Conference on Quality Assurance and Standards in Finite Element Analysis - Brighton 1987.

(3) Piper, D. "CEC Project COSA - Benchmark 3 - Isothermal Free Convergence Calculation - Preliminary Results" - W S Atkins Engineering Sciences June 1987.

(4) Piper, D. "CEC Project COSA - Benchmark 3 - Heated Pressure Probe Test 1 Specification" - W S Atkins Engineering Sciences September 1987.

(5) Knowles, N.C., Lowe, M.J.S. & Piper, D. "An update on Project COSA" - Paper BL12/1 SMIRT 9 Lausanne August 1987.

(6) Knowles, N.C. & Piper, D. "Some computational experiences of a Geomechanical Benchmark in Rock Salt" - Paper accepted for 6th International Conference on Numerical Methods in Geomechanics Innsbruck April 1988.

(7) Knowles, N.C. & Come, B. "A Progress Report on Project COSA" Paper to NEA Workshop on "Excavation Responses in Deep Repositories" Winnipeg April 1988.

References

/1/ BROYD, T.W., et al. CEC EUR Report 8669 (1985)

/2/ LOWE, M.J.S.L., KNOWLES, N.C., CEC EUR Report 10760 EN

Table I : List of organisations involved in COSA II

W.S. ATKINS E.S. - Epsom (UK)	Co-ordinator
FORAKY - Brussels (B)	Calculation Team
LGC - Louvain-la-Neuve (B)	Calculation Team
KfK - Karlsruhe (D)	Calculation Team
RWTH - Aachen (D)	Calculation Team
CEA-DEMT - Saclay (F)	Calculation Team
EMP - Ecole des Mines - Fontainebleau (F)	Calculation Team
LMS - Ecole Polytechnique - Palaiseau (F)	Calculation Team
ISMES - Bergamo (I)	Calculation Team
ECN - Petten (NL)	Calculation Team
GSF - Braunschweig (D)	Salt Specialist
Technical University Delft (NL)	Salt Specialist

Geomechanical behaviour of Boom clay at ambient and elevated temperature conditions

Contractor : SCK/CEN, Mol, Belgium
Contract No. : FI1W/0055/B
Duration of contract : from October 1986 to December 1989
Period covered : January 1987 -December 1987
Project Leader : A. A. Bonne

A. OBJECTIVE AND SCOPE

The aim of the work is to investigate experimentally the mechanical and thermo-mechanical behaviour of Boom clay for predicting its behaviour under the real conditions at various stages of the construction and operation of an underground disposal facility and after closure of it. Emphasis will be upon the in situ research in the existing underground HADES-laboratory.

The test excavation of a small shaft and drift in intact Boom clay at Mol and monitoring of this experimental work demonstrated that, at reduced scale, tunnelling and mining of a plastic clay is feasible.

To improve the understanding of the basic geomechanical behaviour of the Boom clay during the construction of real galleries and during the post-operational phase, whereby a temperature increase of the host rock is expected due to the heat dissipation from HLW, a series of "in situ" geomechanical experiments will be performed as well as ordinary geo-mechanical laboratory tests.

The test will also provide the necessary data for improving and validating the modelling of the in situ geomechanical behaviour of clay around excavated cylindrical structures under normal and elevated temperature conditions.

B. WORK PROGRAMME

1. Stress measurements in non-frozen clay
2. Fracturing of clay
3. Long-term dilatometric tests
4. Heated tube test

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Most of the research issues to be dealt with in this research contract are linked or related to in-situ experiments in the underground HADES laboratory. Due to construction activities in it, lasting about 6 months more than originally planned, some of the in-situ experiments are now scheduled to be installed in the course of 1988. However in-situ experiments related to geomechanics followed the original calendar. The first stress measurement and long term dilatometer tests are installed and orientative trials of a fracture observation technique was performed.

Progress and results

1. Stress measurements in non-frozen clay

The stress and pressure evolution of the two Glötzl cell cylinders (emplaced in two parallel horizontal bore holes in ring 9 and 19 at 16 m distance from the URL) reached a stabilisation in the course of the year. It can be concluded from these test that :

- the total pressure appears to be too low; comparison with pore water pressure confirms this point of view ;
- the main stress direction is horizontal or within 45° w.r.t. the horizontal ;
- the configuration of the cells and the characteristics of the embedding material may cause local artefacts and a readout deviating from the actual in-situ conditions.

2. Fracturing of clay

A preliminary trial with an endoscopic device for examining the fractures on the walls of a non-cased bore hole in the clay has shown that fractures are present in such a bore hole and that this technique needs to be implemented. Therefore complementary trials upon the possibility to use for this purpose camera/video chains and PC-image processing techniques have been performed. It is expected that by this technique a more accurate observation and documentation will be possible and that statistical treatment of various characteristics (e.g. strike and slope of the fractures, density, aperture) will be simplified.

A programme for remote auscultation of fracturing of clay in a transient heating environment has been established and an order has been placed for performing this auscultation. The programme foresees the following loggings : nuclear logging (gamma-ray, gamma/gamma, and neutron/neutron), seismic logging (single hole and cross-hole) and resistivity measurements.

3. Long term dilatometric tests

Two long term dilatometric tests (type: Mazier) of the joint SCK/CEN-ANDRA proposal were emplaced this year :

- A vertically downward emplaced device in ring 9 of the URL, between 16.75 and 17.75 m from the URL. The cell was inflated immediately to a pressure of 3.8 MPa, stress assumed to act in the clay mass.
  The test is of the "retracting" type and consists of following up, in function of time and for decreasing pressure levels, of the volumetric and radial deformations of the measuring device under constant internal pressure at each pressure level considered ;

- A horizontally eastward emplaced device in ring 25 of the URL, between 15.5 and 16.5 m distance from the URL. The procedure for this test was to follow in function of time and for decreasing cell volume steps the pressure build-up exerted by the clay mass on the device at each volume step. Also radial deformations are monitored of course.

4. Heated tube experiment

This experiment, a joint SCK/CEN - ANDRA test, will be developed in order to investigate the pressure build-up and deformation of clay at elevated temperatures. Only preparatory activities (e.g. design, scale, positions) have been tackled.

LIST OF PUBLICATIONS

A. BONNE "Geotechnology investigations", in Mol Research Division Report, BLG 601, p.75-83, 1987

A. BONNE, P. HENRION, J. MARIVOET, B. NEERDAEL, et al. "R&D programme on radioactive waste disposal into geological formations (study of a clay formation)", EUR 11025 EN

D. DE BRUYN, et al. "Time Dependent Behaviour of the Boom Clay at Great Depth. An Application to the Construction of a Waste Disposal Facility", Computers and Geotechnics 3, 3-20, 1987

B. NEERDAEL, et al. "In situ testing programme related to the mechanical behaviour of clay at depth", Proc. 2nd Int. Symposium on Field Measurements in Geomechanics, Paril 6-9, Kobe, Japan, 1987, pp. 763-774

THERMO-MECHANICAL BEHAVIOUR OF BOOM CLAY.

Contractor: ISMES S.p.A. - Viale Giulio Cesare, 29 - 24100 BERGAMO ITALY
Contract n.: FI1W/0150
Duration of contract: 29 months, from 1.11.1987 to 1.2.1990
Period covered: 1.11.1987 to 1.1.1988
Project Leaders: Dr. A. Peano, Ing. G. Baldi

A. OBJECTIVES AND SCOPE

The understanding of thermal effects due to decay heat like pore pressure rise, change in mechanical properties and in the hydraulic field under high lithostatic pressures is fundamental in the evaluation of safety and in the design of nuclear waste repositories in clay.
For this purpose a thermo-hydro-mechanical model has been developed in ISMES. Its suitability in reproducing the thermo-mechanical response of the samples tested under different loading conditions has been positively verified with experimental tests performed on the HITEP triaxial cell operating in ISMES laboratories on various types of stiff clays, either remoulded and undisturbed.

Furthermore, the interpretation procedures of thermal tests shew that for some of the clays tested the Campanella and Mitchell procedure can lead to inconsistent results.

In order to study possible reasons for this inconsistency, first thermal expansion coefficient values will be studied referring to the conditions of water in stiff clays, which are suspected to affect significantly its thermal behaviour.This study will be conducted with AECL of Canada.

The results of this research could affect also the predicted undrained response of clay in terms of pore pressure rise.
In the meantime a better understanding of thermo-mechanical Boom clay behaviour is foreseen in order to improve the model.
Thermo-mechanical effects on clay due to realistic disposal geometries will be then studied with this model with the cooperation of SCK/CEN.
Similar studies are planned also for sand/betonite mixtures, widely adopted for backfilling.

B. WORK PROGRAMME

1. Microstructural studies
2. Sampling of the Boom clay in the Mol site.
3. Experimental tests in the HITEP apparatus on natural clayey and artificial soils.
4. Identification of material parameters on the basis of experiments on Boom clay.
5. Introduction of the options expected from activity 1 in the mathematical model.
6. Check on the results of the laboratory tests using the above model.
7. Definition of the boundary value problems to be treated on the basis of prospective in-situ experiments and/or typical disposal technology at Mol site.
8. Simulation of clay mass behaviour with reference to the problems envisaged in activity 7.
9. Evaluation of test results.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Microstructural activities performed together with the Atomic Energy of Canada Ltd. are in progress. ISMES is studying improvements on the HITEP apparatus for the experimental campain on Boom Clay and on a Sand/Bentonite material.

PROGRESS AND RESULTS

1.1 Work has commenced on the development of a model to describe the properties of bound and free water in clay systems. A preliminary model will be ready for a presentation at the next group meeting in April 1988.

1.2 A pressure plate and pressure membrane extraction device has been selected and ordered by AECL. Delivery is expected in Feb. 1988 and initial equipment trials should be completed by April 1988.

1.3 Design of the 1-D thermal cell has been completed, ancillary equipment has been ordered and construction of the cell itself is expected to begin in February 1988.

1.4 A preliminary laboratory testing program has been developed for the Pressure Plate and 1-Dimensional equipment and will be initiated following equipment delivery and installation. Preliminary testing will include testing of low activity clays (Illite or Pontida silty clay) to determine their suction moisture content equilibria and thermal expansion properties. Later testing will progress to active clay materials (Boom clay, Reference Buffer Material (Bentonite)). Comparison of the results of testing high and low activity clays should provide a means of determining the influence of surface forces on water movement and expansion, and hence, material performance at an actual disposal site. These laboratory tests will also provide information needed for the development of a constitutive model describing the thermal expansion characteristics of saturated clay soils.

STUDY OF THE CLAY BEHAVIOUR AROUND A HEAT SOURCE

Contractor: ME2i, 8 Rue Eugène Oudiné, 75013 PARIS
Contract n°: FI1W.0152.F
Duration of contract: 1/12/87 to 31/12/89
Period covered: december 1987
Project leader: P. De Sloovere

A. OBJECTIVES AND SCOPE

Wave propagation into soft rock is not completely described by purely linear elastic theory. Through spectrum analysis of a wave propagated into such a medium, one can see that several frequencies are selected by the ground. This behaviour is not forecasted by linear elasticity but is related to mechanical characteristics of the medium. Any change in the mechanical characteristics modifies the frequency content of a signal passing through the medium. This agrees with the behavior of a wave propagated into a Biot medium or a viscoelastic medium. Therefore one can detect by spectrum analysis of propagated wave any change in mechanical characteristics of a medium. Around an underground storage in clay, displacement or swelling will provoke a shift in main frequencies.

We use the general concept of cross-hole method in order to produce or receive the signal. Previous experiments confirmed that an improvement of the soil characteristics is easily shown by this method. One can detect the lack of grouting in alluvium, sands, etc. One can detect a cavity and its filling after grouting. Cracks on piles have been detected by this method.

One can imagine that such a method is well adapted to detect any change around a radioactive waste deposit, mainly in clay or in soft rock. Around a borehole heated by a corrosion tube, we will set up a cross-hole system and follow the frequency content during the heating of the clay.

B. WORK PROGRAMME

1. Construction of a new shock transmitter for horizontal borehole and three receivers
2. Boring of four holes on the Mol site (CEN/SCK)
3. Setting up transmitters in the boreholes (taken in charge by CEN/SCK)
4. First measurements
5. Realization of the big borehole for corrosion tube (CEN/SCK)
6. Measurement of the effect of the excavation
7. Heating of the clay
8. Measurement of the heating of clay effect
9. Interpretation

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Due to the fact that the boreholes are horizontal, we had to construct a new shock transmitter able to work in any position. This "borehole shear-hammer" will be similar to compressed air rifle. It is the first step necessary to conduct the experiment.

FRACTURE MECHANICS FOR HARD ROCK

Contractor: J.Gramberg, The Netherlands

Contract No.: FI 1W-0153-NL

Duration of contract: July 1987 - Dec. 1988

Period covered: July 1987 - January 1988

Project leaders: J. Gramberg

A. OBJECTIVES AND SCOPE

This report is a sequel to the report WAS-454-NL, to be published as EUR 11134 EN: "A non-conventional view on rock mechanics and fracture mechanics" /2/.

The present report FI 1W-0153-NL is focussed upon observed fracture phenomena in mine workings and in tectonics, whereby the primary fracture phenomenon of the "axial cleavage" or "extension fracture" forms the central point.

One of the objectives is the framing of a General Law of Primary Brittle Fracturing.

Graphical constructions, based upon stress theory will be shown as well as their application in the analysing of "case histories".

Some extrapolations with respect to the cataclastic equilibrium within the earth's crust and also concerning a possible cause of local uplifts will be discussed.

B. WORK PROGRAMME

1. A very concise version of the phenomenology, leading to the Principal Law, Part (1) and Part (2).
2. A very concise treatment of the theory on the axial cleavage fracture
3. A review the features of brittle fracturing in block diagrams
4. Analysis of the various observed types and patterns of brittle fracture; the result of pressure only; the combination with small shearing movements; the effect of relaxation.
5. The application to cases in underground mining
6. On Tectonics:
   a) Vertical and sub-vertical joints in the Earth's crust
   b) The C.P.E. equilibrium in parts of the continental Earth's crust (the influence of the internal self-confinement pressure σ_{3i}).
   c) A mechanism of fracture cleavage and of certain kinds of schistosity.
   d) A possible mechanism of local uplifts in the Earth's crust

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

A concise review of the development of the considerations which resulted into the "Ellipse-with-Notch-and-Variable-Axis-Ratio" model for the axial cleavage or extension fracture is ready.
Not less than five different views on the (man-made) idea "stress" are involved in the description of this natural phenomenon by means of our (man-made) stress theory and theory of elasticity.
In connection with the researches of Maury /1/ about the failure mechanisms around underground excavations it appeared relevant to approach the term "brittle" for the quality of solid rock in a more differentiated way: In connection with the different fracture mechanisms the quality should be pointed out by the terms "ideal-brittle", "true-brittle" and "not-true-brittle", depending on the measure of presence or absence of traces of elements of plasticity in the material.
It is tried to frame the proposed "General Physical Law of Primary Brittle Fracturing at Tensile as well as at Compressive Loading" properly.
A Thesis on the reversibility of this Principal Law is put in order to dispose of an entrance for the application of the Principal Law in "Fracture-and-Fracture-Plane-Analysis" in order to connect observed brittle fracture planes with the then prevailing stress distribution.
Curved fracture planes in rock are discussed briefly.

REFERENCES

/1/ MAURY, V., Observations, researches and recent results about failure .... mechanisms around single galleries (Report of the I.S.R.M. Commission on Failure mechanisms around underground excavations) in: Proceedings of the Sixth Int. Congr. on Rock Mechanics of the I.S.R.M., Montréal 1987. pp. 1119-1128

/2/ GRAMBERG, J., A non-conventional view on rock mechanics and fracture .... mechanics (EUR 11134 EN, 1987, Ed. Balkema, Rotterdam (1988), 271 pp.

/3/ GRAMBERG, J., and ROEST, J.P.A., A vision on the problem of rock .... fracturing; Workshop on Failure Mechanics Around Underground Working, Sept. 2, 6th J.S.R.M. congress, Montréal, Quebec, Canada.

Experimental study of the mechanical behaviour of argillaceous rock

Contractor: Commissariat à l'Energie Atomique, Fontenay-aux-Roses, France
Contract N°: FI1W.0163.F
Duration of Contract: October 1987 - December 1988
Period covered: October 1987 to December 1987
Project Leader: J.Y. BOISSON

A. Objectives and Scope

Changes in the mechanical behaviour of clays according to the temperature are not yet well known.If, for the short term behaviour studies, one can admit that there is no drainage effect and that a temperature rise leads, at the short term, to a clay volume increase, this cannot be stated concerning the long term, where the drainage effect must be taken into account.

Recent studies have shown that, thanks to their texture rearrangement, saturated remoulded porous soils, replaced in a normal consolidated state, exhibit, in the long term, a volume decrease, with, as consequences, settling effects and crackings.

It is possible that the long term response of the clays at such thermal prompting is a fonction of their over consolidation degree : normal consolidated clays will decrease, in fact, in volume under thermal sollicitation but this could be different for the over consolidated clays. The aim of this study is to bring clear and quantitative experimental answers to these questions both with a theoretical interpretation of these phenomena.

This research will be performed with scientific support of the Centre de Géologie de l'Ingénieur (ARMINES-Ecole des Mines de Paris).

B. Work Programme

2.1. Choice of the sites, and sampling of clay

The selection will be made first considering that the sites answer to some textural granulometric criteria (clays silts) and mechanical criteria (normally or over consolidated clays).

After that, we will take these materials under predetermined conditions to avoid remolding and overconsolidation due to surficial dessication.

We will determine then, in a precise way, their initial overconsolidation degree and their texture, considering that these two points are essential for this study of the behaviour of clays towards thermal sollicitations.

2.2. Responses study of the selected material towards the thermal mechanical sollicitations

These responses are mainly textural rearrangements which will be studied in the laboratory by precise texture identifications and by comparisons between initial and final state.

2.2.1. Basic petrographic, mineralogic and textural identification

Different procedures will be used : X ray diffractometry analyses, adsorption tests with methylene blue, Atterberg limits, porosimetry, observations with scanning electron microscope, and permeabilities.

2.2.2. Determination of the overconsolidation degree.

2.2.3. Control thanks to blank tests of the thermal behaviour of the experimental apparatus used

The aim will be to well separe, in the experimental results, the information concerning the clay geomechanical behaviour from artefacts due to the thermal behaviour of the tests apparatus itself.

2.2.4. Creep tests in oedometer cells and permeability measurements

An axial counterpressure will be applied so as to be able to scan the temperature range between 20°C and 120°C without pore water loss. The stress will be equivalent to the one in situ, and will not be less than 0.01 MPa.

In case of swelling during the sample saturation, the applied stress will be equivalent to the swelling pressure. The thermal prompting applied to each selected clay sample will correspond to the 4 following temperatures : 20, 50, 80 and 120°C. Different temperature rises will be applied, favouring the exploration of parameters linked to the thermal prompting and to the creep :

a) direct temperature rise (creep study at mid term during 3 months, tests with the four mentionned temperatures).
b) direct temperature rise, (creep study at long term during 9 months, tests at 20° and 80°).
c) progressive temperature rise at 20° and 120°C (for each temperature level, creep study at mid term for 3 months).
d) progressive temperature rise and then progressive decrease, creep study during 3 months (for each temperature level) : 1 test from 20° to 50°C and then from 50°C to 20°C ; 1 test from 20°C to 80°C and then from 80°C to 20°C ; 1 test from 20°C to 120°C and then from 120°C to 20°C.

A certain number of these tests will be repeated (two or three times) so as to ascertain the reproducibility of the results.

2.2.5 Textural study

This study will be done by applying the mercury porosimetry tests, scanning electron microscope, permeability tests for each test (initial and final state). The compared analysis of the whole results will certainly give a contribution to the thermal mechanical behaviour knowledge related to the texture and overconsolidation degree.

The basic equipement for the textural study and for the mineralogical, petrological identifications and classical geotechnical tests is available. Nevertheless, for the thermomechanical tests it will be necessary to use adapted devices.

C. Progress of Work and Obtained Results

As this study has just begun, no experimental results can be provided at this stage.

Preliminary tests with a modified oedometer cell including a heating device have been performed, and have revealed that this apparatus was not completely adequate : structure deformations due to the thermal effects were not compatible with the proposed tests.

As a consequence, a new specific device has been designed and built.

At the same time, a selection of six possible clay sites has been made. The complete characterisation of the theses clays will be achieved before the tests.

4.2. REPOSITORIES AND ENGINEERED BARRIERS

4.2.A. Repository design and disposal techniques

N.B. : No particular research contracts have been concluded on this subject

4.2.B.1) HLW container development (COMPAS)

ASSESSMENT OF STRUCTURAL PERFORMANCE OF HLW CONTAINERS (COMPAS)

Contractor : Ove Arup and Partners, London, England
Contract No. : FI 1W/0111
Duration of Contract : April '87 - Dec '89
Period Covered : April '87 - Jan '88
Project Leaders : J Miles; S Hendry

A. OBJECTIVES AND SCOPE

The COMPAS project has been designed to look at the mechanical performance of those containers which will be used for overpacking and disposing of high level radioactive waste. By agreement of the Partners*it will be retricted to the examination of containers for vitrified waste rather than containers for the direct disposal of spent fuel. The project is not concerned with the production of a specific design for licensing purposes; it is only intended to investigate the characteristics of representative designs.

The objectives of the COMPAS project are to look at the mechanical performance of these containers and develop an understanding of how they will behave when subject to the most extreme conditions which can be foreseen in realistic disposal scenarios.

In order to predict the ultimate mechanical performance of the disposal containers it will be necessary to use computer aided modelling techniques. The early part of the COMPAS project therefore includes a considerable amount of computational work which is aimed at developing confidence in the use of these techniques.

B. WORK PROGRAMME

The first exercise to be carried out following initiation of the project was a planning study. A detailed project plan was produced and presented to the Partners and, following a meeting in July, it was officially adopted. It comprises the following activities:-

(i) Directory of Computer Codes

(ii) Containment Concepts
(iii) First Benchmark Exercise
(iv) Second Benchmark Exercise
(v) Prediction of Ultimate Performance

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

The following subsections set out the progress to date against the headings identified in the project plan. The project is on schedule and is within the original budget tendered for the work which has been completed. However, following discussions with the CEC in December, proposals were made to extend the programme of work and this has been approved by the CEC.

* Partners are: SCK/CEN (B), STEAG Kernenergie GmbH (D) Equipos Nucleares (E), CEA (F), Paul Scherrer Institute (CH), ENRESA (E), NAGRA (CH).

(i) Directory of Computer Codes

The purpose of this study is to create a directory in which all those codes seen by the Partners as being useful within the COMPAS project are identified, described, and commented upon. The exercise has involved discussions with the project partners and the circulation of a standard questionnaire. The codes which have been included in the survey are: PAFEC, BOSOR 5, MARC, ANSYS, ADINA, ABAQUS, CASTEM, NIKE, DYNA, HONDO, COSMOS and CASTOR. All but three of these codes (BOSOR 5, MARC and ABAQUAS are in current use by the partners.

The necessary information has now been received from the partners and the directory is in the course of being written up.

(ii) Containment Concepts

The purpose of this study is to confirm the state of development of repository plans for the various project partners. It has involved a series of meetings at which the partners have described their intended scenarios and this has been complemented by a literature survey. The work is now near completion and is being written up. Little new information has been unearthered compared to that which was already available at the start of the project.

(iii) First Benchmark Exercise

The purpose of this study is to set up a series of example problems against which the partners could test their favoured computer codes. The problems posed have included non linearities such as elastic/plastic material response and creep behaviour.

The problems were set up in two "families". One family was oriented towards thick walled container concepts and the other was oriented towards thin walled concepts. In all some 18 problems were specified.

All of the partners took part in the exercise although not all of them attempted 18 problems. Results were received just after Christmas 1987 and a presentation summarising the findings was made to the partners in January 1988. The work is now in the course of being written up.

(iv) Second Benchmark Exercise

The purpose of the first benchmark exercise was to gain experience in the use of advanced computer techniques. The purpose of the second exercise is to acquire some experimental data against which those computer techniques can be validated. An experimental programme is due to be carried out in the latter part of 1988 and the early part of 1989. Some preliminary planning has been carried out and, in particular, a number of potential test sites have been contacted with a view to ascertaining their ability to carry out the work. Beyond this, however, most of the work related to this task has yet been done.

(v) Prediction of Ultimate Performance

This study is intended to predict the ultimate performance of the containers under extreme disposal conditions. By its nature, it can only be attempted once the majority of the work in the second benchmark exercise has been completed. However, some preliminary hand calculations have been done in order to give a general appreciation of the problem and this has formed part of the preliminary planning studies for the second benchmark exercise mentioned above.

(vi) Extension to the Original Programme

At the invitation of the CEC, proposals were made to extend the original programme of work. The proposal involved an increase in the number of experiments associated with the second benchmark exercise. Originally it had been intended to make a small number of reduced scale replica models of thin and thick walled containers. It was expected that two, or maybe four, models would be made and tested to destruction. (The tests would involve pressurisation from the outside and heating of the container in order to simulate geological pressure and steady state temperature under disposal conditions). This programme represented a small number of difficult and specialised tests.

In the extension to the program, it was decided that a larger number of relatively simple tests should be included in the programme prior to the final testing of replica scale models. The proposals in this extension have been accepted by CEC and the project plan is currently being modified in recognition of this. Discussions have been held with the partners and their views on the specific nature of the test work are being sought.

4.2.B.2) Backfilling ans sealing of radioactive waste repositories

In situ reduced scale backfill and heater experiment

Contractor : SCK/CEN, Mol (B)
Contract n° : FI1W/0055/B
Duration of contract : October 1986 to December 1989
Period covered : January 1987 - December 1987
Project leader : A.A. Bonne

A. OBJECTIVE AND SCOPE

The interactions between a heating high-level waste canister, backfill, lining and host rock are to be investigated in order to predict the behaviour of these components, in a final repository. In this context an integral reduced scale in situ experiment (with a simulated heat source) will be performed in clay at great depth. The characteristics of the components, emplacement techniques and instrumentation of backfill and/or buffer material(s) for such test will be defined and studied in collaboration with CEA-DRDD and finally tested in situ in the underground HADES-laboratory (see contract FI1W/0061).

B. WORK PROGRAMME

1. Preliminary investigations about materials and instrumentation
2. Integral reduced scale in situ experiment (Bacchus)
3. Validation of heat transfer and thermo-mechanical computer models

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

For the reduced scale in-situ backfill/heater experiment the design and selection of materials are completed. Fabrication and purchase of instrumentation for this experiment was started.

Progress and results

1. Preliminary investigations about materials and instrumentation

SCK/CEN and CEA-DRDD agreed upon the choice of two natural materials to be tested in the joint BACCHUS experiment. A first mixture is based on a Ca-smectite (50%) and quartz (45%) (quartz will reduce the swelling pressure of the smectite to a value of around 5 MPa) and with graphite added in order to obtain a thermal conductivity in the mixture about equal to that of the Boom clay (1.69 W/m.°C). The second material is grounded Boom clay.

The instrumentation for the monitoring of the experiment in the surrounding clay mass is foreseen to include: two composite Glötzl cell cylinders with pre-orientated pressure cell embedded in a cement/bentonite mixture (modulus 500 MPa, incorporating along different orientations 2 disk pressure cells, 3 rectangular cells, 1 piezometer) and an array of individual piezometers (hydraulic cells and closed screens), Pt-100-probes and moisture sensors. Some research is still required for the final choice of the moisture sensors, the selection of the other sensors being set already. The measuring devices in the backfill and the heating device is taken care of by CEA-DRDD.

For detailed characteristics and test results on the materials and sensors in the experiment core see contract FI1W/0061-F.

2. Integral reduced scale in situ experiment (BACCHUS-experiment)

The design of the experiment, as it stands end 1987, is given in figure 1. It is planned to install this experiment mid-1988 in ring 12 of the Hades-URL. Complementary holes have already been bored for emplacement of the sensors array.

3. Validation of heat transfer and thermo-mechanical computer codes

The actual validation is of course only possible once the experiment is run. For the time being modelling efforts give support for the design and dimensioning of the experiment. With the MPGST-heat transfer code it has been calculated that the temperature increment to be expected at the interface between the heater (at constant power of 300W) and the backfill cylinder is 70 °C.

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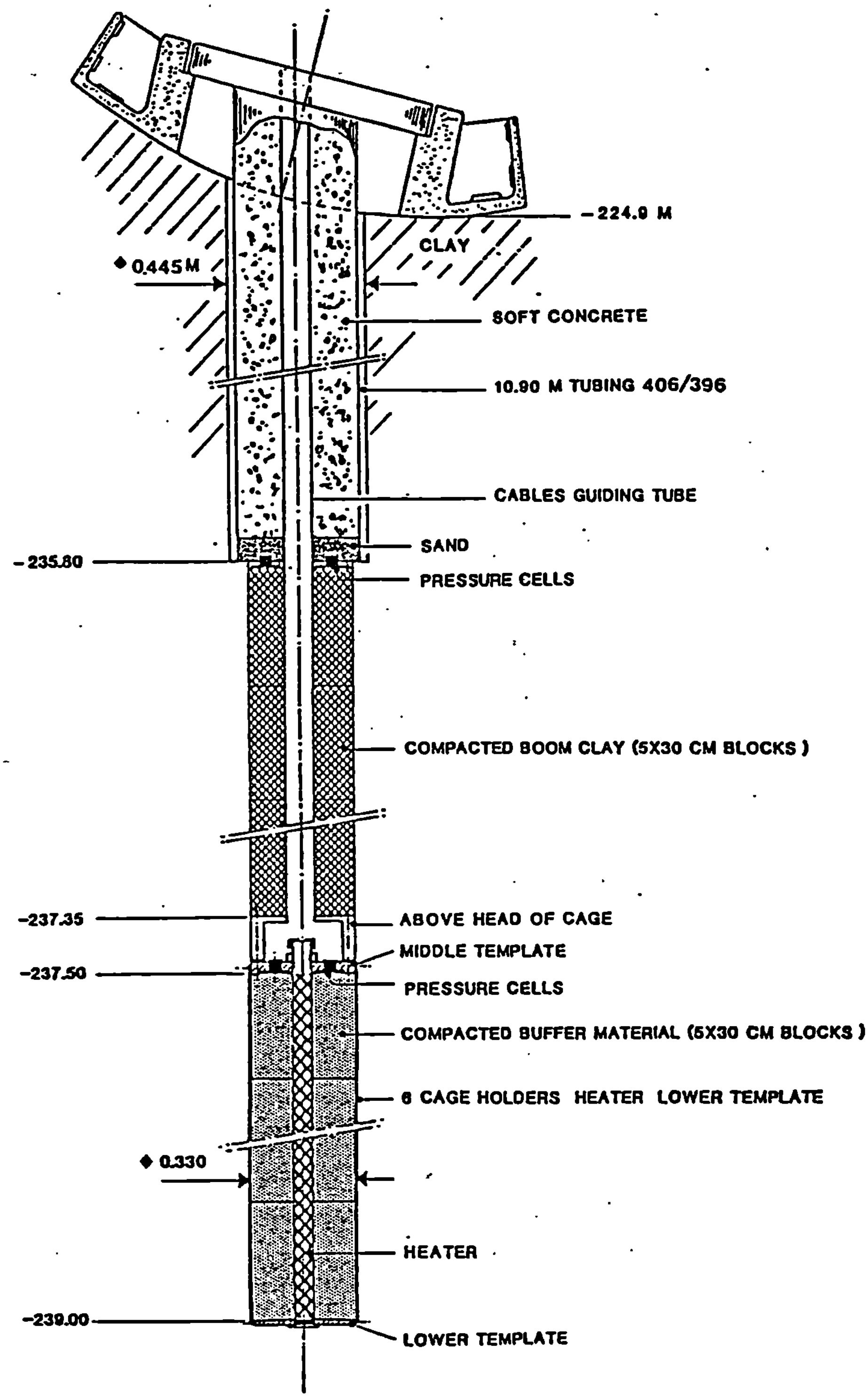


SCK/CEN

Fig 1. Concept of the BACCHUS-experiment

FEASIBILITY STUDY FOR HIGH LEVEL RADIOACTIVE WASTE DISPOSAL IN DEEP BOREHOLES DRILLED FROM THE SURFACE

Conctractor : ENEA,CRE CASACCIA , ROME (ITALY)
CONTRACT No. : FI1W/0056-I
Duration of contract : Jannuary 1987 - December 1988
Period covered : Jannuary 1987 - December 1987
Project leader : E.Tassoni

A. OBJECTIVES AND SCOPE

A preliminary feasibility study has been carried out in the frame of a previous contract (215-80-7 WASI) on the disposal of high level and cladding hull waste in the Plio-pleistocenic blue clay of Italy. Two preliminary repository models have been assessed :

- mined repository
- deep boreholes drilled from the surface

Of the two models, assessed for the same reference power programme (10 GWe) , the deep borehole facility seem preferable if compared to the mined repository from severals points of view but expecially as regards total cost and flexibility. The deep borehole facility is also modular, it does'nt involve large initial investment andmoreover it does'nt heavily interferes with local land use; even if inacceptable geological conditions are encountered in one borehole, operations can be moved to another part of the site with little cost penalty. The main goals of this project are the following :

- elaboration of a preliminary demonstration test of high level radioactive waste disposal in deep boreholes drilled from the surface; this study will be the first step towards the final test of full scale disposal of simulated radioactive waste containers.
- determination of the in laboratory and in situ behaviour of plugging and backfilling materials for deep borehole disposal.

B. WORK PROGRAMME

1. Feasibility demonstration test of deep borehole plugging.

1.1. Laboratory permeability tests, carried out both in small triaxial cells and in big oedometric cells, on samples formed by natural clay as well as on samples formed by clay sealed with different materials (cement, bentonite, etc).

1.2. On site plugging test of a deep borehole (100÷150 m.), sealed with the material selected under item 1.1.

2. Project of a demonstration test for high level waste disposal in deep boreholes drilled from the surface.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Several tests have been carried out in a special device designed to simulate on site conditions. In these tests, the variations of permeability caused by central plugs of sealing materials within a sample of undisturbed clay were studied. Samples of undisturbed Plio-pleistocenic clay, coming from Central Italy, has been used as host material. The sealing materials have been obtained by mixtures with varying quantities of remoulded clay, bentonite and water or by an expansive cement mortar. After testing, some samples were also examined with an electron microscope to study the nature of the clay-sealing material interface. A detailed project of feasibility test of geological disposal in a deep borehole drilled in a clay formation has been developed. Particular attention has been devoted to preliminary investigations like stratigrafic borehole, laboratory analyses on samples coming from borehole and the on site plugging test.

PROGRESS AND RESULTS

1.1. Permeability tests on different homogeneous samples have been carried out in a standard oedometric cell, which can contain samples 2 cm high and 5 cm in diameter. The composition of the samples and results of the tests are shown in table I. Special test cells have been used to consolidate large clay samples (Φ=10÷24 cm) under high vertical loads (10 MPa) and laterally constrained conditions. A feature of these devices allows a central hole to be drilled in the sample and subsequently filled with a plug material , the vertical stress being maintained on the sample; the plug can be indipendently subjected to an adjustable vertical load to obtain the required stress. Permeability tests have been performed on both intact samples before coring and on samples after the emplacement of plugging material. The plugging materials used in the permeability tests are the following :

- Cement mortar with expansive additive
- Bentonite

The plugs composition and the tests results are shown in table II. The results obtained from the permeability tests can be summarized as follows :

- The sealing mixtures based on clay and bentonite have permeability ceefficients like that one of undisturbed clay.
- The permeability coefficient decrease with increasing bentonite content of the mixture.
- The clay samples sealed by means of a cement mortar with expansive additive has permeability coefficient like that one of undisturbed clay.
- The tests carried out with a joint piston actlng on both clay and sealing material show an increase of permeability coefficient; this is due to the small consolidation pressure on the sealing material.

1.2. The instrumentation for on site testing of plugged boreholes, developed in the frame of a previous contract (199-82-7 WASI), is being modified. The permeameter will be formed by a water injection unit, by a pressure transducer and by an acoustic data transmission system, wich must be located nearby in a second borehole. The in situ plugging test will be carried out in a Plio-pleistocenic clay formation, overlain by a permeable volcanic rock. Geophysical prospecting is being performed on the choosen site to know the exact geological stratigraphy and the thickness of the clay formation.

2. The disposal of HLW in deep boreholes has some advantages .However full scale demonstration is needed for the feasibility of this technique as well as for the complete cycle of hole preparation, waste emplacement and borehole sealing. A detailed project has been developed to define the steps of the emplacement demostration test (fig. 1). The most qualifying steps of the project are the following :

- Borehole plugging test to measure the hydraulic performance of the sealing material, of the type determined under item 1.1., to isolate the waste in the clay formation.
- demonstration of the complete cycle of hole preparation,of simulated waste emplacement and borehole plugging at full scale. Nine or twelve waste packages simulating those produced by nuclear industry, will be emplaced in a borehole at a depth of between 200 and 300 m., the borehole will be sealed and the disposal zone will be cored, after a suitable time, to obtain data on the in situ behaviour of the different components.

TABLE I : PERMEABILITY TESTS ON HOMOGENEOUS UNDISTURBED AND REMOULDED SAMPLES

SAMPLE	COMPOSITION	TEST	CONSOLIDATION PRESSURE (MPa)	PERMEABILITY COEFFICIENT (cm/sec $*10^{-10}$)
E1	UNDISTURBED CLAY	E1/1	2.4	3.1
		E1/2	6.4	2.7
		E1/3	9.6	1.9
E2	100% clay W = 40%	E2/1	0.05	80.0
		E2/2	0.2	41.0
		E2/3	0.8	10.0
		E2/4	2.4	7.6
		E2/5	4.8	3.1
E3	90% clay 10% bentonite W = 40%	E3/1	0.05	33.0
		E3/2	0.2	17.0
		E3/3	0.8	6.3
		E3/4	2.4	3.2
E4	80% clay 20% bentonite W = 40%	E4/1	0.05	19.0
		E4/2	0.2	8.2
		E4/3	0.8	3.7
		E4/4	3.2	1.7
E5	70% clay 30% bentonite W = 40%	E5/1	0.05	12.0
		E5/2	0.2	6.6
		E5/3	0.8	3.1
		E5/4	3.2	1.2
E6	100% bentonite W = 120%	E6/1	0.05	4.4
		E6/2	0.2	2.1
		E6/3	0.8	1.3

TABLE II : PERMEABILITY TESTS ON HOMOGENEOUS UNDISTURBED AND SEALED SAMPLES

SAMPLE	TEST	COMPOSITION OF SEALING MATERIALS	CELL DIAMETER CM	PISTON POSITION	Va MPa	Vs MPa	Kl cm/sec $*10^{-10}$	Ks cm/sec $*10^{-10}$
2	2/1	–	24	Joint	5	--	2.8	
	2/2	EMACO		Indipend.	5	5		2.8
3	3/1	–	24	Joint	5	--	2.8	
	3/2	A = 100% W = 30%		Indipend.	5	5		2.8
4	4/1	–	24	Joint	1.8	--	2.4	
	4/2	–		Joint	5	--	2.0	
	4/3	A = 60% B = 40% W = 30%		Indipend.	6	5		2.1
5	5/1	--	24	Joint	5	--	1.9	
	5/2	A = 60% B = 40% W = 30%		Indipend.	5	5		1.9
	5/3	A = 60% B = 40% W = 30%		Joint	5	N.D.		2.3
6	6/1	–	10	Joint	5	–	4.9	
	6/2	B = 100% W = 100%		Joint	5	N.D.		5.8
7	7/1	–	10	Joint	2.5	–	2.3	
	7/2	B = 100% W = 280%		Joint	2.5	N.D.		4.3
9	9/1	–	10	Joint	3	–	4.8	
	9/2	A = 70% B = 30% W = 40%		Joint	3	N.D.		5.9
10	10/1		10	Joint	3	–	4.1	
	10/2	A = 100% W = 40%		Joint	3	N.D.		9.6
11	11/1	–	10	Joint	3	–	5.2	
	11/2	A = 50% B = 50% W = 40%		Joint	3	N.D.		5.6
12	12/1	–	10	Joint	3	--	4.6	
	12/2	A = 80% B = 20% W = 40%		Joint	3	N.D.		6.1
	12/3	A = 80% B = 20% W = 40%		Indipend.	3	3		5.7
	12/4	A = 80% B = 20% W = 40%		Indipend.	3	6		4.4

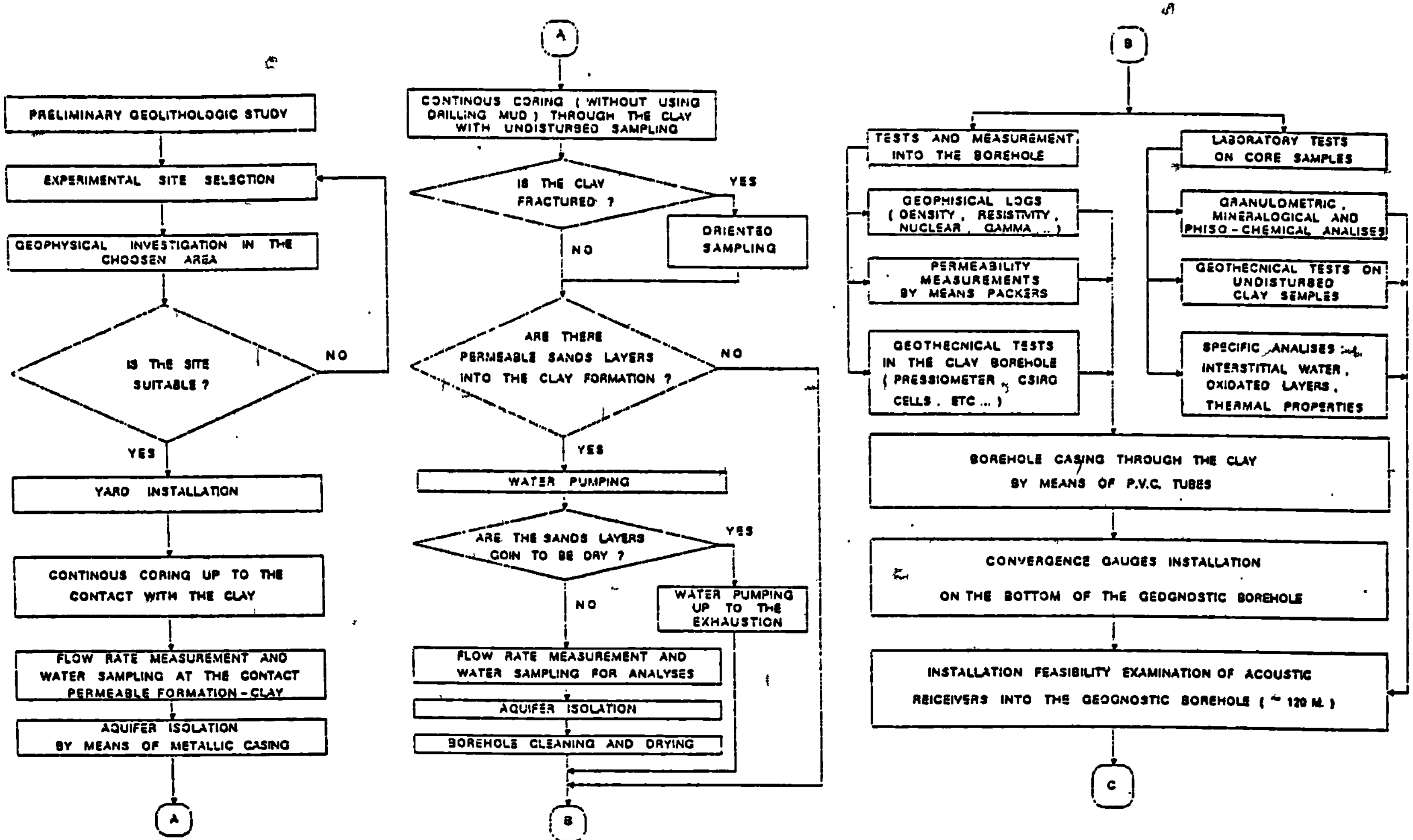
A = Remoulded clay content — W = Water content (by weight)

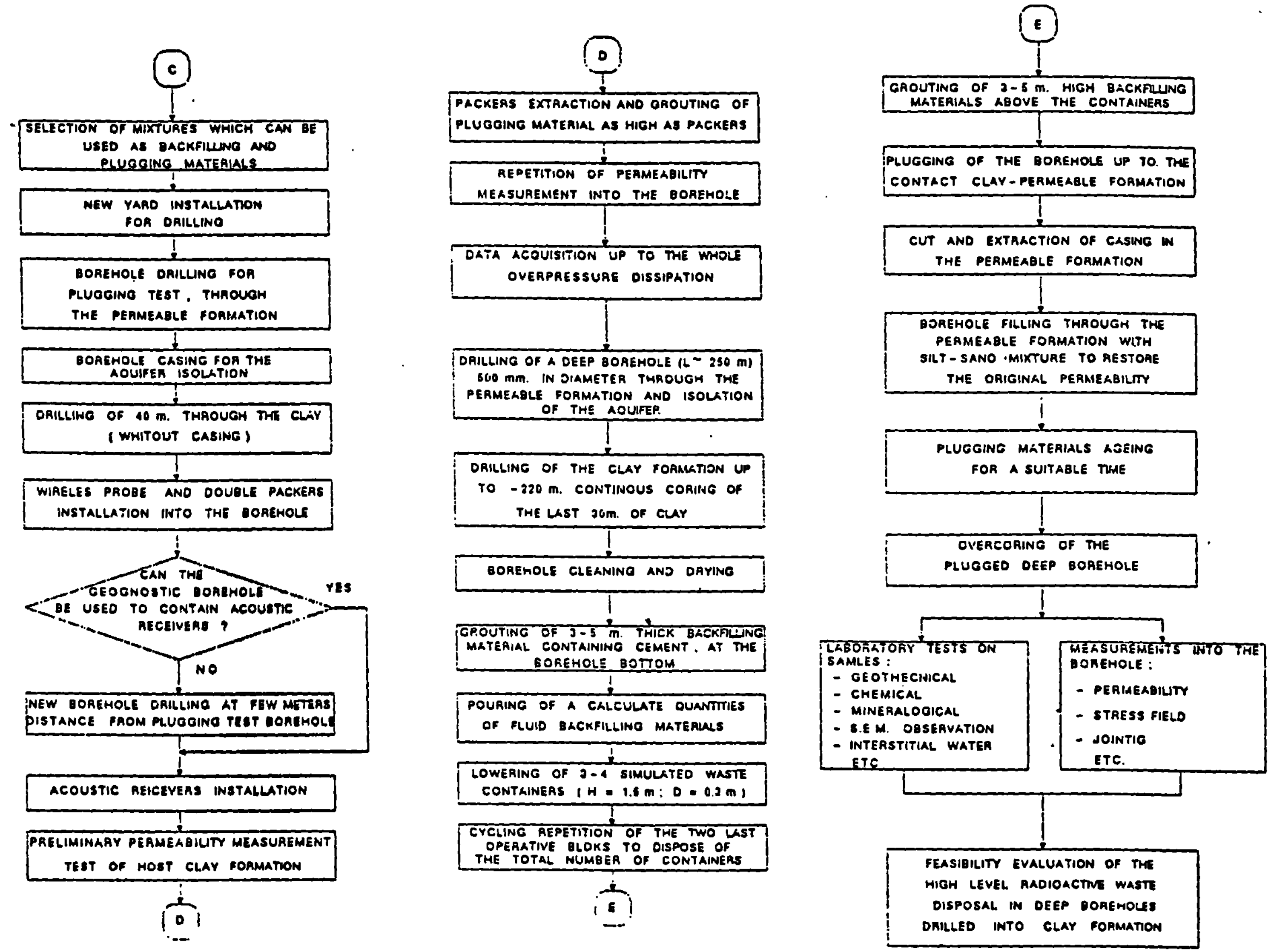
B = Bentonite content — Vs = Vertical load on the sealing material

Ks = Permeability coefficent of sealed sample — Va = Vertical load on the sample

Kl = Permeability coefficent of undisturbed sample — N.D. = Not determinated

Fig 1. - BLOCK DIAGRAM OF THE STAGES RELATED TO THE FEASIBILITY TEST OF SIMULATED HIGH LEVEL RADIOACTIVE WASTE DISPOSAL IN A DEEP BOREHOLE DRILLED FROM THE SURFACE.




C
SELECTION OF MIXTURES WHICH CAN BE USED AS BACKFILLING AND PLUGGING MATERIALS
NEW YARD INSTALLATION FOR DRILLING
BOREHOLE DRILLING FOR PLUGGING TEST, THROUGH THE PERMEABLE FORMATION
BOREHOLE CASING FOR THE AQUIFER ISOLATION
DRILLING OF 40 m. THROUGH THE CLAY (WHITOUT CASING)
WIRELES PROBE AND DOUBLE PACKERS INSTALLATION INTO THE BOREHOLE
CAN THE GEOGNOSTIC BOREHOLE BE USED TO CONTAIN ACOUSTIC RECEIVERS ?
YES
NO
NEW BOREHOLE DRILLING AT FEW METERS DISTANCE FROM PLUGGING TEST BOREHOLE
ACOUSTIC REICEVERS INSTALLATION
PRELIMINARY PERMEABILITY MEASUREMENT TEST OF HOST CLAY FORMATION
D
D
PACKERS EXTRACTION AND GROUTING OF PLUGGING MATERIAL AS HIGH AS PACKERS
REPETITION OF PERMEABILITY MEASUREMENT INTO THE BOREHOLE
DATA ACQUISITION UP TO THE WHOLE OVERPRESSURE DISSIPATION
DRILLING OF A DEEP BOREHOLE (L ~ 250 m) 600 mm. IN DIAMETER THROUGH THE PERMEABLE FORMATION AND ISOLATION OF THE AQUIFER
DRILLING OF THE CLAY FORMATION UP TO -220 m. CONTINOUS CORING OF THE LAST 30m. OF CLAY
BOREHOLE CLEANING AND DRYING
GROUTING OF 3-5 m. THICK BACKFILLING MATERIAL CONTAINING CEMENT, AT THE BOREHOLE BOTTOM
POURING OF A CALCULATE QUANTITIES OF FLUID BACKFILLING MATERIALS
LOWERING OF 3-4 SIMULATED WASTE CONTAINERS (H = 1.6 m ; D = 0.3 m)
CYCLING REPETITION OF THE TWO LAST OPERATIVE BLOKS TO DISPOSE OF THE TOTAL NUMBER OF CONTAINERS
E
E
GROUTING OF 3-5 m. HIGH BACKFILLING MATERIALS ABOVE THE CONTAINERS
PLUGGING OF THE BOREHOLE UP TO THE CONTACT CLAY-PERMEABLE FORMATION
CUT AND EXTRACTION OF CASING IN THE PERMEABLE FORMATION
BOREHOLE FILLING THROUGH THE PERMEABLE FORMATION WITH SILT-SAND MIXTURE TO RESTORE THE ORIGINAL PERMEABILITY
PLUGGING MATERIALS AGEING FOR A SUITABLE TIME
OVERCORING OF THE PLUGGED DEEP BOREHOLE
LABORATORY TESTS ON SAMLES :
- GEOTHECNICAL
- CHEMICAL
- MINERALOGICAL
- S.E.M. OBSERVATION
- INTERSTITIAL WATER
ETC
MEASUREMENTS INTO THE BOREHOLE :
- PERMEABILITY
- STRESS FIELD
- JOINTIG
ETC.
FEASIBILITY EVALUATION OF THE HIGH LEVEL RADIOACTIVE WASTE DISPOSAL IN DEEP BOREHOLES DRILLED INTO CLAY FORMATION

TRIALS AND CONTROL OF PLACING FILLING AND SEALING MATERIALS FOR DEPOSITS IN SCALE MODELS

Contractor : SOLETANCHE ENTREPRISE S.A.
Contract n° : FI 1W/0057
Duration of contract : February 1987 to March 1990
Period covered : February 1987 to December 1987
Project leader : D. GOUVENOT

A. OBJECTIVES AND SCOPE

The containers of radioactive wastes of high or low level activity will be disposed of in vertical shafts or horizontal galleries. In order to avoid any groundwater circulation in contact with the containers the void between the rock and the containers will be filled with sealing materials.

The materials, subject of this study, are cement based mortar formulations wich are the results of previous studies and experiences of SOLETANCHE and C.E.A. These materials made of water, cement, clay and additives have to exhibit various mechanical characteristics as stability, imperviousness, durability, possible retention towards radioactive cations and above all easy placing in order to assure a good quality filling and sealing.

The first, objective is to evaluate the hereabove characteristics of various mortar formulations, through lab tests, in order to select four formulations best suited to the filling and sealing.

The second objective is to improve and finalize the placing method of materials in scale models. To that aim each of four scale models will be, one after each other, filled, cured at various temperatures, tested and dismantled for examination in order to define the best material placing technique.

B. WORK PROGRAMME

1. Laboratory studies

1.1 Theoretical studies. From the previous studies and experiences, choice of filling material formulations.

1.2 Preselection tests (based on the placing criteria). The rheological properties of the hereabove formulations are measured in fluid state (viscosity, shear strength, bleeding, workability limit).

1.3 Final selection of formulations. Measurements of characteristics of hardened materials (strength, shrinkage, water content, permeability, thermal conductivity, microstructure, retention and diffusion of caesium ions) cured at various temperatures (20, 50 and 80°C).

2 Experimental studies

2.1 Vertical scale models. Filling and quality controls of two successive vertical scale models.
- Study and improvements of materials placing and instrumentation.
- Controls of fresh and hardened materials in lab and in situ.
- Controls and tests of filling and sealing properties of materials in the scale models.

2.2 Horizontal scale models. Filling and quality controls of two successive horizontal scale models.
- Same tests and controls as vertical models.
- Finalization of materials placing technique. Particular specifications for horizontal scale models.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The initial formulations tested are made of cement (CPA,CLK,CLC), silica fume, clays, silica sand and various additives. The rheological characteristics of fresh state formulations (viscosity, shear strengh, bleeding, workability time) were measured on materials cured at 20, 50 and 80°C. The maximum temperature initially stated at 120°C was reduced to 80°C due to the modification of the forecast initial temperature of the waste containers. In order to reduce radiolysis, water content had to be as low as possible. Additions of water reducing agents allowed high dry matter to water ratios to be reached. At last, retarders were added to comply with the placing criteria i.e. long workability time along with low viscosity.

On the hardened materials the following characteristics were measured : unconfined compressive strengh and temperature influence, free water content, temperature rise during setting, shrinkage, permeability and thermal conductivity. Tests are in progress at C.E.A. facilities to evaluate the caesium retention behaviour by various materials, as well, the microstructure is studied by Armines (other cocontrator) by means of SEM and porosimetry tests.

PROGRESS AND RESULTS

1. Laboratory studies

1.1 Theoretical studies. In order to minimize the water content of the filling and sealing materials the formulations to be tested had to have the highest possible dry matter content. The rheological criteria (viscosity and workability time) implied to use various additives (water reducing agents and set retarders). The choice of the preliminary formulations was made from Soletanche Petrisol patented materials and from C.E.A mortar formulations.

1.1.1 Constitutive materials. The formulations tested are made of the following basic materials :

- Three types of cement : CPA 55 (Portland)
  CLK 45 (Blast furnace)
  CLC 45 (Portland, BLF and fly ash blend)
- The cement/water ratios (C/W) were as follows :
  1.5 to 2.0 for Petrisol
  2.78 for CEA mortars (only with CLC 45)
- Sand. Fontainebleau sand (silica sand, 0 to 0,3 mm) was used for the regularity of its composition and grain size distribution. The sand/water ratios (S/W) were as follows :
  2.8 to 3.0 for Petrisol
  0.7 for CEA mortars
- Additional materials. Different types of materials were added (one or several) to the Petrisol in order to improve various final characteristics of the materials (strength, permeability, microstructure, durability, retention behaviour) according to the following ratios (AM/W) :
  Clays : 0.1 to 0.2
  Silica fume : 0.05 to 0.08
  Zeolithes : 0.1 to 0.2

1.1.2 Dry matter and water contents. The dry matter and water contents are in the following ranges :

Petrisol - DM : 1670 to 1760 kg/m3
- WC : 340 to 370 kg/m3

CEA mortars - DM : 1565 kg/m3
- WC : 450 kg/m3

1.2 Preselection tests

From the hereabove ranges of ratios the water reducing and fluidifying agents contents were adjusted in order to get the correct rheological characteristics. All together more than 50 formulations were tested to get the following characteristics (workability criteria) with the various constitutive materials :

- Viscosity : 20 to 60 s (LCPC cone, 10 mm diameter outlet tube)
- Shear strength : less than 1 g/cm2 (100Pa)
- Bleeding : nil
- Workability limit : 4 hours at 30°C and 1 hour at 50°C.

The 100Pa maximum shear strength was stated from the civil engineering works. Further tests, in progress, may show that this limit is too low so that the sand content could be increased.

1.3 Final selection

1.3.1 Unconfined compressive strength. The U.S.C. measured after 90 days of cure are ranging between 40 to 60 MPa.

1.3.2 Permeability. The permeability was measured by means of a triaxiel cell according to lateral pressure and percolation pressures respectively of 0.95 and 0.85 MPa (hydraulic gradients from 1000 to 1500).

The permeability was found between 10-11 to 10-13 m/s.

1.3.3 Durability. The test consists of measuring the concentration of chemical products possibly dissolved from the tested material in the water forced through the test sample, by means of a triaxial cell as permeability tests. The flow of water recovered was so small, even with gradient of 3000, that the water analysis was impossible.

1.3.4 Free water content. Percent of water evaporated from the material samples after 24 hours curing in an oven at 105°C.

- Petrisol : 13.5 to 19.2 %
- C.E.A. mortars : 19.5 %

1.3.5 Materials behaviour at 80°C. When the filling material comes in contact with the containers its temperature may rise to 80°C. Materials samples cured 90 days in a water bath regulated at 80°C exhibited strength increases ranging from 15 to 30 %.

1.3.6 Freezing and thawing cycles. In the aim of a possible qualification of these sealing materials to surface waste disposal, two formulations were tested for 5 cycles between - 20° and 5°C and then 5 cycles between 5 and 40°C. The UCS drop was less than 10 %, whereas flexural strength was not significantly changed.

1.3.7 Temperature rise during setting. The temperature of material samples (1 kg) placed in adiabatic conditions was measured for two days. The temperature rises and the corresponding power of 1 kg samples are approximately as follows :

- CLK and CLC Petrisol (C/W = 2.0) : 20 to 30°C and P = 1W
- CPA Petrisol (C/W = 2.0) : 40 to 50°C and P = 1.8W
- CLC C.E.A. mortars (C/W = 2.78) : 55 to 60°C and P = 2.2W

1.3.8 Thermal conductivity. These measurements performed in Armines facilities gave the following results :

- Petrisol : 2.3 to 2.4 W/m°C
- C.E.A. mortars : 1.6 W/m°C

1.3.9 Shrinkage. The dimensional variations of samples cured at 20°C in water and in 50 or 80 % moisture air were measured versus time.

- Water : + 300 to + 600 10-6 (swelling)
- 80 % moisture air : - 300 to - 500 10-6 (shrinkage)
- 50 % moisture air : more than - 1000 10-6 (shrinkage)

Shrinkage is also depending secondly of the types of cement and clay. In the disposal shafts and galleries the confining conditions should be close to saturated conditions or, even to water immersion, so that one can expect a swelling.

1.3.10 Caesium retention. In order to select formulations to be tested in the C.E.A. facilities lixiviation tests were carried out on materials presaturated with inactive caesium chlorid. After 28 days the fraction of caesium lixiviated was 3 to 45 % of the initial caesium. These results are closely depending on the natures of cement and clay. The tests are still in progress.

Sealing of fractures and boreholes

Contractor: Commissariat à l'Energie Atomique, Fontenay-aux-Roses, France
Contrat N°: FI1W.0058.F
Duration of Contract: October 1986 - December 1989
Period: October 1986 - December 1987
Project Leader: J.Y. BOISSON, S. DERLICH

A. Objectives and Scope

Radioactive wastes disposal into deep cristalline rocks requires to carry out important underground works or geological investigations by the means of boreholes which might induce direct pathway or short circuits for water, between repository and ground surface. It is essential to use specific technics and methods allowing the sealing of these potential pathways.

Among several other possibilities, clay materials have been considered to fill the boreholes and shafts. One of these clays, montmorillonite, is widely studied because of its qualities : good adsorbsion towards radionuclides , swelling properties in contact with wastes.

The aim of the study, it to determine, in laboratory and in situ, the behaviour of such a clay, used as a plug in a borehole in contact with an hydraulic fracture, and to study the possible erosion of such a plug so as to be able to estimate the longevity of the sealing.

B. Work Programme

2.1. Laboratory studies

2.1.1. An experimental erosion apparatus with bentonite is used, thanks to a scale model simulating a fissure. Appropriate technics are carried out for the determination of the eroded clay mass by a water flow inside the model fissure.

Tests will be performed with two or three types of representative clays, i.e. those which are presentely investigated and could be used as sealing material in a real repository :

- the Na bentonite "Green Bond", from Wyoming (USA) (equivalent to the MX 80).
- one or two bentonites extracted in France.

The waters which will be used, will be of different types, either natural (from cristalline formations), or reconstituted with different percentages of relevant ions.

2.1.2. The behaviour study of this sealing material is completed with direct observations of the clay in the fissure, with granulometric analysis, and mineralogic X rays analysis, and scaning electron microscope.

We intend to ascertain the influence of the nature andvelocity of the water flow. The experimental parameters will be then ions concentrations caracteristics and water flow rates.

2.2. In situ study

A fracture with a significative water flow, in a well known direction, will be selected, in situ, in a mine or quarry. The geometric position of this fracture will be identified thanks to boreholes, used themselves for hydraulic studies and sealed with bentonite at the fracture level.

The resulting water flow will be characterised by the means of tracers, water flow rates measurements at the free surface of the drift or on the face of the quarry.

After the experimentation, for a time depending upon the amount of the recovered clay mass, an over coring operation will be done, perpendicular to the fracture plane, both at the plug level, and around.

Modifications of the clay plug will be analysed in the laboratory, using the same technics as those for the scale model tests.

The clay, used for this test, will be one of those used in the laboratory.

2.3. Numerical model

The evaluation of the transported clay mass will be analysed and quantified both for the laboratory and in situ experimentations.

The results will be compared, and it is intended to establish a correlation between the two configuration.

This must lead us to provide a numerical model concerning the erosion behaviour and the durability of such bentonite plugs in boreholes in contact with water.

C. Progress of Work and Obtained Results

State of advancement

In the preliminary part of this work a general overview is presented concerning the main mechanismswhich govern theoretically the clay behaviour towards water inside a fracture.

The behaviour of a clay wich seals a fracture and which is submitted to the water flow effects is a complex phenomena. First, the clay swells in contact with water : there is constitution of a colloïdal material in front of the clay block. Interparticular bonding strengths depend on particules arrangement and chemical composition of the pore water.

The main objective of this laboratory part of our work is to simulate the behaviour of the clay, sealing a fracture and then, in contact with underground water. The first stage is hydratation of samples with a water content higher than the liquidity limite (W_L).

Given this, the laboratory study is carried out to evaluate the two phenomena : swelling and erosion of the clay.

The clay is a Na bentonite, "Green Bond", for this first part of the laboratory study.

Progress and Results

3.1. Free swelling of the clay in the laboratory

Clay samples are introduced into glass cylindrical container (Ø 56 mm) and covered with water. The swelling of the clay is measured versus time.

The parameters fixed for this study are :

- Thickness of the samples : 1,3 and 6 cm.
- Water content of each samples : 367 %, 399 % and 422 %.
- Two types of water (used either for the clay preparation, and the swelling test) :
  - demineralised water
  - underground water from Volvic (Massif Central, France)

The "Green-Bond" Na bentonite swells rapidely when in contact with the water, although it is at a water content higher than the liquidity limit (cf. fig.n°1).

The initial thickness of the clays seems to be of little importance, during the test period probably due to the high values of the water content.

The kinetics of the swelling is little influenced by the chemistry of the water, particulary with the highest water content used for the clays in these tests. In this last case, the swelling is more important with the demineralised water.

Finally, using the ratio (swelling at a given time/final experimental 1000 h swelling), all the results obtained during these tests seem to fit on a single curve, leading us to think that these results are independant of the fixed parameters within the limits of our experimentation (cf. fig.n°2).

Nevertheless, we might think that, if this swelling phenomenon remains intrinsically the same, its kinetics under the conditions of a natural crack could be different from the laboratory results with the tests in cylinder, due to differences in the geometrical characteristics and differences of surfaces effects.

This remarks have been partially confirmed by other specific tests in laboratory : instead of glass cylinders, swelling tests have been performed using an plexiglass device, simulating the geometry of a crack (300, 30,5 mm). The results with the same initial conditions appear to be different (less swelling for the simulated crack).

3.2. Erosion process in a scale model of a fissure

The aims of these tests in laboratory are to study physical and chemical phenomena governing the behaviour of clay in contact with a water flow, inside a simulated crack.

For this purpose, a scale model of a crack filled with clay has been built, in plexiglass (length : 300 mm, heigth : 50 mm, thickness : 5 mm) allowing to create a controlled water flow at the contact surface with the clay (cf. fig.n°3).

The same "Green Bond" Na bentonite has been used for these experimentations than the one for the swelling tests.

The clay is tested with the same three initial water contents.

Only the demineralised water is used for this first part of the study.

The range of the water flow rates is between 0.6 cm^3/min to 30 cm^3/min (corresponding to water flow velocities between 4.10^{-4} m/s and 2.10^{-2} m/s).

The evolution modes of the erosion process are analysed into two ways :

- inside the scale model, by :
  - . evolution of the profile at the contact between clay and water.
  - . identification (mineralogy and granulometry) of the clay material at this interface.
- outside the scale model by :
  - . eroded clay mass quantification
  - . eroded clay granulometric distribution

It is noticed that, in any cases, the "Green Bond" clay can be more or less eroded with demineralised water. The erosion mechanisms of the clay with a water flow are well identified. They can be interpreted as the succession of the following phenomena : swelling, particules release, and transport.

Once they have been released, the biggestparticules are sedimented, this phenomenon is the most obvious for the lowest water flow rate.

It can be observed that, for a given constant volume of water, the clay erosion is more important for the weakest rate flow (cf. fig.n°4) this phenomenon can be amplified with the highest initial water contents : this can be explained by the fact that the interparticular strengths decrease when the clay water content increases.

The fact that, for a given constant water volume, the clay erosion appears to be relatively more important for the weakest rate flow, has led us to suppose that the chemical phenomena are of major importance.

During the erosion process, clay structure modifications can be observed at the clay/water interface. These modifications occur with low rate of flow. Two zones can be described :

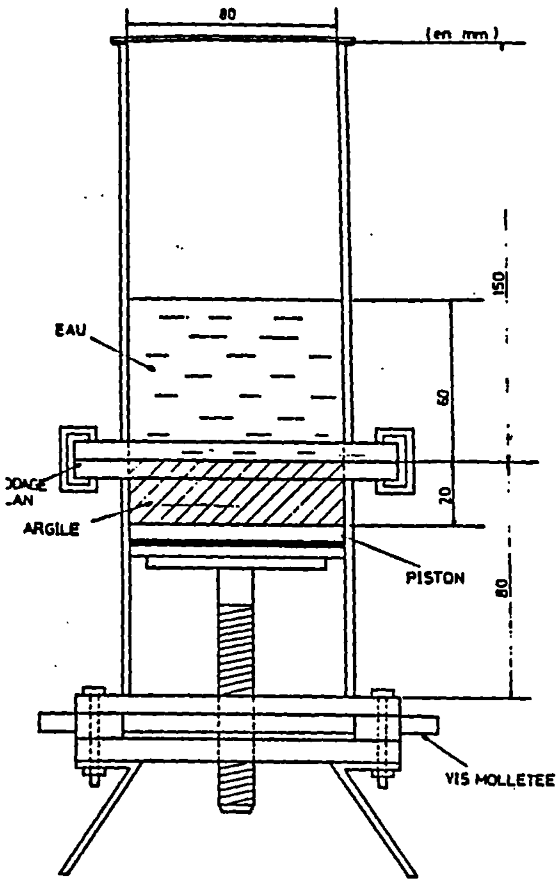
- a "grey zone", which appears to be constitued of fine grain size, dispersed, particules of clay.
- a "black zone", which appears to be constitued of detritic particules (Quartz, Feldspars, with clay) with greater grain size distribution.

Below these zones, the initial aspect of the clay remains. The dispersed state of the clay has made easier the heaviest particules sedimentation from the "grey zone" to the "black zone".

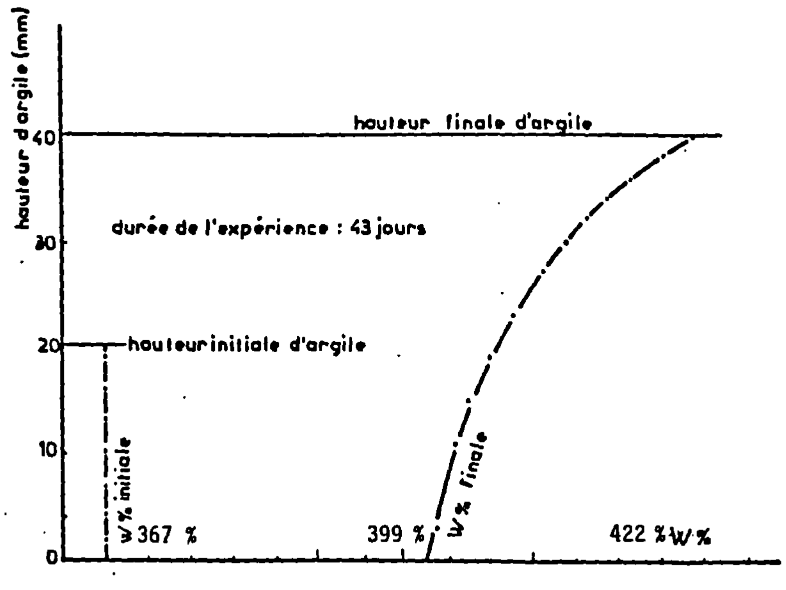
The fact that, for the weakest volumes of water, the carried clay mass is relatively more important for the weak flow rates implies that the chemical phenomena are of a major importance for the first stages of the erosion (cf. fig.n°5).

Actually, if these erosion mecanisms were only governed by the mechanical processes, considering that the pull forces due to the water flow increase with flow speed, the results should have been opposite to those observed.

The clay particules release appears when the interparticular bonding forces decrease. This weakening is related to ions exchanges between clay and water.



Dispositif expérimental pour l'étude de la distribution verticale de la teneur en eau dans l'argile



Evolution du gonflement et du taux d'humidité sur l'épaisseur d'argile pendant 43 jours

Fig. 1 : Essais de gonflement en laboratoire

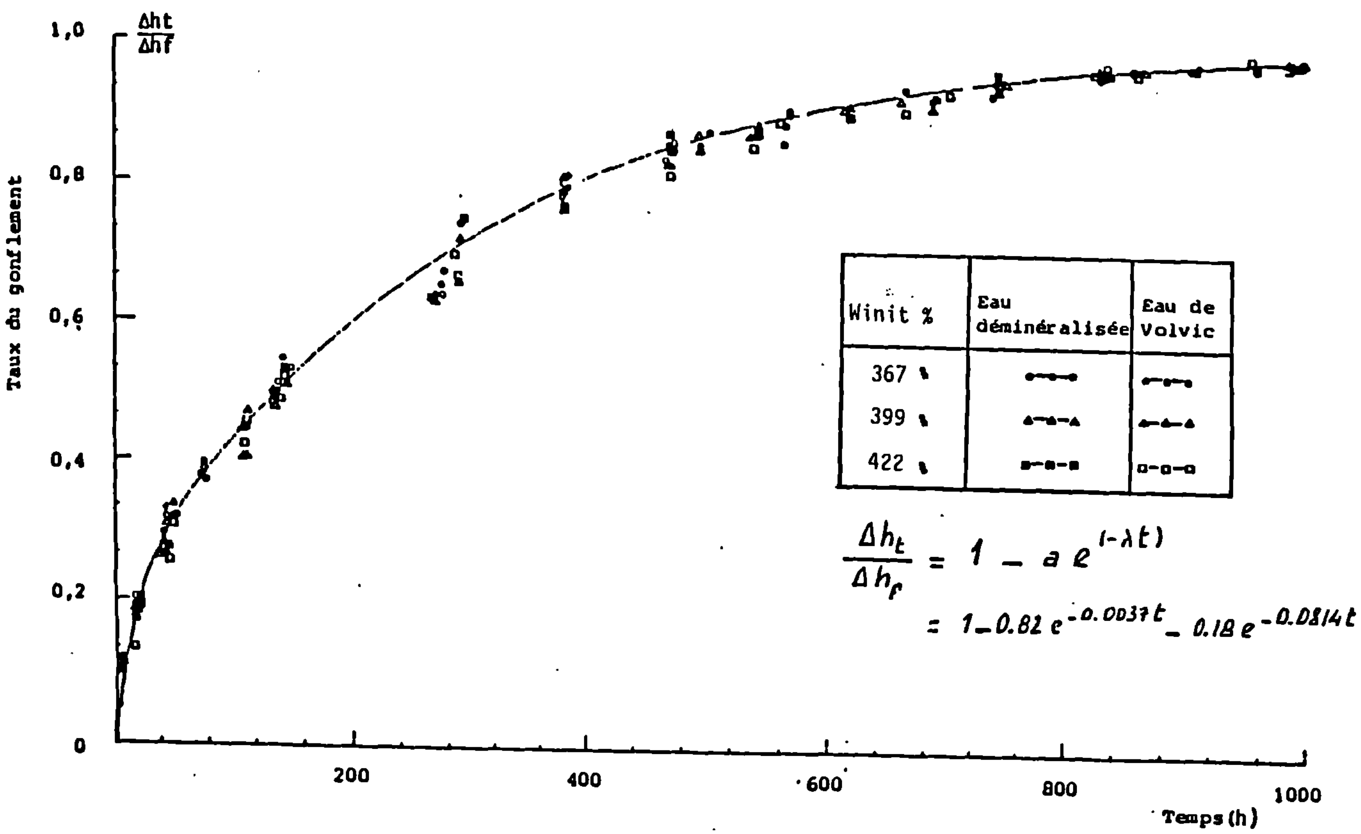


Fig. 2: Taux du gonflement (rapport du gonflement instantané Δht au gonflement à 1000 heures Δhf)

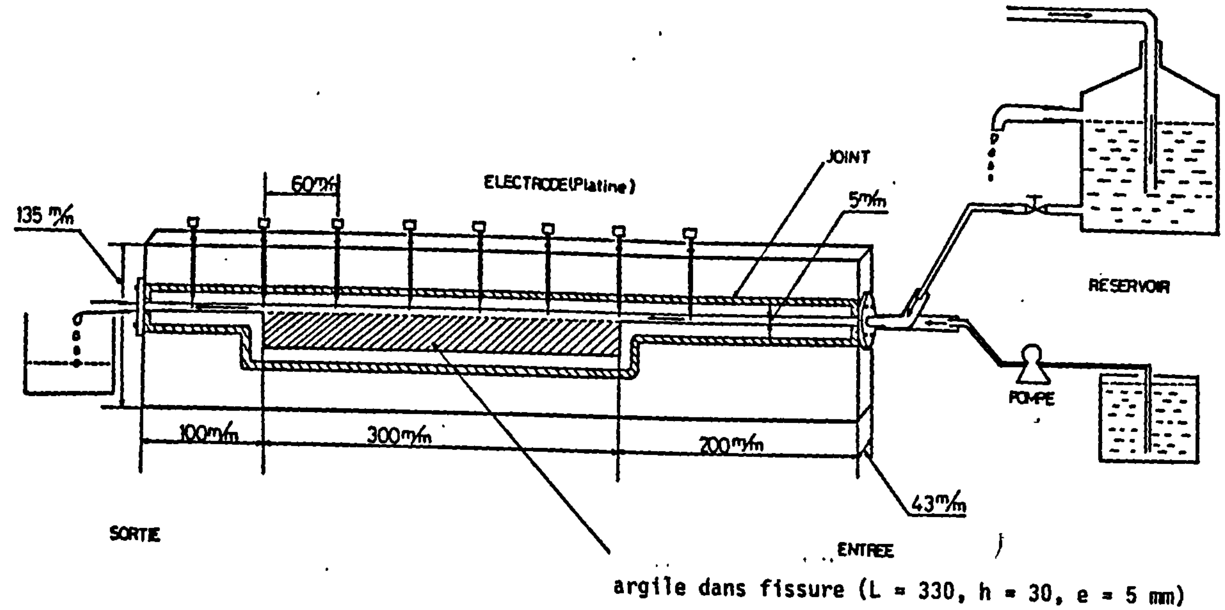


Fig.3 : Maquette de fissure avec argile expérimentale

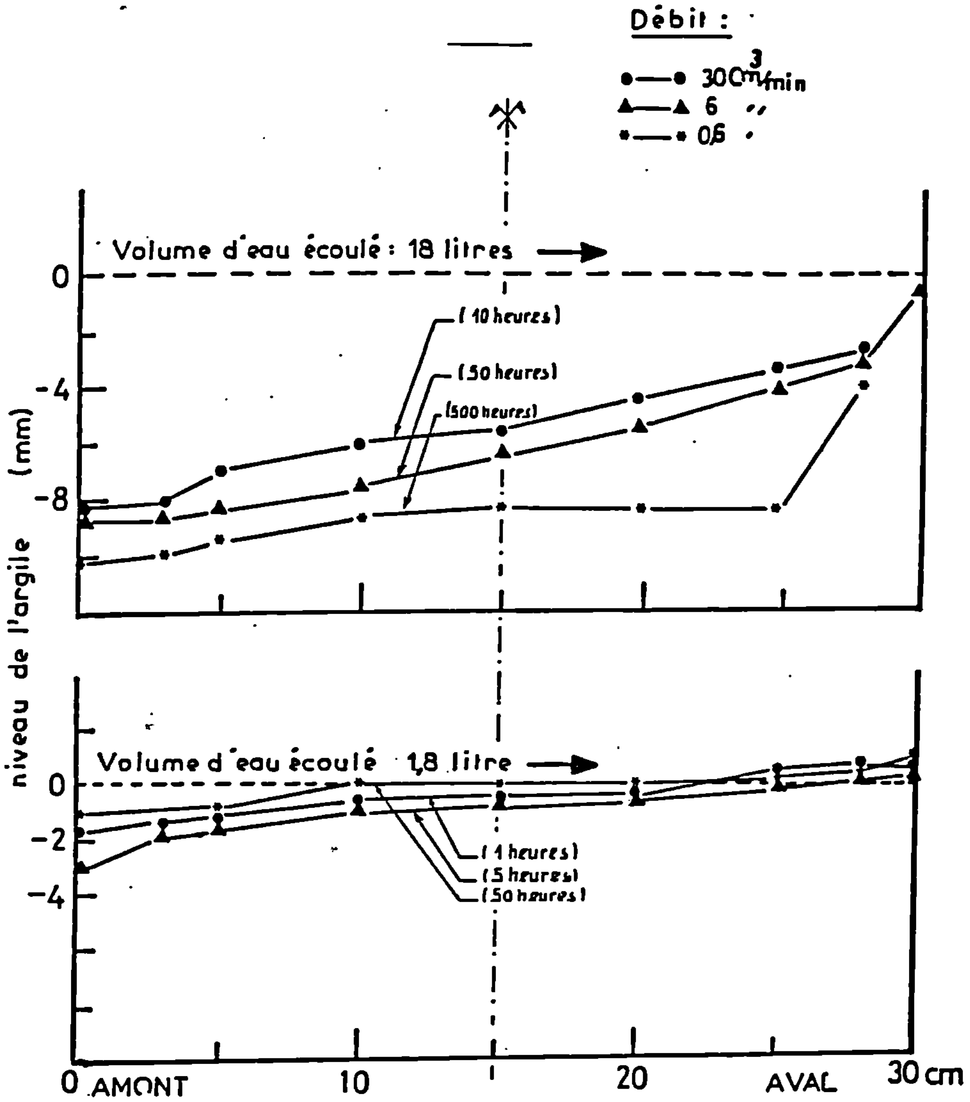


Fig.4 . Evolution du profil de la surface d'argile en fonction de la distance à l'entrée
(Influence du débit pour deux volumes d'eau écoulés -Winit % = 399 %)

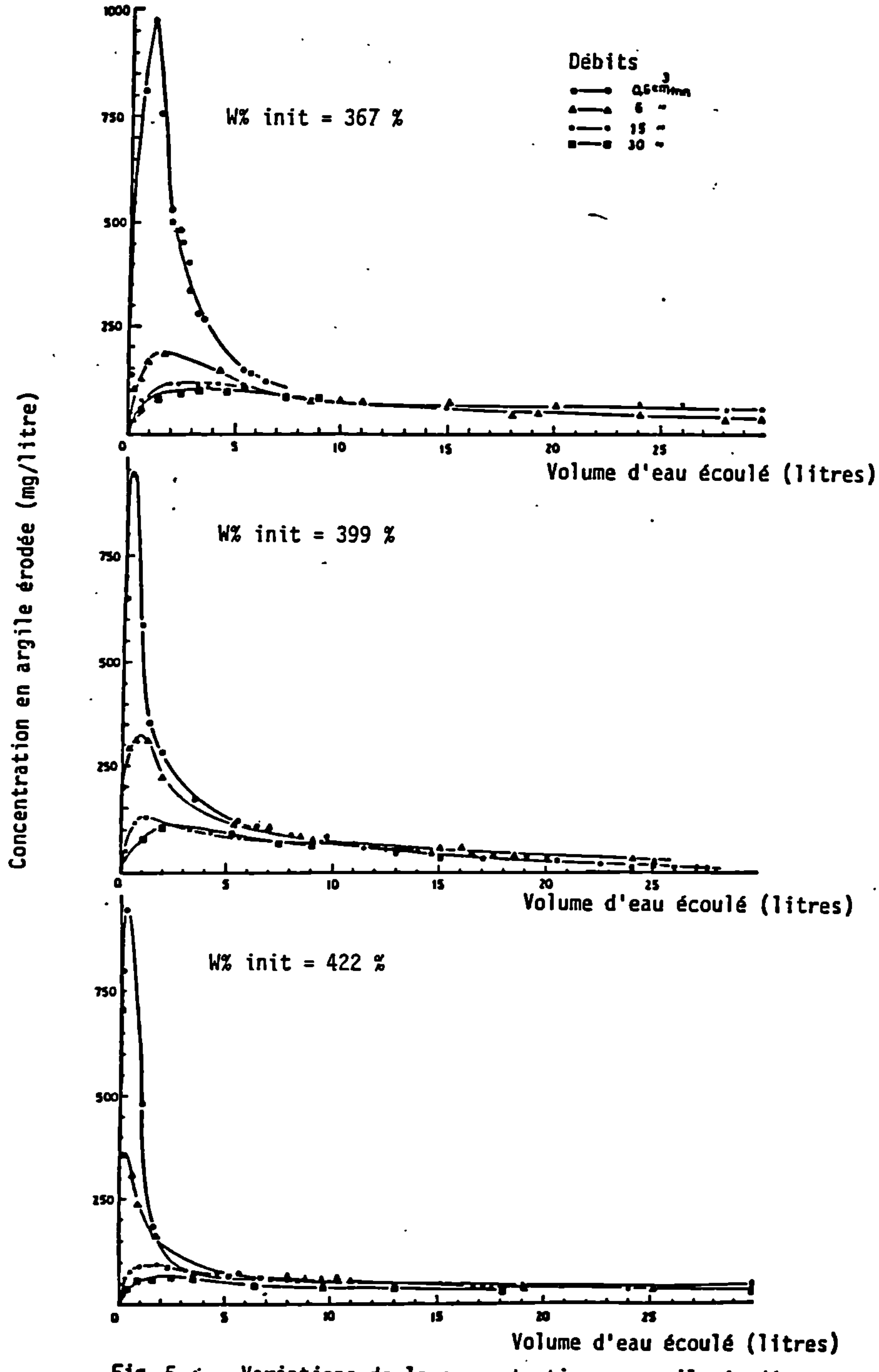


Fig. 5 : Variations de la concentration en argile érodée en aval de la maquette en fonction du volume d'eau écoulé (Influence du débit, pour trois taux d'humidité initiaux)

RESEARCH ON BACKFILLING AND SEALING OF ROOMS AND GALLERIES IN A REPOSITORY IN SALT

Contractor : GSF/Inst. f. Tieflagerung (IfT), Braunschweig, F. R. Germany
Contract No. : FI1W/0059/D
Duration of contract : 01.09.1986 - 31.12.1989
Period covered : Jan. - Dec. 1987
Project Leader : W. Fischle

A. OBJECTIVES AND SCOPE

Backfilling and sealing materials are important elements in a multibarrier concept to prevent resp. to delay an inflow of water or brine into a repository or to reduce transport velocity of nuclides in case of a hydrogeological incident. The backfilling material is also to act as a mechanical stabilizer and to serve as filling agent for voids (i.e. between waste containers). Technical concepts for backfilling are to be developed and tested under in situ conditions with supporting laboratory tests. Maintenance-free sealing systems for chambers and galleries have been developed, constructed and are still monitored. Newly developed sealing systems need to be tested in situ as well.

B. WORK PROGRAM

B.1. Laboratory investigations to determine the soil mechanical behaviour of crushed salt as a backfilling

B.2. Geotechnical in situ measurements in backfilled chambers and carnallite stopes in the Asse salt mine

B.3. Performance of (large-scale) load consolidation tests on backfilling materials in the Asse salt mine and in the laboratory

B.4. Laboratory and in situ investigations and monitoring of chamber and gallery sealings

B.5. Development of an evaluation matrix to examine backfilling materials (especially crushed salt)

C. <u>PROGRESS OF WORK AND OBTAINED RESULTS</u>

The main task of the soil mechanical researches in backfilling chambers and galleries is to determine the load consolidation behaviour of the bulk material (crushed salt ± clay) in laboratory and under in situ conditions.

Additional results are

- decrease of permeability by admitting clay-minerals (10 -30 %) to the crushed salt
- decreasing consolidation behaviour with increasing clay content

No final results are available for the geotechnical control measurements in the surroundings of the backfilled chamber 8a/532 m level and in the chamber itself. It can be said that there is a very slow settlement of the backfilling (crushed salt), decreasing with time. The pressure build-up in the pillars left for support rises to about 2000 KPa in E-W direction and to 4900 KPa in N-S direction. The maximum deformations of the pillars, which are measured automatically by extensometers, are 1,6 mm/a in the eastern pillar.

About 60 years old backfilling material from the 750 m-level shows an identical compaction behaviour corresponding to convergence rate. Eight chamber and gallery seals are monitored with about 200 pressure gauges at the 750 m-level at three months interval. After about 400 days a first increase of pressure with a maximum of 5,5 MPa could be observed.

One of a various number of sealings for chambers and galleries are salt bricks (briquette). These bricks, formed out of crushed salt, were rock-mechanically investigated in the laboratory. Some results are

- uniaxial pressure strength σ_D = 23,2 MPa
- Young's modulus E = 21,4 MPa
- Poisson's ratio μ = 0,23

To determine suitability of backfilling materials a valuation matrix was developed according to safety-relevant and technical criteria. This pattern is suited to compare different backfilling materials. In a next step more or less relevant criteria for a valuation of crushed salt as a backfilling are to be determined (Fig. 1).

<u>List of publications</u>

FISCHLE, W., STARKE, C. et al., Untersuchungen zum Versatz und Verschluß von Kammern und Strecken in einem Endlager im Salz, Abteilungsber. IfT 3/87 (1987)

GIES, H., KAPPEI, G, STARKE, C., The German backfilling and sealing concept for a salt repository : present state and first results of testing activities, Geochem. Workshop, Albuquerque, N. M., USA, 21 -25 Sept. (1987)

KAPPEI, G., Untersuchungen zum Verdichtungsverhalten von Steinsalzhaufwerk, Kali und Steinsalz, Bd. 9, Nr. 12, S. 415 - 420 (1987)

KAPPEI, G., Ermittlung bodenmechanischer Eigenschaften von Salzhaufwerken als mögliche Versatzmaterialien in einem untertägigen Endlager. IfT, Projektabteilung, TL 60/87, GSF-Bericht 1/88 (1988)

Criteria for Assessment		Backfill Material		
		X	Y	Z
Material Behaviour	Geotechnical			
	Geochemical			
	Physical			
	Mineralogical			
Availability	Descent			
	Preparation			
	Transport			
	Bunkering			
Stowing Method	Hand Packing			
	Gravity Stowing			
	Slinger Stowing			
	Pneumatic Stowing			
	Hydraulic Filling			
	Pump Stowing			
	Other Techniques			
Handling Aspects	Transport in the Mine			
	Dust Exposure			
	Water Insertion			
	Mobility			
	Efficiency			
Safety Aspects	Gas Accumulation			
	Temperature			
	Compatibility			
	Long-term Safety			
Economy				

Fig. 1: Matrix to Evaluate Backfill Materials in a First Step

CRUSHED SALT BEHAVIOUR UNDER EFFECT OF A HEAT SOURCE IN BOREHOLES DRILLED IN A SALT MINE

Contractor : ANDRA
Contract n° : FI 1W/060
Duration of contract : 24 months
Period covered : 01/10/86 - 01/11/88
Project leader : R. ANDRE JEHAN

A - OBJECTIVES AND SCOPE

The study concerns the final stage of a nuclear waste disposal in deep salt formations : the partial or complete closing of a site. Sealing of drifts and shafts must be performed as tight as possible to set up a barrier as similar as possible to the natural geological barrier.

As crushed salt backfilling corresponds to one of the considered concepts a research program is actually developed on the basis of the following axis :

- thermomechanical behaviour of crushed salt during thermal climax and during cooling,
- mechanical interaction between crushed salt and rocksalt,
- evolution of fluids, especially trapped air in crushed salt pores.

This study led to performing an in-situ experiment by heating crushed salt in several boreholes drilled in a salt layer in an Alsace Potash Mine.

ARMINES (Association pour la Recherche et le Développement des Méthodes et Processus Industriels) is contractor for ANDRA to support the experiment which is conducted by LMS (Laboratoire de Mécanique des Solides) and the Engineering Department of MDPA (Mines de Potasses d'Alsace).

B - WORK PROGRAM

1. Preparation of the test site
   Drilling of the boreholes :
   - six 240 mm diameter boreholes destined to be heated,
   - small measurement boreholes : four around each of the heated ones.
2. Instrumentation

2.1. Setting up of the computer controlled system developed by LMS for data acquisition and data transmission (from the test site to LMS).

2.2. Equipment of the boreholes :
   - heated holes :
     + introduction of the framework supporting the electric wires and several transducers (for measurement of temperature, interstitial pressure of trapped air, total pressure of crushed salt, borehole closure),
     + backfilling of crushed salt in five of them, the sixth one leaving without backfill in order to check natural closure of heated salt and to compare its behaviour to the others',
   - small holes : introduction of the temperature and extensometry measurement transducers.

3. Modelling

3.1. Preliminary calculations in order to define the following points :

- thermal power to be supplied in each borehole to reach a wall temperature of 110° C,
- geometrical shape and position of the heating sources,
- heating process,
- range of the transducers.

3.2. Interpretation of the in-situ results.

4. Laboratory experiments

The following experimental study has been conducted in order to determine mechanical and thermal properties of crushed salt :
- physico-chemical analysis,
- mechanical properties at ambient temperature,
- mechanical behaviour under temperature (up to 100° C),
- thermal study.

C - PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Complexity of proceedings concerning conception of instrumentation, monitoring and data transmission system led to start the first experiment on a single borehole, borehole n° 1. It was decided not to start other experiments before two months of heating in that borehole. Respectively 16 days and 49 days after beginning of the experiment, failure occured in two of the three paires of electrical wires installed in the borehole.

This brought to a tempory interruption and postponed instrumentation of the other boreholes.

Several actions were undertaken :
- to overcome the failures ; heating could finally continue 63 days after beginning of the experiment,
- to recognize the origin of the failures ; simulations were performed and proved :
  + the existence of corrosion points on the INOX shealth of the electrical cire,
  + a partial cristallisation of crushed salt.

Both phenomena appeared to be strongly dependent upon crushed salt humidity content (<3 %) and led to take following decisions for the backfilled boreholes n° 2 to n° 5 :
- the substitution of electrical wires protected with INOX by others protected with INCONEL,
- drying crushed salt before backfilling.

Field instrumentation is planned to continue according to the following schedule :
- borehole n° 6 (non backfilled) at the beginning of February 1988,
- boreholes n° 2 to n° 5 at the end of March 1988.

There by the encountered problems have two main consequences :
- the abandon of humidity content as a parameter of the study,
- a lengthen of about six month for the duration of the in-situ experiment.

Progress and results

3. Modelling

3.1. Preliminary calculations

3.11. Thermal calculation

In the first calculation a single electrical heater was located along the axis of the boreholes. This resulted in an excessive temperature increase on the heating source, due to small conductivity of crushed salt. However the temperature on the wall of the borehole remained without any significant modification. This result guided to the positionning of six heat sources near to the borehole wall. Morever non axisymmetric calculations showed concentration of heat only over a few centimeters of the wall. Beyond 10 cm, isotherms remained circular as already obtained by axisymmetric model. This is why an axisymmetric representation was adopted, which allowed to consider more realistic boundary conditions, especially in the galleries where high thermal convection is possible due to ventilation.

On the whole it was proposed on the basis of the calculations results to deliver a 3kW heat power to each borehole ; the steady-state thermal output is reached after 10 days.

3.12. Thermomechanical calculation

The borehole without backfill converges more than those subject to backfilling pressure. This case was studies using closed form solutions based on non linear viscoelastic behaviour of heated rocksalt.

Pessimistic situation corresponds to application of final values of temperature related to steady-state thermal behaviour to a borehole after a sudden drilling.

The calculated values of closure allowed to define a + 20 mm range for convergencemeters.

3.2. Interpretation of the in-situ results

Interpretation of results is postponed due to the difficulties mentionned above. For the time being only some gross plots can be given for some measured parameters in borehole n° 1. All of them are affected by the power supply interruption.

A modelling of the boreholes will be undertaken, using finite element thermal and thermomechanical codes :

- backfilling mechanical influence will be studied with axisymmetric models,
- rocksalt will be considered to be non linear viscoelastic with properties in accordance with creep tests already performed,
- crushed salt behaviour will be supposed to be elastoplastic with parameters as defined by laboratory tests in addition to field measurements.

4. Laboratory experiments

The experimental study has been conducted on three varieties of crushed salt having different grain sizes :

- a refined fine grained salt,
- a refined coarse grained salt,
- a "natural" salt, which is a by-product of the MDPA potash processing;

4.1. Physico-chemical analysis

- grain size measurement, with an average value of 1.1 mm, 2.2 mm, .4 mm respectively,
- density measurement, 1.38, 1.22, 1.36 respectively ; further compaction tests led to a gain in porosity of about 6 %,
- mineralogical composition, 99.95 %, 99.95 %, 90.90 % NaCl respectively.

4.2. Mechanical properties at ambient temperature

- isotropic triaxial test in order to follow volume change due to an increase of the confining pressure in the range of 0 to 1.8MPa ; the maximum of volume deformation was about 9 %,
- compressive triaxial tests under constant confining pressure from 0.1MPa to 0.9Mpa,

- two basic results were obtained :
  + a non linear and irreversible mechanical behaviour,
  + a volume decrease under the effect of isotropic stress and fairly high values of confinement associated to deviatoric stress,
  + on the contrary a volume increase due to deviatoric stress under the effect of small confining pressure.

4.3. Mechanical behaviour under temperature (up to 100°C)

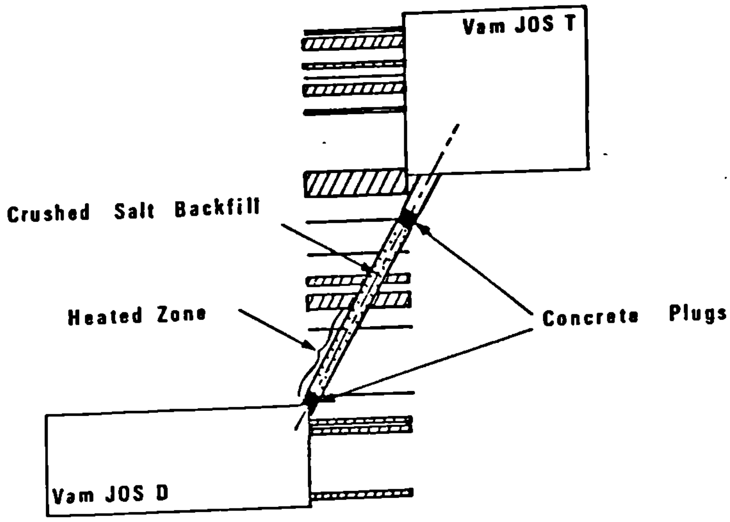
- oedometric tests allowed to measure time dependent compaction under different normal stresses,
- the results showed a significant difference between rocksalt behaviour and crushed salt behaviour ; rocksalt is a viscoplastic material and its viscosity depends highly upon temperature ; for crushed salt, at least for the ones studied, we did not observe a clear viscosity influence during 1 month tests ; therefore those crushed salt seem to be similar to sand, usually condidered to be elastoplastic.

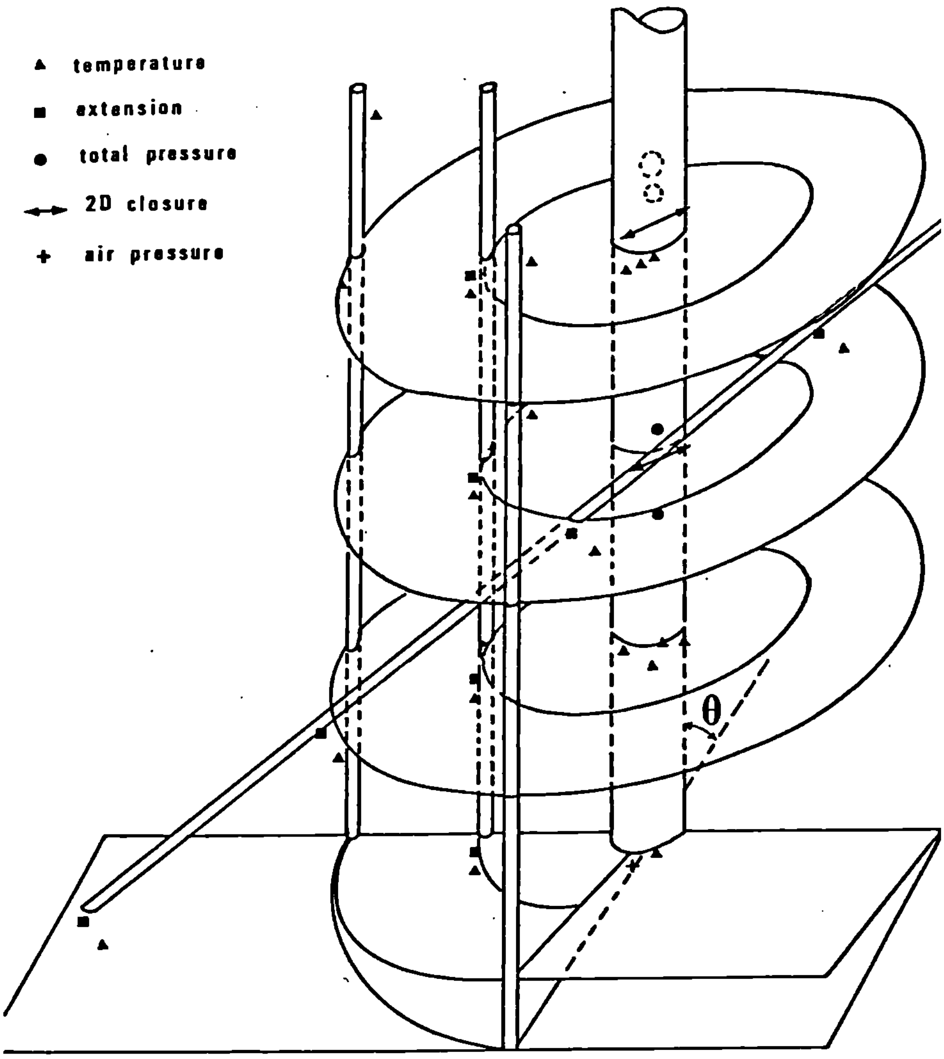
4.4. Thermal study

- in order to determine thermal conductivity, the distribution of temperature was recorded at different radii of a spherical sample, at the center of which a heat source had been placed,
- the values of steady-state temperature proved that thermal conductivity of crushed salt was smaller than rocksalt conductivity (5.25W/m/°C) by one order of magnitude ; the results seem to be sensitive to grain size, porosity and specific surface of crushed salt.

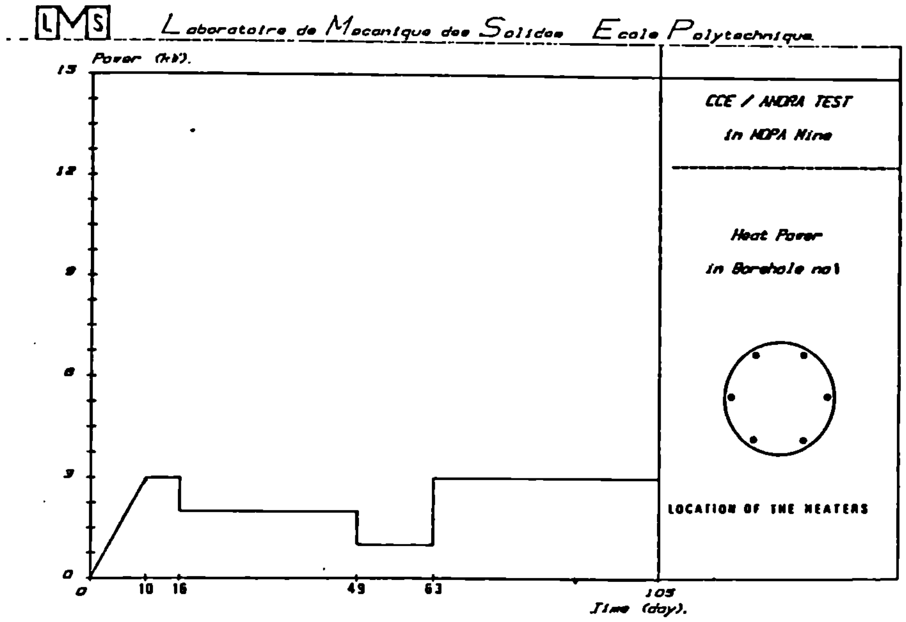
CCE / ANDRA TEST
in MDPA Mine

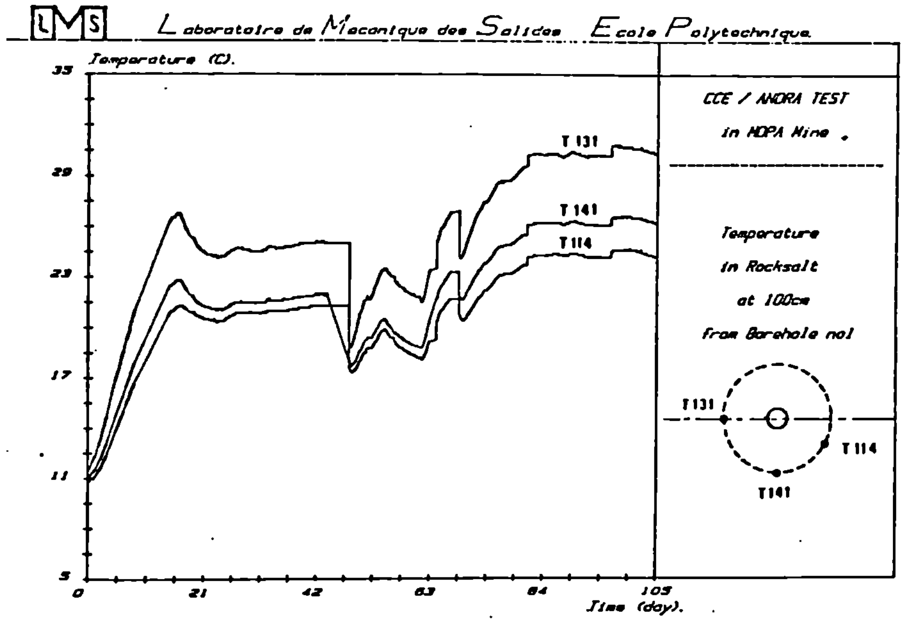
VERTICAL SECTION
OF BOREHOLE N° 1

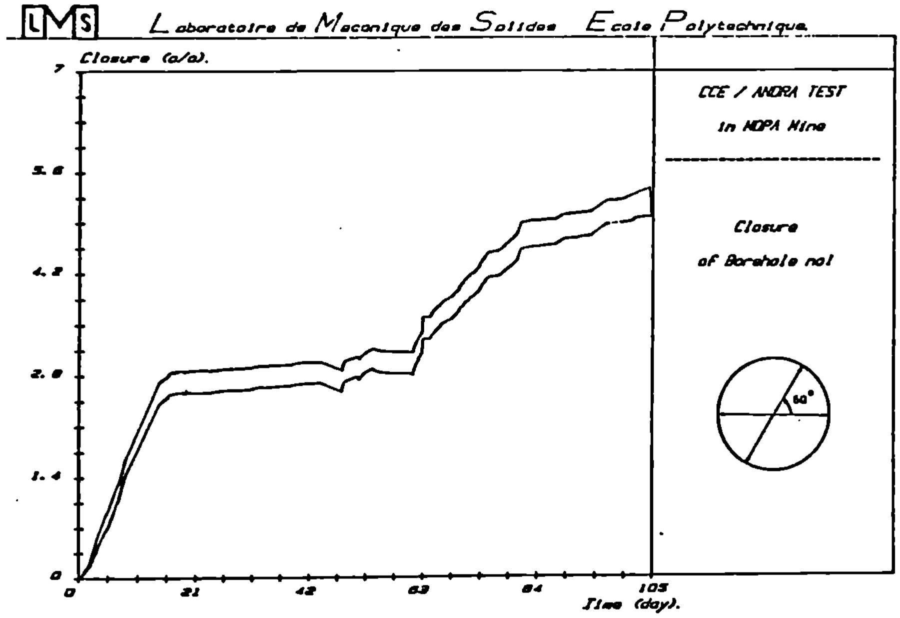




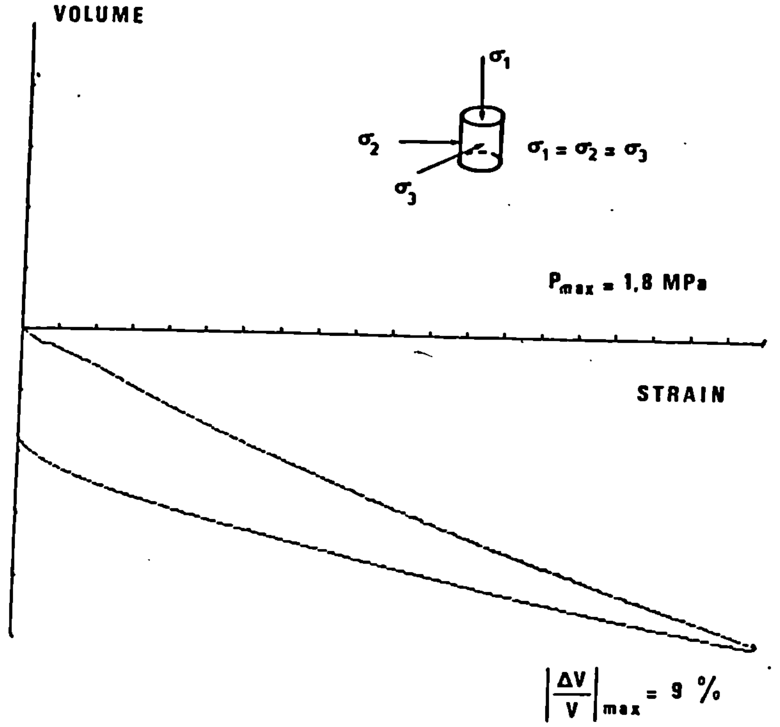
LOCATION OF THE BOREHOLES
INSTRUMENTATION


LMS
Laboratoire de Mécanique des Solides Ecole Polytechnique
Power (kW).
CCE / ANDRA TEST
in HOPA Mine
Heat Power
in Borehole no1
LOCATION OF THE HEATERS
Time (day).


LMS
Laboratoire de Mécanique des Solides Ecole Polytechnique
Temperature (C).
T 131
T 141
T 114
CCE / ANDRA TEST
in HOPA Mine
Temperature
in Rocksalt
at 100cm
from Borehole no1
Time (day).

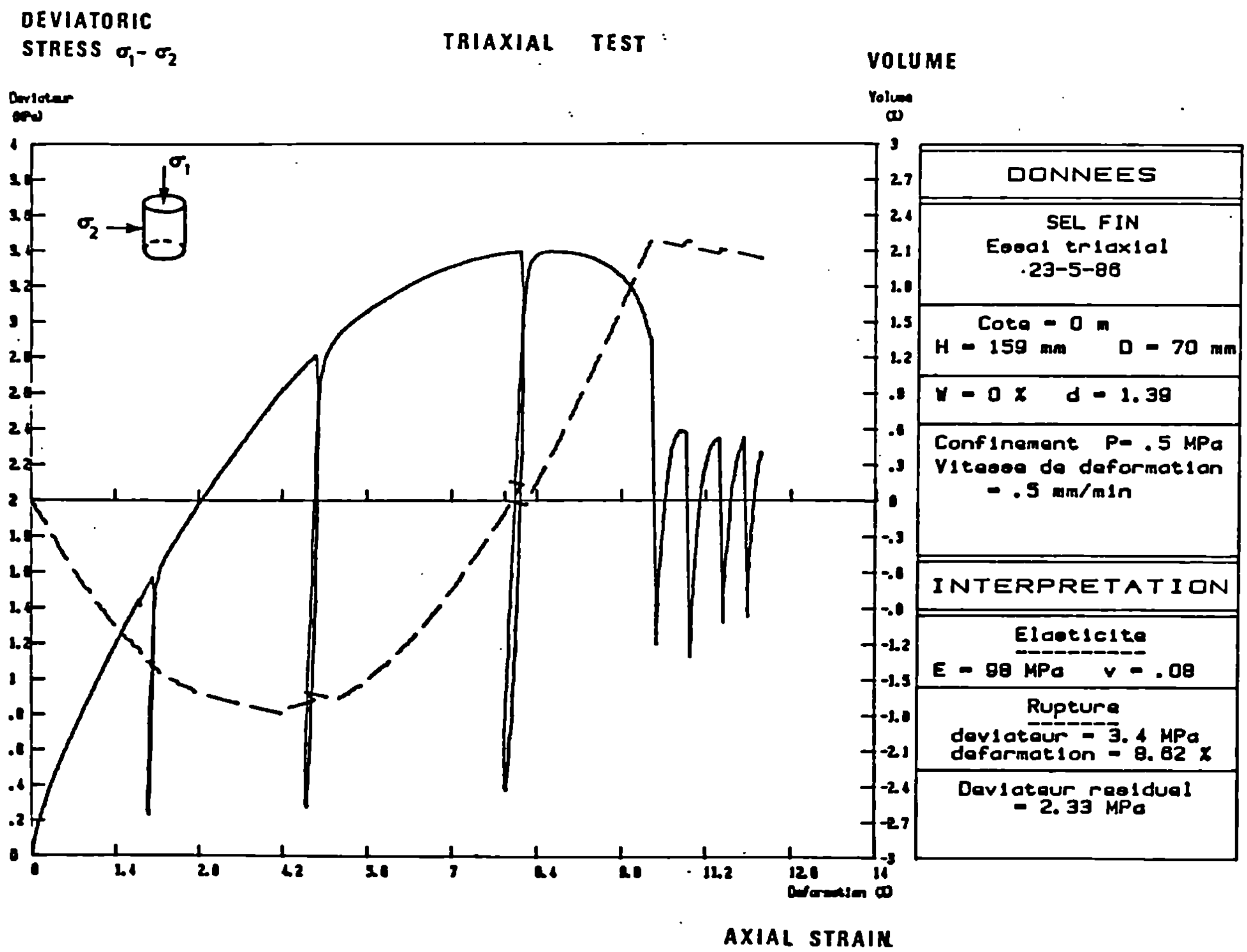

LMS
Laboratoire de Mécanique des Solides Ecole Polytechnique
Closure (o/o).
CCE / ANDRA TEST
in HOPA Mine
Closure
of Borehole no1
60°
Time (day).

ISOTROPIC TRIAXIAL TEST



Fine grained salt

TRIAXIAL TEST



Study of the thermal behaviour of clay-based buffer materials on reduced scale mock-ups and in an underground laboratory

Contractor : CEA, CEN Fontenay-aux-Roses
Contract n° : FI1W - 0061 F
Working period : July 1986 - December 1989
Period covered : January 1987 - December 1987
Project leader : M. DARDAINE

A. OBJECTIVES AND SCOPE

Clay materials could be used as components of engineered barriers placed between high-level waste canisters and host rock.

The purpose of this work is to compare the behaviour of different types of materials, both homogeneous and heterogeneous, simultaneously subjected to heat and humidity gradients. Only the initial stage of storage, the so-called " dried stage ", is simulated.

The study, which involves instrumentation, first involves the desing and construction of an experimental device to reproduce the actual physical conditions of waste disposal : temperature and water content. Subsequently, in collaboration with CEN/SCK, an in-situ heat transfert experiment will be carried out in the Mol underground experiment facility. An electrical heater will be surrounded with buffer and backfill materials. The entire system will be instrumented with temperature, moisture and pressure sensors. The test will be supported by heat transfer modelling.

B. WORK PROGRAMME

B.1 Research and development work on water content sensors :
- . thermal conductivity sensor,
- . capacitance sensor.

B.2 Design and construction of an experimental heat transfert device. Experiments and modelling.

B.3 Properties of backfill materials, determined in the underground experiment facility at Mol (Belgium). In-situ experiments on heat transfer and modelling.

C. STATE OF PROGRESS AND RESULTS OBTAINED

State of progress

The research and development work concerning the thermal conductivity sensors is now finished. Twenty sensors have been made, of which twelve have been used for instrumentation of the thermal test rig. The measurement system consists of a stabilized power supply, a multimeter and a computer which simultaneously interrogates the twelve sensors.

The research and development work concerning the capacitance probes has principally consisted of measurement by three different methods (Q-metre, oscillator method and the Wayne-Kerr bridge) of the dielectric constant of samples of compacted clay of different dry specific densities and water contents.

The experimental setup for studying thermal transfer in the engineered barriers in the facility has been completed and the qualification experiment is in progress.

The last part of the study consists of measuring the characteristic properties (compacting pressure, thermal conductivity, hydraulic conductivity and swelling pressure) of the materials to be used in the Bacchus (Backfill Control for HLW Underground Storage) experiment to be conducted in the Mol underground experiment facility in 1988. The substances involved are processed Boom clay and a ternary mixture consisting of 4a clay, quartz sand and graphite. The study is conducted in collaboration with CEN-SCK under EEC contract FI1W - 0055.

Progress and results

B.1 Research and Development work on water content sensors.

The thermal conductivity sensors

The twelve thermal conductivity sensors positioned radially in the intermediate ring of the thermal test rig have made it possible to take a large number of readings and to assess their characteristics.

At ambient temperature, the reproducibility of the readings of all the sensors is excellent. For about fifty readings, the typical deviation is less than 1% of the average value. Between the twelve sensors, the dispersion between the respective average values does not exceed 4%.

When the readings are taken in the presence of a temperature gradient (maximum temperature 55°C), a slight increase in dispersion is found which is attributable to degraded contact between the probes and the surrounding material.

The capacitance sensor

The different measuring techniques used have made it possible to assess change in the dielectric constant of the compacted clay as a function of its dry specific density and water content. A few additional tests have also shown the extreme dependence of measurement on temperature rise.

Furthermore, the Wayne-Kerr bridge method is the only one in which a miniature sensor can be connected to the measuring bridge by a sufficiently long cable.

Nevertheless, it remains necessary to optimize the reliability of the sensor and to obtain an automatic admittance bridge applicable to the measurement situation.

In conclusion, as the thermal conductivity sensor is now in its operational phase (other sensors of higher performance are ready in production for the in-situ experiment), the importance of continuing the studies concerning the capacitance sensor diminishes, especially as the problems which remain to be solved will necessitate the further investment of a large amount of time and resources.

B.2 Desing and construction of an experimental heat transfer device. Experiments and modelling

The experimental setup essentially consists of the thermal test rig and a control and instrumentation power supply unit, is designed for laboratory tests of heat transfer through engineered barriers has now been built and assembled. The qualification experiment is in progress. The engineered barrier consists of a stack of three rings of French 4a clay, with a water content of 10% and an apparent specific gravity of 2.12 placed round a heating mandrel instrumented with thermocouples and thermal conductivity sensors.

Analysis of the temperature and heat conductivity over a four-mounth period, during which the rings were subjected to a practically stationary temperature gradient (maximum temperature 80°C), has demonstrated that there is no significant migration of water within the material. This is confirmed by water content measurements made on a radial sample from the lower ring.

B.3 Characterization of the material used in the Bacchus experiment

The processed Boom clay possesses excellent compactiblity properties. The apparent specific gravities obtained are range from 1.83 to 2.35, as the compacting pressure increases from 15 to 200 MPa.

For a dry specific gravity of 1.74, the swelling pressure that it exercises on saturation varies between 1.9 and 2.5 MPa when the water injection pressure increases from atmospheric pressure to 1.0 MPa. It reaches 3.1 MPa at a temperature of 60°C.

The hydraulic conductivities measured under the same gradient (2 x 10^3) at ambient temperature and at 60°C are respectively 3.5 and 6.5 x 10^{-12} m/s.

The proposed engineered barrier consists of a mixture of 50% 4a clay, 45% quartz sand and 5% Carbone-Lorraine graphite. When compacted at 20 MPa, the mixture has a specific density of 2.07 and its thermal conductivity already reaches 1.7 W/m.K. However, the swelling pressure that it exercises peaks at around 5 MPa at 150°C. Its hydraulic conductivity is ther about 2.10^{-12} m/s.

Preparation of five rings of the required size (cf Progress Report EEC FI1W-0055) has been completed in the Bacchus operation. Their apparent specific gravity is in the region of 2.07.

DEVELOPMENT OF EFFECTIVE CONCEPTS FOR ATTENUATING THE NEAR FIELD EFFECTS OF HLW IN ARGILLACEOUS HARD ROCKS

Contractor: SCK/CEN, Mol (B)
Contract n°: FI1W/0145/B
Contract period: July 1987 - December 1989
Project leader: A. A. Bonne

No progress report made available

TITLE: The Construction of Laboratory Scale Mock-ups for studies of back-filling shafts & tunnels with concrete.

Contractor Taylor Woodrow Construction Ltd.
Contract No.: FI 1W/0157.UK
Duration of Contract: February 1988 to January 1990
Period Covered: Pre-contract period to December 1987.
Project Leader: Mr. I. Ll.Davies.

A. OBJECTIVES & SCOPE

The aims of this study relate to investigating the use of concrete as the means of backfilling and sealing underground radwaste repositories and comprise :-

* optimisation of concrete mix characteristics consistant with the functions of backfilling and sealing
* evaluation of alternative techniques of concrete emplacement
* the provision of experimental data to develop a mathematical model capable of predicting long term behaviour of a sealed repository system (see report on Contract No.FI.1W.0159.UK)

The study extends previous laboratory small scale tests to the use of large scale models which will provide a much higher degree of representivity when compared to actual repository designs.

B. WORK PROGRAMME

The work programme shall comprise:-

1.0 Literature Survey:This will evaluate the potential use of chemical admixtures and their applicability to pre-placed aggregate concretes (PAC).

2.0 Backfilling Trials:

2.1 Concrete Mix Development: Utilising output from 1.0 above PAC mixes will be developed and controls prepared and tested.

2.2 Backfilling: Large scale models of repository segments will be constructed and filled with both pumped and pre-placed aggregate concretes. The models will be instrumented and subject to a comprehensive series of tests including the recovery of core samples for reference purposes.

3.0 Model Tests:A series of comprehensive tests will be completed to produce data for use in the development of mathematical models.

3.1 Model Construction: These will be representative of segments of repositories in both rock and clay formations. The models will be stressed to appropriate levels and subject to thermal gradients consistant with that expected in repository environments.

3.2 Testing: The models will be monitored to measure internal strain and temperature, and representative samples will be recovered for comprehensive physical testing. The data will be used as input to the thermal and stress analytical model being developed as a parallel study contract.

4.0 Reporting: In addition to a factual report on the model testing programme, recommendations will be prepared concerning concrete mix design and specifications for repository backfilling and sealing requirements.

C. PROGRESS OF WORK & OBTAINED RESULTS

Contracts are expected to be signed and work commence during the first weeks of 1988 as the UK NIREX & UK Department of Environment have agreed to fund the balance of monies required to complete this research project. No technical progress can therefore be reported for this period.

TITLE: Studies of Historic Concrete
Contractor Taylor Woodrow Construction Ltd.
Contract No.: FI1W/0158.UK
Duration of Contract: January 1988 to December 1988
Period Covered: Pre-contract period to December 1987.
Project Leader: Mr. I. Ll.Davies.

A. OBJECTIVES & SCOPE

Durability of concrete materials, either as matrix for low and intermediate level waste, or as backfilling/sealing materials for repositories, is a major concern in the preparation of both designs and safety assessments.

The objective of this study is to examine ancient concretes, and modern ones with proven durability; to identify the parameters which contribute to their durability. The work is an extension to that previously undertaken in a previous phase and will be used to provide data to enable life predictions on modern concretes to be made.

B. WORK PROGRAMME

The following sources of samples will be investigated :

1.1. Ancient Materials
Preference will be given to obtaining samples from concretes containing natural pozzolanic materials, where the sample is partially buried and from zones of the concrete where carbonation may be incomplete.

1.2 Medieval materials (up to 1824)
Preference will be given to materials where a hydraulic binder is likely to have been used.

1.3 Modern Portland Cement Based Concretes (1824 - present)
Preference will be given to securing samples from large masses of underground concrete located in a moist environment and with a likely pozzolanic content.

2. Examination & Testing
The procedure set out below will be followed where appropriate, depending on the size and nature of the sample and the outcome of previous tests:

2.1 Visual examination
2.2 Assessment of depth of carbonation
2.3 Optical microscopy of thin sections taken at positions representing fully carbonated material, the carbonation front and uncarbonated material.
2.4 Scanning electron microscopy of polished sections and fracture surfaces in the same zones.
2.5 Individual phases identified above analysed by electron probe microanalysis.
2.6 Chemical and XRD analysis of portions representative of the different zones of the sample.
2.7 Pore structure analysis of similar portions.
2.8 Analysis of pore fluid expressed from the portions used in the previous analysis.
2.9 Other tests may also be made to resolve issues arising from the results of the above procedure.

C. PROGRESS OF WORK & OBTAINED RESULTS

Contracts are expected to be signed and work commence during the first weeks of 1988 as the UK Department of Environment have agreed to fund the balance of monies required to complete this research project. No technical progress can therefore be reported for this period.

TITLE: The Development & Application of Mathematical Modelling approaches to interactive effects for concrete backfill in hard rock and argillaceous hosts.

Contractor: Taylor Woodrow Construction Ltd.
Contract No.: FI 1W/0159.UK
Duration of Contract: April 1988 to June 1989
Period Covered: Pre-contract period to December 1987.
Project Leader: Mr. I. Ll.Davies.

A. OBJECTIVES & SCOPE

The main objective of this study is to develop a mathematical model utilising the ADINA CODE which can predict interactions between concrete backfill and host geologies for underground radwaste repositories.

The work is a parallel programme to the contract FI.1W.0157 UK and may use physical test data derived from that programme for analysis development and unification purposes.

B. WORK PROGRAMME

The work programme shall comprise:-

1. Literature review of recent international work to ensure that the mathematical models developed using ADINA represent a reasonable state of the art in terms of both analytical approach and representation of the physical phenomena.
2. Investigation of the newly available features provided in the latest release of the ADINA code and consideration of their appropriateness to modelling repository interaction behaviour.
3. Agreement, in consultation with Community partners, upon appropriate generic disposal scenarios in both hard rock and argillaceous hosts.
4. Study of range of mechanical and thermal interactions between the host material, the backfill and canistered waste,including long-term creep effects.
5. Assessment of the development of damage in and adjacent to the backfilling material, and how the damage may increase with time both short-term from early thermal effects from cement and waste and very long-term from lithostatic creep effects.

C. PROGRESS OF WORK & OBTAINED RESULTS

Contracts are expected to be signed and work commence during the first weeks of 1988 as the UK NIREX & UK Department of Environment have agreed to fund the balance of monies required to complete this research project. No technical progress can therefore be reported for this period.

QUALITY ASSURANCE ASPECTS OF WASTE EMPLACEMENT AND BACKFILLING IN ILW AND LLW REPOSITORIES

Contractor:	Bullen and Partners Consulting Engineers 188 London Road Croydon CR9 1PT England
Contract:	FI 1W - 0161 - UK
Duration of Contract:	From February 1988 to February 1989
Period Covered:	Pre-Contract
Project Leader:	Dr J.A. Allison

A. OBJECTIVES AND SCOPE

The objectives of the study are:

- o To critically examine existing conceptual design proposals for the deep underground disposal of ILW and LLW in water-bearing (non-saliferous) host rocks, with particular reference to the quality control/quality assurance aspects of waste emplacement and backfilling.
- o To examine the extent to which existing proposals enable effective monitoring and remedial action to be achieved
- o To identify the parameters which are most effective in describing backfill material properties and waste unit characteristics, both before and after placement.
- o To identify appropriate measurement techniques and the means of application of such measurements in the development of a coherent quality control system.
- o To examine the ways in which repository design details, methods of waste unit/backfill placement and the sequence of operations involved may be adapted to ensure that an effective quality assurance system can be established.

B. WORK PROGRAMME

1 **Phase 1.** will comprise a brief review of the following aspects of the ILW and LLW disposal concepts developed in member states of the European Community:

- o The types of waste units envisaged for deep underground disposal and the quality control/quality assurance systems currently adopted or envisaged for the pre-disposal stages.
- o The waste emplacement systems currently proposed and the extent to which quality control/quality assurance procedures have been specified.
- o The range of backfill materials under consideration, and the properties which relate most effectively to their intended functions.

2 **Phase 2** will concentrate upon the generic deep-level repository design concepts for ILW and LLW disposal (including plutonium-contaminated wastes) which are incorporated within the current UK waste disposal strategy.

Consideration will given to a range of backfill materials, reflecting the scope of current Community research and development.

For these reference conditions, more detailed evaluation of quality control/quality assurance measures will be carried out, itemising the procedures and measurements required at each stage of development.

Where appropriate, the need for repository design modifications is to be considered as a means of improving the exercise of quality control in the waste emplacement/backfilling processes.

The following are among the factors to be considered:

- o The extent to which backfill materials can be prepared in solid 'fill block' from or as pre-batched 'fluid form' fills at off-site production centres, or at an adjacent surface facility.
- o The scope for palletising waste units in appropriate spatial arrays, with partial interstitial filling, prior to emplacement and final sealing.
- o The scope for exercising control over the geometry of waste unit arrays such that required fill volumes are accurately known and directly comparable with volumes actually emplaced.
- o Means of separate monitoring for groups or 'cells' of emplaced waste units/backfill, such that the origin of defects may be identified, and recovery or appropriate remedial action achieved.
- o The extent to which the emplacement processes for different categories of waste (incorporated in a single repository) may require different approaches in exercising a consistent level of control.

3 The study will include recommendations concerning the development of quality control/quality assurance procedures for waste emplacement, backfilling and monitoring to complement and extend those which are being (or have been) developed in relation to the pre-disposal stages. Supplementary recommendations concerning the correlation of readily measured quality control parameters and specified performance properties will be provided.

C PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

A contract for the implementation of the project has been concluded with the Commission, the anticipated start date being 1 February 1988.

PROGRESS AND RESULTS

Work has not commenced at the time of preparation of this progress report.

RESEARCH ON SWELLING CLAYS AND BITUMEN AS SEALING MATERIALS FOR UNDERGRUND REPOSITORIES FOR RADIOACTIVE WASTE

Contractor:	Bullen and Partners Consulting Engineers 188 London Road Croydon CR9 1PT
Contract:	FI 1W - 0162 - UK
Duration of Contract:	From February 1988 to July 1989
Period Covered:	Pre-Contract
Project Leader:	Dr J.A. Allison

A. OBJECTIVES AND SCOPE

Work previously carried out within the CEC's research and development programme indicates that swelling clay together with bitumen could be used to form a highly effective waste containment barrier for use in deep underground radioactive waste repositories.

This project seeks to identify relevant material properties and sealing mechanisms. Its objectives are:

- o To assess the potential behaviour of combinations of swelling clays and bitumen, and the potential effectiveness of synergistic combinations of these materials for sealing underground repositories against groundwater ingress, radionuclide release and gas release.
- o To assess the potential level of confidence in the long-term behaviour of such seals in the perspective of the quality assurance procedures that could be associated with the emplacement of backfill and seal materials.

B. WORK PROGRAMME

The work programme consists of the following activities:

1 A review of available information on properties and behaviour of swelling clays (including bentonite and magnesium oxide) and information on bitumens as used in engineering structures.

2 Control tests on samples of swelling clays and bitumen to establish the range of compatibility between clay swelling properties and the rheological properties of bitumen.

3 Construction and operation of a test rig to monitor water uptakes and swelling pressures in combinations of swelling clay and bitumen.

4 Examination of combinations of the materials to establish whether seals are formed and the nature of the seals.

5 Calculation of the water, radionuclide and gas permeabilities of the seals: with particular reference to the radionuclides iodine, technetium and neptunium and to the gases hydrogen, methane and carbon dioxide.

6 Assessment of test results in the context of material properties and free swelling space that could be achieved in practice with current quality control systems in potential repositories.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

A contract for the implementation of the project has been concluded with the Commission, the anticipated start date being 1 February 1988.

PROGRESS AND RESULTS

Work has not commenced at the time of preparation of this progress report.

EMPLACEMENT FEASABILITY OF OPTIMIZED AIR PLACED MORTARS

Contractor : CEA, Fontenay-aux-Roses, France
Contract No. : FI1W/0166
Duration of contract : October 1987 - December 1989
Period covered : October 1987 - December 1987
Project leaders : A. Bernard, R. Atabek.

A. OBJECTIVES AND SCOPE

Air placed techniques - Gunite and Shotcrete - are commonly used in civil engineering for wall reinforcement with cement based materials. Gunite is a trade name to designate a mixture of PORTLAND cement and sand thoroughly mixed dry, passed through a cement gun and conveyed by air through a flexible tube, hydrated at a nozzle at the end of such flexible tube and deposited by air pressure. In the case of shotcrete, a proportioned combination of PORTLAND cement, aggregates and water is mixed by mechanical methods and pumped in a plastic state to the nozzle where air is added to expel the material.

These techniques are likely to be used for engineered barrier emplacement due to the facts that :

- spraying machines are commercially available and easily automatized for nuclear applications,
- their delivery ($\simeq$ 10 m^3/h) is compatible with the french needs of T.R.U. waste disposal in galleries.

The research program, developed within the framework of this contract, is devoted to test air placed mortar ability to fill up the voids between the waste packages and the host rock. Materials and techniques will be optimized taking into account air placed mortar properties such as density, permeability, water transfer, radionuclide retention, etc...

B. WORK PROGRAMME

B.1 Literature survey : choice between the two processes (dry or wet) ; recommendations for the selection of the most appropriate equipment ; definition of the test specifications.

B.2 Feasability tests : choice between different types of materials, taking into accountcement types, additives (clays, silica fume), plasticizers, aggregates granulometry distribution.

B.3 Full scale study of the selected material : spraying cycle definition, rebound influence on air placed material homogeneity.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Literature survey is in progress using SOLETANCHE knowledge of civil engineering. Results will be available in April 1988.

4.3. RADIONUCLIDE MIGRATION IN THE GEOSPHERE (MIRAGE)

4.3.A. Actinide and fission product geochemistry in natural acquifer systems

Characterisation of the Boom clay and its multi-layered hydrogeological environment with a view to radionuclide migration

Contractor : SCK/CEN, Mol (B)
Contract n° : FI1W/0055/B
Duration of contract : October 1986 to December 1989
Period covered : January 1987 - December 1987
Project leader : A.A. Bonne

A. OBJECTIVES AND SCOPE

The effectiveness of the geological barrier is a key function for the long-term safety of the disposal of nuclear wastes. The assessment of its barrier performances can only be done by modelling, provided that reliable in situ data is available.

The underground experimental HADES-laboratory in the Boom clay at Mol allows to sample the clay according to various procedures and to perform experiments aiming at characterizing the clay in situ and at determining in situ migration parameters. The hydrogeological observations and sampling network around the site enable to verify if the local site data is in agreement with the regional groundwater flow regime and hydrochemistry. Research previously carried out has shown that organic matter and compounds in clay are of prime importance for trapping various radionuclides in the argillaceous barrier. The characterisation of the organic substances in the Boom clay, their specific retention capabilities and stability with regard to irradiation are therefore of particular interest in the near-field. A collaboration in this matter with the University of Louvain (KUL, Prof. Cremers) is on-going.

The research will be backed by migration tests simulating in situ conditions (diffusion experiments on reconsolidated clay plugs) and by hydrogeological studies, both not being part of the contract, but the results of these will be made available for sake of confirmation or completion.

B. WORK PROGRAMME

1. Study of the organic substances in the Boom clay, with emphasis on their affinity for Eu and Tc.
2. In-situ short-term migration experiments in the Hades-URL
3. Application of isotopic techniques and hydrochemistry for the characterisation of a multi-layered aquifer system

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The characterisation of the organic substances in the Boom clay and their retention specificities continuing on the line of the research on that matter already started in the previous multi-annual programme. For the in-situ migration experiments, emphasis was on a precise understanding of the very local hydraulic conditions of the test. For the various possible experimental set-ups the mathematical formulations have been worked out. A few in-situ migration experiments were already installed. Carbon-14 groundwater dating and hydrochemical studies, based upon of the groundwaters analyses of the past years, are also continued on the line of the previous work.

Progress and results

1. Study of the organic substances in the Boom clay, with emphasis on their affinity for Eu and Tc.

In the effort to measure quantitatively the HA's in dilute extracts of Boom clay it appears that the cobalti-hexamine saturation yields very satisfying results. This method gave 1.45 meq/g at pH=7 and 1.89 meq/g at pH=8 for the functional group capacity.

By an experimental approach aiming investigating the time-dependence of the reductive complexation of Tc in three Boom clay samples, the hypothesis has been confirmed that under in-situ conditions in the Boom clay Tc is quantitatively reduced to a lower oxidation state and, in the process, becomes associated with the humic acid components. Consequently the only migration mechanism of Tc through the Boom clay is to be related to the HA migration pattern.

Concerning the Eu-HA-complexes the research results obtained up to now allow to state that under in-situ conditions, effective HA-levels in the interstitial pores are high enough (<500 ppm) as to lead to the formation of a 3-Eu-HA-complex. Therefore, the solid-liquid distribution of Eu under in-situ conditions, i.e. the potentially mobile fraction of Eu, is exclusively dependent on these HA levels and the stability constant of the 3-Eu-HA-complex. Moreover, if we assume that, in the solid phase Eu is quantitatively associated with the humic phase, then the in situ fraction of Eu in the liquid phase could be identified with the fraction of HA present in the interstitial fluid.

2. In-situ short-term migration experiments in the HADES-URL

Two types of in-situ migration experiments are actually performed or in preparation :

- percolation experiments with clay cores wherein a labelled filter-paper is sandwiched so that migration is allowed to proceed in both halves of the clay core on both sides of the source (core A and core B) ;
- direct injection of non- or weekly retarded tracers in the clay mass.

The table below gives an overview of the in-situ migration tests of the percolation type emplaced in the URL.

access hole	radio-isotope	activity (Bq)	emplacement date	retrieval date
55	152+154 Eu	1.78 E+6	85.10.15	87.12.07
43	152+154 Eu	1.78 E+6	85.10.16	87.02.17
44	Sr-85	3.7 E+6	87.08.12	87.11.27
53	Cs-134	3.0 E+6	87.07.03	-
62	U-233	3.5 E+4	87.11.24	-

From these experiments it can already be concluded that for the in situ experimental set-up diffusion is still the overruling phenomenon (even with a 30,000 to 75,000 higher seepage rate).

From the first retrieved Eu-experiment it can also be concluded that an extremely small fraction of the tracer is almost not retarded while the bulk of the activity remained sticking on the source.

Autoradiographs of slices of the cores of the first Eu-experiment showed that the migrated activity is not disseminated homogeneously over the cores but spots with higher activity were detected.

The tracer injection experiments were performed in a piezometer nest beyond the two metres thick concrete end wall of the URL. The piezometer nest is composed of a series of 10 small filters which are embedded in the clay mass between 1 and 10 meters distance from the concrete end plug. This experiment which involves migration distances on the metre scale in undisturbed clay may be considered as a good exercise for model validation. As the distance between the filters in this piezometer nest is 90 cm, migration experiments with only non-retarded tracers have to be considered here (injection planned in 1988). It is expected that such tracer injected under such circumstances will migrate with almost spherical symmetry. The technique for tracer injection has been tested with a 100 micro-Ci I-131 source. Mini-piezometer nests with filters 1 cm long and at 5 cm interval are under construction. They are intended for migration experiments with weakly retarded tracers.

3. Application of isotopic techniques and hydrochemistry for the characterisation of a multi-layered aquifer system

Hydrochemical data, collected during several years, have been analysed for possible interrelations. These relations might provide indications on the processes determining the chemical behaviour of the overall hydrological system. It has been found that the geochemistry is controlled by the $CaCO_3$-CO_2-system, and that the higher pCO_2 observed (pCO_2 = around 10 E-2) is due to the dissolution of $CaCO_3$. According to the equilibrium calculations, carbonate minerals are probably important secondary minerals. However Ca++ concentrations tend to be smaller than expected from those calculations. This is probably due to the exchange of Ca++ for Na+ by the clay minerals in the water-bearing formations.

The impoverishment of SO_4^{--}, derived from the SO_4/Cl-ratio in the confined aquifers of the Brusellian and the Rupelian sands, has been related to the oxidation of organic matter. The oxidation processes thus produce also CO_2, which contributes also to higher pCO_2-values.

When calculating the chemical equilibrium with some common minerals, as a function of depth or along a flowpath, one observes that the saturation index steadily increases with depth but remains undersaturated with respect to dolomite, calcite or gypsum; However, for all minerals considered the equilibrium abruptly changes in the rupelian aquifer, where an oversaturation is observed for calcite and dolomite and a quasi complete absence of gypsum; those observations provide evidences that the aquifer over- and underlying the Boom clay are totally distinct subsystems.

Samples taken from the piezometers installed in the Boom clay around the URL, were send to the ETH-Zürich for determination of C-14 activity by tandem accelerator mass spectrometry. All samples yielded apparent ages older than 28,000 years, which is the detection limit for 1 mg samples. It is expected that this limit will be extended to 38,000 years for the 5 mg samples which are prepared now. Orientating tests on stable isotopes in the groundwaters did not yield firm conclusions or strong directives for further research which could help to confirm by stable isotope hydrometry the hydrodynamic concept of the multi-layered system.

LIST OF PUBLICATIONS

J. PATYN, "Contribution à la recherche hydrogéologique liée à l'évacuation de déchets radioactifs dans une formation argileuse", EUR 11077 FR

J. PATYN, P. del Marmol, M. Monsecour "Environmental Tracers for validating Predictive Models", EUR 11037 EN, Vol. 2

J. PATYN, A. BONNE, E. LEDOUX "Geohydrologisch onderzoek in Noord-België in verband met de berging van radioactief afval", Water, aug. 1987, nr. 35

T. MIMIDES, J. PATYN "Dispersivity determination in the neogene aquifer of the Campine Belgium with the help of a regional hydrogeochemical method", Mining Metallurgical Annals, Nr. 64, aug. 1987

P. DE REGGE, A. CREMERS, P. HENRION, M. MONSECOUR, M. PUT "Facts and features of radionuclide migration in Boom clay", International Confer. on chemistry and migration behaviour of actinides and fission products in the Geosphere, Munich, 14-18 September 1987

P. HENRION, M. PUT "An improval method to evaluate radionuclide migration model parameters from flowthrough diffusion tests in reconsolidated clay plugs", Poster, International Confer. on chemistry and migration behaviour of actinides and fission products in the Geosphere, Munich, 14-18 September 1987

A. MAES, P. HENRION, J. DE BRABANDERE, A. CREMERS "Europium humic acid complexes in reducing conditions", Poster, International Confer. on chemistry and migration behaviour of actinides and fission products in the Geosphere, Munich, 14-18 September 1987

The Role of Organics in the Migration of Radionuclides in the Geosphere

Contractor: Risø National Laboratory, DK
Contract N°: FI1W/0066
Working Period: july 1986 - december 1989
Project Leader: Lars Carlsen

A. Objectives and Scope:

A review on the possible role of organic species in the ground water on the migration behaviour of radionuclides in the geosphere is required. Considerable amounts of data are available. They are, however, rather scattered throughout the literature.

An experimental study as well as theoretical considerations on the influence of organic complexing agents on the sorption, and hence migration behaviour of radionuclides are of fundamental interest in attempts to evaluate the possible transport of released radioactive waste with ground water.

Characterization of naturally occurring organics, e.g. humic and fulvic acids is of general interest, due to the omnipresence of these polymeric species in the terrestrial environment and to their known complexing abilities towards metal ions.

B. Work Programme:

B.1. Review of available literature on the influence of organic compounds including experimental and theoretical data obtained at Risø.

B.2. Batch-type experiments to elucidate the influence of organics on radionuclide sorption.

B.3. Column-type experiments to elucidate the influence of organics on radionuclide migration.

B.4. Theoretical study to elucidate the effect of complex formation on radionuclide migration.

B.5. Characterization of humic acids partly within the frame of the joint european programme on humic acid characterization.

C. Progress of Work and Obtained Results

Summary

The preparation of the review paper is nearly ended. The first four chapters, comprising 'Introduction', 'Organic Compounds in the Geosphere', 'Behaviour of Organics in the Terrestrial Environment', and 'Complex Formation' are available in draft version. The final chapters, e.g. the evaluation and discussion of available literature are in progress. It is expected that the draft version will be available by the end of march.

Column experiments have been carried out. The influence of complexing agents appears clear, as an increased mobility of the radionuclides could be observed.

Theoretical considerations on the influence of complexing agents on the migration behaviour of radionuclides will be included in the final report.

The laboratory has during 1987 invested considerable effort in participating in the joint european intercomparison study on humic acids.

Progress and Results

1. Review (B.1.)

In accordance with the proposed structure of the review report the first four chapters have been written. A short introduction to the subject is given as chapter 1.

Chapter 2 describes organic compounds in the geosphere. This includes naturally occurring as well as artificially introduced organic species. The naturally occurring organics can be divided into the high molecular weight species as humic and fulvic acids and the low molecular weight organic compounds. In the case of the latter type especially the organic acids received attention due to their ability to complex metal ions. In connection with the artificially introduced organic compounds the multidentate species as e.g. the "EDTA-family" are of major concern, as they form extremely stable complexes with metal ions.

Chapter 3 summarizes the behaviour of organic species in the terrestrial environment, which includes subjects as sorption and persistence in the environment. The latter subject are further subdivided, owing to the nature of the possible degradation, i.e. chemical or microbiological degradation.

Chapter 4 gives the basics of complex formation including some rather simple calculations to evaluate the possible presence and influence of certain types of complexes. This method can also be used to evaluate the speciation of metal ions in the presence of a manifold of complexing agents, which typically will be the case in ground water.

The final two chapters discussing available literature on the influence of organics as well as experimental and theoretical results obtain in the frame of this study will available within the first months of '88.

It should be noted that the review relies heavily on available literature. Thus, the text will be kept to a minimum, however, with extentive refences to the literature.

2. Experimental and Theoretical Work (B.2. - B.5.)

Column-type experiments have been carried out, especially studying the transport of Co through model ion-exchange columns. It can be concluded that apart from the possible presence of organics, the pH of the "ground water" appeared to be crucial. Only at rather low pH Co was retained. At pH around neutral no retention of Co by the Dowex50 ion exchange resin could be observed. It was concluded that the presence of the acidic hydrated Co ions was involved in the sorption process. The presence of organics mobilized part of the Co, the amount depending of the pH. The organic species used were EDTA and citric acid.

A substantial effort has during 1987 been put into the interlaboratory comparison study on humic acids.

Humic acid samples (commercially available as well as from the Gorleben site) have been characterized based on their content of functional groups, i.e. carboxylic groups and phenolic groups. These groups are of special interest, since the protons from these groups may participate in the complexation with metal ions. The content of a wide range of metal ions in the humic acid samples has been determined by AAS and ICP-MS techniques. The laboratory also tried to study the size distribution of the samples applying a liquid chromatography technique using light scattering detection. However, it appears that due possible to fluoresence phenomena the technique is not very well suited for humic acid samples. However, our participaion in the size distribution study was not foreseen.

Studies on the interaction between humic acids and trivalent europium ions, especially focussing on the formation of soluble complexes have been initiated. The ion-exchange technique is used to determine interaction constants. Results are not yet available. A study to evaluate the possible applicability of a modified dialysis technique has been initiated.

ACTINOIDE MIGRATION PHENOMINA IN GROUNDWATER: COLLOID GENERATION AND COMPLEXATION WITH NATURAL ORGANICS

Contractor: Institut für Radiochemie, TU München

Contract No.: FI 1W/0067

Duration of contract: Sept. 1986 - Dec. 1989

Period covered: 1. Jan. 1987 - 31. Dec. 1987

Project leader: J.I. Kim

A OBJECTIVE AND SCOPE

Important geochemical processes that govern the migration of actinides in deep geological aquifer systems are: hydrolysis reaction, redox reaction, complexation with inorganics as well as organics and colloid generation. The colloid generation and complexation with natural organics, e.g. humic substances, appear to be the most significant geochemical phenomena with regard to actinide migration in many different aquifer systems.

The contract research deals, therefore, with the colloid generation of representative actinides and their complexation with natural organics, particularly humic substances in different groundwaters. The results are expected to give an insight into the migration mechanisms of actinides in the geosphere.

B WORK PROGRAMME

B 1. Actinide colloid generation in groundwater

- Characterization of colloids
- Generation mechanisms of actinide pseudocolloids
- Quantification of colloid generation in a migration medium for actinides

B 2. Actinide complexation with natural organics

- Characterization and complexation study
- Humic substances as organometallic colloids
- Mobility of complex species and colloids in aquifer systems
- Quantification of actinide mobility

B 3. Interlaboratory comparison exercise on complexation with natural ligands (COCO-group: TUM, CEN/SCK, KUL, CEA-FAR, Risø Nat. Lab., BGS, JRC-Ispra and other new members)

- Intercomparison of characterization methods
- Separation and production of natural humic acids present in the reference sites
- Intercomparison of stability constants

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The dissolved organic carbon (DOC) has been analysed in various groundwaters from the Gorleben area. Humic and fulvic acids from a few selected groundwater have been separated and characterized for their protonation capacity, size distribution, element composition, contents of inorganic impurities and spectroscopic properties. The study has been also extended to a commercial humic acid of ALDRICH and incorporated in the interlaboratory comparison exercise in the COCO-group work of the CEC projekt MIRAGE II.

The colloid study has been carried out for natural colloids in a wide variety of Gorleben groundwaters, particularly for their chemical composition and the generation process of Am-pseudocolloids.

Progress and results

1. DOC concentration and its composition

In 44 different groundwaters taken from various deep aquifers in the Gorleben area the DOC concentration is found to be varying from the minimum at 0.1 mg C/L to the maximum at 99.1 mg C/L. Characteristic features observed are as follows:

- Dissolved organics in these groundwaters are mainly composed of humic and fulvic acids
- Separation of organics shows that in higher DOC concentrations (>10mg C/L) humic acid is predominant, wheras fulvic acid appears to be the major component in lower DOC concentrations
- They are heavily loaded by inorganic metal ions and hence present as colloidal form which is called as natural humic colloid
- Concentrations of tri and tetravalent metal ions in groundwaters are closely correlated with DOC concentrations

2. Am humic colloid generation

Upon introducing the Am^{3+} ion in groundwater containing natural humic colloids, the generation of Am pseudocolloids is observed as illustrated in fig. 1. The concentration of humic substances in groundwater is quantified as the DOC-concentration in this figure. In groundwater with more than 10 mg C/L DOC, the solubility of Am^{3+} reaches up to 10^{-4} mol/L. By ultrafiltration with decreasing pore size, the Am concentration in the solution decreases gradually, implying that the Am^{3+} ion is bound to natural humic colloids present. The spectroscopic speciation shows that there is no Am humate complex ions but Am humic colloids present. In groundwater with lower concentration of DOC (<3 mg C/L), the Am^{3+} solubility appears substantially decreased, e.g. $< 10^{-6}$ mol/L. A reversible exchange process of Am^{3+} on natural humic colloids is demonstrated in fig. 2. This groundwater contains 7.8 mg C/L DOC as humic substances. The filterable amount of Am at 1.3 nm pore size increases with a pH decrease, showing the desorption of Am^{3+}. While increasing pH from 2 to 8 the Am^{3+} ion becomes sorbed again on humic colloids. Natural humic colloids appear to be a soluble ion exchanger in groundwater.

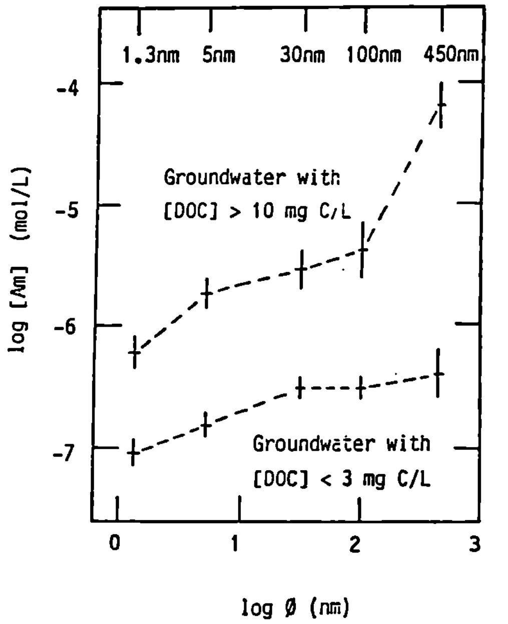


Fig. 1: Ultrafiltration of Am(III) humic colloids in groundwaters with different DOC concentrations. The Am(III) concentration in filtrate varies with filter pore size.

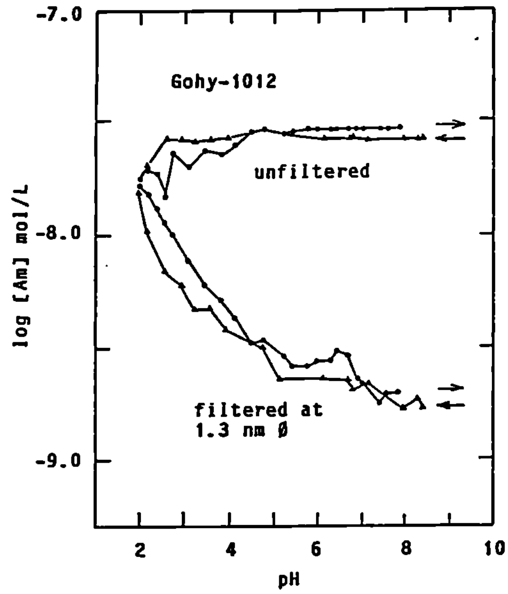


Fig. 2: Generation of Am(III) pseudocolloids (humic colloids) in the Gohy-1012 groundwater by dissolving the Am hydroxide precipitate and diluting it with the fresh groundwater. The pH titration is made from pH = 8.4 to 2.0 and back titrated. The Am concentration is determined in unfiltered solutions and filtrates at 1.3 nm pore size.

3. Spectroscopic characterization of humic complex and humic colloid of Am(III).

The Am humate complex is speciated as shown in fig. 3 by spectrophotometry, since its absorption at 506.5 nm can be well distinguished from the main absorption of the Am^{3+}ion at 503 nm. The Am humic colloids, which are produced by sorption of the Am^{3+}ion on natural humic colloids in groundwater, do not show a distinctive absorption peak, instead generate an intense light scattering. The spectroscopic observation of such a light scattering is demonstrated in fig. 4 (a), which is a photoacoustic spectrum, being equivalent to absorption spectrum, of 2 x 10^{-6}mol/L Am(III) in natural groundwater containing about 15 mg of humic substance. This amount of Am(III) remains stable in the groundwater at pH 8.2 due to the formation of Am humic colloids. Conditioning this groundwater with addition of EDTA (Ethylmediamine tetraacetic acid) to one portion and of HCl to the other portion results in the desorption of Am^{3+} from humic colloids as shown by fig. 4(b) and 4(c). On adding EDTA the Am^{3+} ion is de-

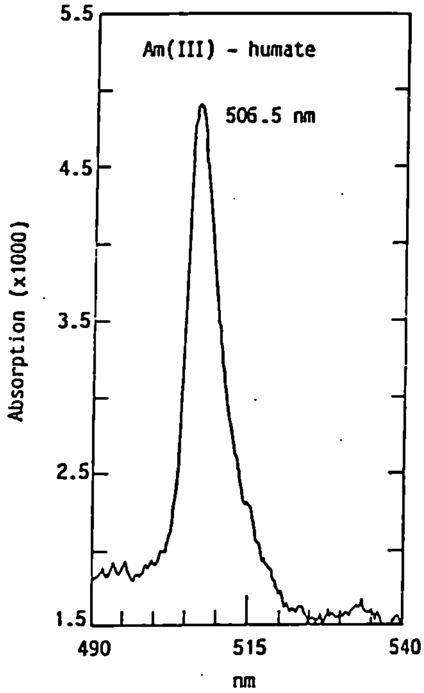


Fig. 3: Absorption spectrum of the Am Humate (1.1×10^{-5}mol/L Am) in 0.1 M $NaClO_4$ (pH 9.2; 10mg/L HA)

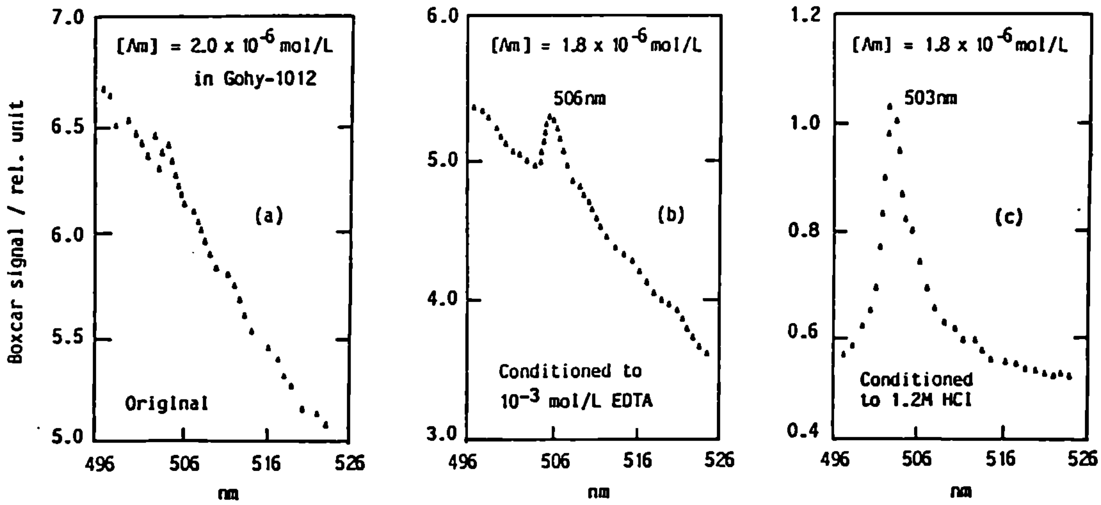


Fig. 4: Photoacoustic spectra of the Am(III) pseudocolloids (humic colloids) in the Gohy-1012 groundwater (a), the Am(III)-EDTA complex (b) and the Am^{3+} ion (c). The latter two spectra are taken after conditioning of colloids for 6 months in EDTA or HCl.

sorbed via EDTA complexation. The natural humic colloids remain unperturbed as illustrated by fig. 4(b) in which the light scattering caused by the presence of colloids is shown by a relatively high baseline. Upon acidification, as seen in fig. 4(c), the Am^{3+} ion is desorbed (absorption peak at 503.0 nm) and at the same time humic substance becomes precipitated by a proton saturation. This is the reason why the baseline is substantially lowered and the absorption band at 503.0 nm becomes clearly pronounced as appeared in fig. 4(c).

4. Interlaboratory comparison exercise

The objective of this exercise is to compare characterization procedures of different laboratories with one another. Three different kinds of humic acids have been prepared by us and distributed to 7 laboratories in CEC member countries. One humic acid is a commercial product of Aldrich Co. in Na-form, which is homogenized and portioned 50 g each. A part of this humic acid is purified, protonated, freeze-dried and portioned 5 g each. The third humic acid is extracted from a groundwater from the Gorleben area (Gohy-573), purified, freeze-dried and protioned 2 g each. All participating laboratories have received the three different humic acids from each of the same batches.

The characterization involves the determination of

- Element concentration: CHONS
- Inorganic impuries of macro- and micro-concentration
- Protonation capacity and pKa
- Spectroscopic properties: IR-spectrum, E4/E6 ratio
- Humidity concentration
- Size distribution

The main part of interlaboratory comparison results is available and will be summarized in a fortherming CEC report.

List of Publications

J.I. Kim, G. Buckau, R. Klenze: Natural Colloids and Generation of Actinide Pseudo Colloids in Groundwater, EUR 11037 EN (1987).

J.I. Kim, G. Buckau, W. Zhuang: Humic Colloid Generation of Transuranic Elements in Groundwater and their Migration Behaviour, Mat. Res. Soc. Symp. Proc. 84 (1987) 747.

J.I. Kim, G. Buckau, R. Klenze: Characterization of Colloids in Groundwater, RCM 01687 (1987) pp 29.

STUDY OF THE INTERACTIONS BETWEEN ORGANIC MATTER AND TRANSURANIUM ELEMENTS

Contractor : CEA-IRDI/DRDD/SESD/SCPCS - FONTENAY-AUX-ROSES - FRANCE

Contract n° : FI1W/0068

Duration of Contract : From 1985 to 1989

Period covered : 1987

Project Leader : Mme MOULIN, M. BILLON

A. OBJECTIVES AND SCOPE

As it has been presented in the previous annual progress report (CEC Report n° 11089) the main objective of this programme is to study the importance of natural organic ligands (humic and fulvic acids) as complexing agents of radionuclides in their migration or retention behaviour in the geosphere. An additional point to this programme previously described is to emphasize the role of the natural colloids (inorganic and/or organic species) present in deep or shallow aquifers, which could have a major importance in the transport of radioelements /1-3/. The goals of this resarch programme are :

- to define the characteristics and properties of the natural colloids including humic substances,
- to determine the formation conditions of organic complexes with radioelements and the interactions with the natural colloids (sorption, complexation, ...)

B. WORK PROGRAMME

B.1. Isolation and characterisation of humic substances

B.1.1. Concentration of humic materials from natural groundwaters : sampling, concentration, fractionation, purification.

B.1.2. Characterisation of humic materials by physical and chemical methods : elementary, mineral, functional, potentiometric and molecular size analysis.

B.2. Interactions between humic coumpounds and transuranic elements

B.2.1. Development of the chromatographic method selected for the complexation studies

B.2.2. Determination of interaction constants by this method (as a function of pH, ionic strength, metal and ligand concentrations). Comparison with other methods (as spectroscopy)

B.3. Interlaboratory comparison exercice on these two research arcas

B.4. Studies on natural colloids

B.4.1. Isolation of colloids from natural waters by ultrafiltration : sampling, water analysis, development of the technique.

B.4.2. Characterisation of the colloids for the determination of their population ; their size and composition : use of Scanning Electron Microscopy.

B.4.3. Interaction with radionuclides : retention studies.

B.4.4. Interlaboratory comparison exercice on these topics.

NB : The part B.4 is on additional point to the previous work programme.

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of avancement

The isolation of humic materials from a natural water (Fanay-Augères ; a granitic mine) is going on with good results : more than 3 g of products have been obtained ; the characterisation of humic and fulvic acids is under investigation.

The chromatographic technique used for the complexation studies between humic materials and americium is in progress. All the system (glove-box, chromatographic system, the on-line detector with the associated electronics) is operational. Preliminary results of complexation experiments have been obtained in acidic medium.

Spectrophotometry has also been used for the determination of formation constants between Am(III) and humic substances at acidic pH.

The characterisation of natural colloids obtained from MARKHAM CLINTON Water (U.K.) by diultrafiltration or dialysis (from the interlaboratory exercice /3/) has been developped by Scanning Electron Microscopy coupled with EDX for the determination of colloid population, size and composition.

The general work progress status is as follows : B.1., B.2., B.3. are progressing normally ; B.4..1 will begin in 1988, B.4.2. and B.4.4. are in development ; B.4.3. is delayed.

Progress and Results

Isolation and Characterisation of Humic Substances

The humic materials are isolated from a natural granitic water (Fanay-Augères/Massif Central) by concentration on an ionic-exchange resin (DEAE-cellulose). Due to the very low concentration of organic carbon in this water (2 mg/l), this step is very long. More than 3 grammes of humic materials have been obtained and this operation goes on in order to have enough coumpounds to be distributed to the different laboratories involved in the intercomparison exercice. The procedure used for the obtention of humic and fulvic acids is shown on Figure 1 (B.1.1.).

The Fanay-Augères water has been analysed under a one-year period. No significant change in the composition has been observed. It is a poorly mineralised water where humic and fulvic acids are present in equal quantities. The characterization is in progress (B.1.2.).

The characterisation of humic materials in the frame work of the interlaboratory comparison exercice (B.3.) is nearly achieved for the "reference product" : the commercial humic acids ALDRICH. Two properties are intensively studied due to the lark of reproductible results for these analysis : the proton capacity related to the complexing capacity is determined by acid-base titration ; the analysis of the molecular size related to the transport, is determined by chromatography and ultrafiltration.

Isolation and Characterisation of natural colloids

The S.E.M. observation of MARKHAM colloids (B.4.2., B.4.3.) /3/ has been done : 1.5 10^6 particles/l have been estimated in this water with sizes from 0.1 to 1 µm (dispersed particles and some agregates). The effect of time on water storage (and so on colloid concentration is under investigation.

Interaction Studies between Transuranic Elements and Humic Substances

The chromatographic technique for complexation studies /4/ is operational in the glove-box : the chromatographic system (pump, injector, column), the on-line detector for alpha detection (a glass scintillator) with the associated electronics. The calibration of the detector has been made for Am, and preliminary studies have been done on the elution of Am in different citrate media on a Sephadex G-15 column to check the reproductibility of the recovery of Am (area of the peak). In the presence of humic acids the typical chromatogram of this technique (a positive peak, followed by a negatived one /4/) has been obtained proving the feasability of the method. However complementary studies are under investigation to explain the lack of resolution of two peaks.

The spectrophotometric study of the system Am(III) humic substances at 503 nm has shown the formation of rather strong complexes at pH 4.65 and 0.1 M ionic strength. Conditional formation constants of this system are given in Table 1 assuming a 1.1 stoechiometry.

List of Publications

- V. MOULIN ; P. ROBOUCH ; P. VITGORGE and B. ALLARD "Spectrometric Study of the Interactions between Americium III and Humic Materials" ; Paper presented at the 2nd ICLA, Lisbon, April 6-10, 1987 and inpress in Inorganic Chimica Acta (1987).
- B. ALLARD ; V. MOULIN ; L. BASSO ; M.T. TRAN and D. STAMMOSE "Americium Adsorption on Alumina in the Presence of Humic Materials" ; Paper presented to the IMPACT Conference, Nancy, June 1987 and in press in Geoderma.
- V. MOULIN ; P. ROBOUCH ; P. VITORGE and B. ALLARD "Environmental Behaviour of Americium in Natural Waters" ; Paper presented in Migration 87, Munich, September 1987 and submitted to Radiochimica Acta.

- V. MOULIN ; P. ROBOUCH ; D.STAMMOSE and B. ALLARD "Interactions between Americium(III) and Humic Materials ; some results" presented at an OCDE/NEA Workshop, Baden, November 1987.

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/1/ RAMSAY J.D.F., AERE R 11823, UKAEA, Harwell (1985)

/2/ DEGUELDRE C.A. and WERNLI B., Anal. Chim. Acta, 195, 211-223 (1987)

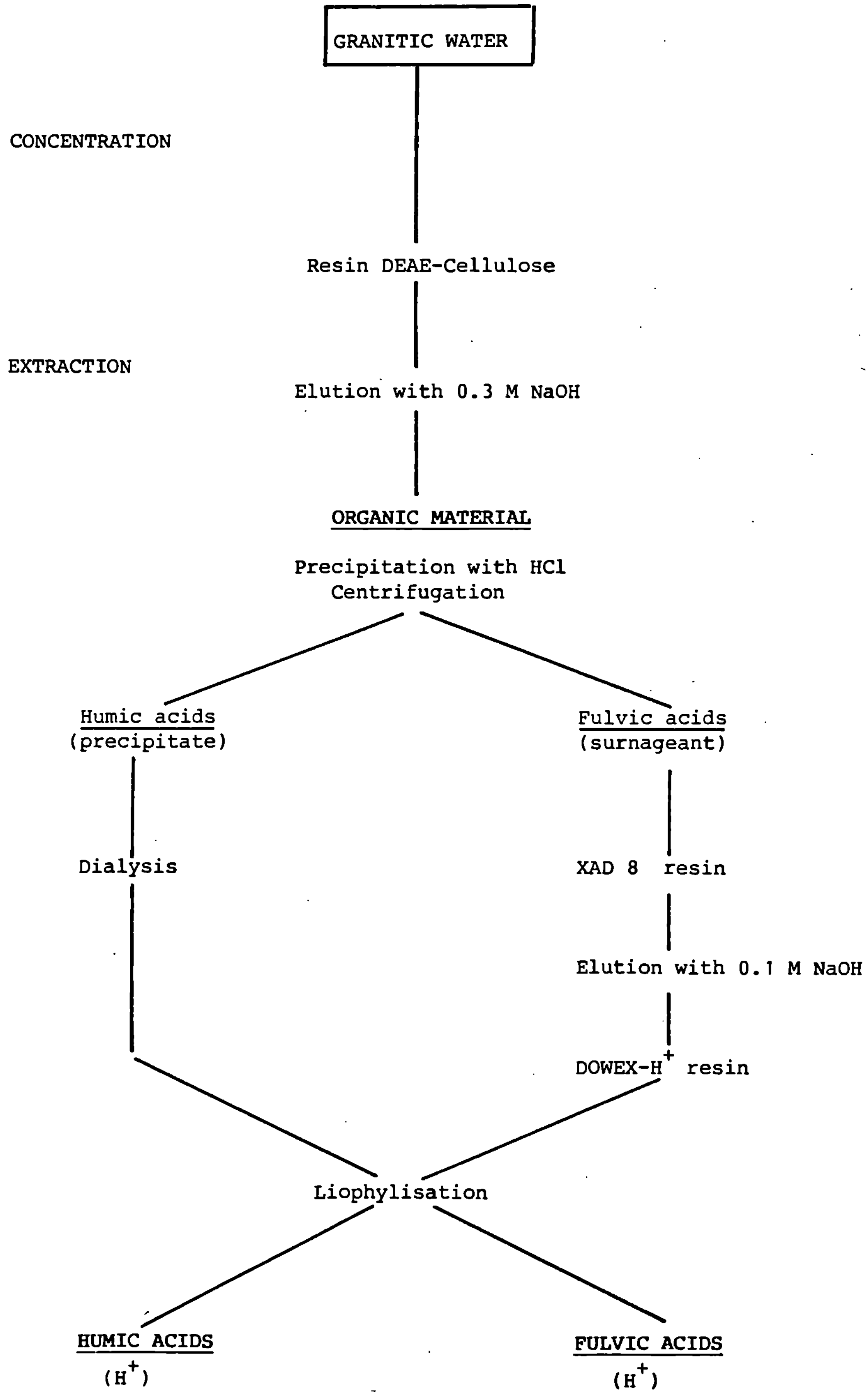
/3/ ROSS C.A.M., DEGUELDRE C., IVANOVITCH M. and LONGWORTH G., Proc. CEC Conf. on Natural Analogues in Radioactive Waste Disposal, Brussels, 1987.

/4/ MOULIN V., Rapport CEA-R-5354 (1986)

Table 1 : Formation constants values of the system Am(III) - Humic substances assuming a 1.1 complex
pH 4.65 - I = 0.1 M $NaClO_4$ - θ = 20°C

Ligand	Origin	log β (l/eq)	log β (l/g)	Equivalent Capacity (meq/g)
Fulvic Acid	Groundwater	6.2	3.1	0.88
Humic Acid	Surface Water	7.0	4.1	1.20
Fulvic Acid	Surface Water	6.0	3.1	1.22
Humic Acid	Lake Sediment	7.0	4.0	1.03
Humic Acid	Soil	(7.5)	(4.7)	(1.40

Figure 1 : Procedure of Isolation, Separation and Purification of Humic Materials from Natural Waters.



DIFFUSION, SORPTION AND STABILITY OF RADIONUCLIDE-ORGANIC COMPLEXES IN CLAYS AND CLAY-ORGANIC COMPLEXES

Contractor: Imperial College - London (UK)
Contract n°: FI1W/00147
Contract period: 01.01.88 - 30.06.90
Project leader: L.V.C. Rees

N.B. Contract started only on 01.01.1988 so no report made available.

Effects of natural organic substances on the geochemistry of a radioactive waste repository.

Contractor: UKAEA, Harwell Laboratory, UK.
Contract No: FI1W/0156
Duration of contract: January 1988 - December 1989
Project Leader: F.T. Ewart

A. OBJECTIVES AND SCOPE

A significant proportion of the dissolved organic carbon in natural groundwaters consists of humic and fulvic acids. There is evidence that these may form complexes with some radionuclides which may result in increased aqueous concentration either due to increased solubility or decreased sorption into surfaces. Previous work in this laboratory has involved the completion of a literature review /1/, an investigation of possible methods of characterisation and some preliminary studies of the effect of humic acid on the sorption of americium on cementitious materials. This programme is for a continuation of that research in those areas relevant to a radioactive waste repository.

There are four main objectives in the programme. Limited humic characterisation forming part of the "CoCo" intercomparison exercise will be made on groundwater samples obtained from geological structures which are typical of reference repository sites. The effects of humic acids on the solubility of Pu, Am and Np in waters representative of a cementitious repository will be investigated and the influence on sorption studied for these elements. A study will be made of the feasibility of including the effects of natural organic compounds in geochemical modelling codes.

B. WORK PROGRAMME

B.1. Characterisation of humic substances.
B.2. Effects of humic acids on Pu, Am and Np solubilities.
B.3. Effects of humic acids upon the sorption of Pu, Am and Np on cement grouts.
B.4. Modelling Studies

C. PROGRESS OF WORK AND OBTAINED RESULTS

No progress to date - contract work to commence January 1988.

References

/1/ EWART, F.T., WILLIAMS, S.J., Harwell Laboratory Report AERE R 12023 (1986)

SIMULATION OF RADIONUCLIDE EXCHANGE BETWEEN AQUEOUS AND MINERAL-ORGANIC PHASES

Contractor: University of Nantes (F)
Contract n°: FI1W/0197
Contract period: 01.01.88 - 31.12.89
Project leader: J. Pieri

N.B. Contract started only on 01.01.1988, so no report made available.

4.3.B. In situ migration experiments and development of measuring techniques

In Situ Determination of the Effects of Organics on the Mobility of Radionuclides in Controlled Conditions of Groundwater Flow

Contractor:	British Geological Survey, Keyworth, Nottingham
Contract No:	FI-1W-0064(UK)
Duration of Contract:	July 1986 - June 1989
Project Leader:	G.M.Williams

A. Objectives and Scope

The broad objective is to verify by means of *in situ* field tracer tests, predictions of the mobility of radionuclides in a shallow glacial sand aquifer, having taken into account the potential effects of organics (natural and introduced) on radionuclide speciation and mobility.

The tracer tests will be undertaken in a remote part of the low level radioactive waste site at Drigg. Prediction of their outcome is based upon detailed hydraulic characterisation of the field site, coupled with laboratory studies of radionuclide sorption and organic complexation. Liaison has been established with Loughborough University (LUT) for direct speciation measurements, the University of Wales Institute of Science and Technology (UWIST) for radionuclide speciation modelling, and Delft Geomechanics for solute transport modelling.

B.Work Programme

The project is divided into a number of research areas as follows:-

(1) Aquifer characterisation and instrumentation - Involves the determination of aquifer hydraulic properties, its geochemistry, mineralogy and groundwater composition, particularly the nature and amounts of natural organics (humic and fulvic acids) and colloids. Development of instrumentation to monitor groundwater composition and radionuclide migration.

(2) Characterisation of complexes and colloids - interlaboratory comparison within the CEC, to characterise, and determine stability constants with selected radionuclides, for commercially available humic acid and natural organics from Drigg, Mol, Ispra etc. A parallel excercise is underway for colloids.

(3) Laboratory sorption studies - includes batch sorption experiments to determine the effects of natural organics on radionuclide sorption, kinetic measurements, and direct speciation determinations of radionuclide complexation in groundwater after equilibration with the sediment.

(4) Modelling - Speciation models will be used to predict the speciation of radionuclides in the sorption experiments and help to determine the important mobile species in the field test. Deterministic flow modelling will aid in the design of the borehole array for the tracer tests and form a basis for reactive mass transport models.

(5) Field tracer experiments - initial tracer tests will compare various conservative tracers (^{131}I, Cl, and ^{3}H) and provide background data on the hydraulic characteristics of the aquifer. Subsequent tracer tests will involve reactive radionuclide species with the addition of organic solutes.

C. Progress of work and results obtained

State of advance

Some delay has been experienced in developing techniques for installing instrumentation in the field array. However, the array has now been sucessfully completed and tracer tests will commence shortly. Apart from this, the remaining work is on schedule, but difficulties are being experienced in extracting reasonable amounts of natural organic material because of its relatively low concentration in the Drigg groundwater (up to 15 mg/l).

Progress and results

(1) Aquifer characterisation and instrumentation (B1)

The array in which the tracer tests are to be undertaken has now been completed satisfactorily using specially developed techniques to minimise disturbance of the aquifer. The array comprises a pair of wells (recharge-discharge duplet 3.5 m apart) between which a tracer release well and three multilevel samplers and γ – probe access tubes are located. Good core recovery has been obtained and cores are being analysed at present for mineralogy, bulk composition by XRF, physical properties, and microbial populations. The system is presently being tested hydraulically and will be followed by a non active chloride tracer test prior to injecting radiotracers ^{131}I and ^{3}H.

(2) Complexes and colloids (COCO excercise, B2)

Characterisation of common samples of humic materials (Aldrich Na and H forms, and Gohy-573(H)) provided within the CEC COCO interlaboratory comparison excercise has been essentially completed. A report has been submitted.

Characterisation by BGS includes:-

- Moisture determination
- Metal determinations
- Elemental analysis (C,H,N)
- IR spectroscopic studies (including FT-IR)
- E_4/E_6 ratios (UV)
- Functional group analysis (total acidity, carboxylic acid and phenolic acidity; carbonyl groups, and quinone groups and hence ketones by difference).
- Particle size distribution by ultrafiltration.

Groundwater from a borehole near the new experimental array has been treated with DEAE-cellulose to extract natural organic material. Measurement of total organic carbon (TOC) in the original water and in the treated water showed that only 55% of the organic material was extracted. (This aspect is discussed further in section B 3)

The natural organic material desorbed from the DEAE with 0.1M NaOH has been separated at pH 1 into humic and fulvic material. However, the sample contained predominantly fulvic material with only a trace of humic. Because of the low concentration of TOC in the groundwater it has not been possible to obtain sufficient sample for complete characterisation or for distribution to COCO club participants. What has been obtained has been fused into a KBr disc for FT-IR analysis. Boreholes have now been installed in a new tracer array at Drigg and a large volume of groundwater has been removed from which natural organic material will be extracted by treatment with DEAE and other resins. This will then be purified and if sufficient is obtained will be distributed to the COCO participants.

The extraction of predominantly "fulvic" organic material from Drigg groundwater presents a problem as no one extraction method is appropriate or free from problems. XAD resins are now being considered in addition to DEAE but it still remains a difficult problem to identify the composition of the material extracted, or that remaining in solution after treatment. Time is therefore required to review extraction techniques in general, and to establish a methodology for subsequent organic characterisation (particularly for low molecular weight components).

As part of the colloid sampling inter-comparison excercise groundwater was taken in January 1987 from a public supply borehole at Markham Clinton in Nottinghamshire, which draws from the confined Triassic Sandstones. Both EIR and Harwell took samples by two different methods (pulsed, cross-flow ultrafiltration, and tangential diafiltration). The characterisation included colloid population, composition and size distribution determined on colloid concentrate samples obtained in the field. Results imply (1) that no artefacts are produced by either sampling method, although some aggregation of colloid particles may occur during storage. (2) Good agreement on populations and size distributuions were obtained by SEM analysis of cross flow filters. (3) limited fractionation of solutes is caused by diafiltration of low salinity water, in particular the uptake of sodium.

This information was presented at the Natural Analogues Symposium in Brussels in April, 1987. Discussions have taken place with AERE Harwell to study colloids at Drigg using similar sampling techniques.

(3) Laboratory sorption studies (B3)

A series of batch sorption experiments has been carried out to assess the effect of organics on the distribution ratio of Co, Sr, Cs and I with Drigg sand. The organics include those naturally present in the groundwater, acetate and EDTA. A number of factors were investigated.

Two primary ground water compositions were used:-
- Natural groundwater
- Groundwater from which organics have been removed using DEAE

Two sand compositions:-
- Natural sand
- Sand from which organics were removed by treatment with 2M NH_4OH.

Acetate or EDTA were added to combinations of natural groundwater and sand and extracted groundwater and sand. However, radionuclide spike was added to the water either 7 days before or 7 days after addition of the EDTA or acetate.

Results for Sr and Cs show that natural and added organics have negligible effect on the sorption values obtained. The results for I experiments are presently being assessed. The results obtained by extracting solid organic material from the sand using 2M NH_4OH are not regarded to be significant since clays and iron oxides which also contribute to radionuclide sorption are also removed.

For ^{60}Co the following results were obtained:-

(1) addition of Co after 7 days gave lower Rd (distribution ratio) sorption values, possibly due to equilibrium not being reached (longer experiments including kinetic measurements are planned).

(2) extraction of natural organic material using DEAE from the groundwater approximately doubled the Rd values for ^{60}Co compared to natural groundwater.

(3) The addition of acetate at 100 mg/l, had no significant effect on ^{60}Co sorption.

(4) EDTA had a dramatic effect on the sorption of ^{60}Co in the following ways:-
a) Rd values for natural and extracted groundwater systems were similar.
b) EDTA at both 10 and 100mg/l, decreased ^{60}Co sorption.

Work has commenced through a sub-contract with Loughborough University, to develop non-invasive techniques to separate bound from free radionuclides in Drigg groundwater. Initially, cobalt which is well known to form organic complexes, has been used as a reference species. Essentially the method uses the weak adsorption properties of Sephadex gel to separate cationic species and preliminary results were presented as a poster at the Munich conference. Results indicate that non-sorbed complexed ^{60}Co is eluted quickly from the column of Sephadex, using groundwater as the mobile phase. The free $^{60}Co^{2+}$ is eluted later. The addition of DEAE cellulose to groundwater removed the majority of the UV 254 nm absorbing species, whereas, 76% of the activity associated with the complexed ^{60}Co remained in solution. Monitoring UV absorbtion at 254 nm therefore, is not a good indicator of the presence of complexing species, suggesting that the organic ligands do not absorb at this wavelength or that the complexes are inorganic.

4. Modelling (B4)

Preliminary hydrogeological data has been discussed with the Delft Geomechanics who are involved in modelling groundwater flow within the array.
Reports on preliminary speciation work are awaited from UWIST.

5. Tracer tests (B5)

Phase two of the work which involves the field tracer tests will commence as soon as possible in 1988. Colloids will be investigated using the AERE filtration rig, and the speciation and laboratory sorption studies will move on to consider other nuclides possibly Eu, Np and Ni for possible inclusion in the field tests. Consideration will be given to the study of the mobility and sorption of iodide and iodate in preliminary tracer tests.

Reports

The following reports have been prepared during the year; a larger number are in the state of advanced preparation:-

Ross C A M, Degueldre C, Ivanovich M and Longworth G, 1987. Colloid Benchmark Excercise: an interlaboratory study of sampling and characterisation techniques for natural colloids in oxidising groundwater. In: Natural analogues in Radioactive waste disposal, Brussels, April 28th - 30th, 1987.

Warwick P, Shaw P, Williams G M and Hooker PJ, 1987. Preliminary studies of cobalt complexation in groundwater. Submitted for publication in the Munich conference proceeding, Migration '87, 12 pp (approx).

Peachey D and Williams G M, 1987. Characterisation of humic material for inter-laboratory comparison. British Geological Survey Fluid Proc. Res. Gp. Rep. No. FLPU 87-5. 19pp.

Title : DEVELOPMENT AND APPLICATION OF A RETENTION PROPERTIES MEASUREMENT SYSTEM IN A GEOLOGICAL ENVIRONMENT USING RADIOACTIVE TRACERS IN THE DRILL-HOLE (self-contained probe FORALAB)

Contractor : CEA/IPSN - CEN CADARACHE
F 13108 St. Paul-lez-Durance

Contract No. : FI1W/ 065

Working period : 36 months

Project Leader : J. PORCHERON

A. OBJECTIVES AND SCOPE

Radionuclides from a subterraneous waste storage place have to force their way through, and interact with, several barriers prior to reaching the geological medium itself.

They are diluted by the suberrraneous water which, by modifying their chemical structure, settles them into a final balance with the medium.

The purpose of this study is to determine the delay term of the radionuclides during their migration through the deep geological environment.

It became evident that it was preposterous to attempt in-laboratory duplication of the prevailing parametric conditions of the natural medium, whether physical, chemical or biologidal.

To avoid the uncertainties connected to laboratory experiments, the probe "FORALAB", whose performances had already been ascertained during the preceding contract (WAS 377-83-7), was developed to permit studying the radionuclide sorption-desorption phenomena in a geological environment in a condition of equilibrium with undisturbed subterraneous waters.

The probe need not simulate the environment as it is plunged into it.

The contract scope is the *"in-situ"* qualification of the probe, using a dual tracing system, i.e. Tritium and Eu on the one hand, Pu and Np on the other hand.

The probe will then be operated in 3 geological sites, of some interest for the Community, i.e. AURIAT (granite), MOL (clay) and GORLEBEN (salt), in order to assess the containment properties of these environments.

The probe is essentially composed of a pump, a syringe, a 20 mm dia., 200 mm long test column and 40 sampling pots. Its double insulation is a safety against drill-hole pollution.

B. WORK PROGRAM

B1. Probe Qualification

The probe will be checked for performance in the hole drilled in the granitic site of AURIAT.

The column, filled with Fontainebleau sand, will be traced by means of Europium and Tritium.

The drill-hole water will be circulated in the column for one day before the tracer injection.

B2. Tests on the Reference Sites

The tests will be performed in the deep holes at AURIAT, MOL and GORLEBEN.

The columns will be filled with a mixture of Fontainebleau sand and 1 to 3 % clay from the site.

The radionuclides used will be Am, Pu and Np.

Each column will be Tritium-calibrated before each individual test.

B3. Finally the results from each individual test will be mathematically processed to yield the delay terms and the adsorption isotherms of each pollutant used.

C. WORK PROGRESS AND RESULTS OBTAINED

C1. State of Advancement

After being entirely tested in the laboratory, the probe has been tested for qualification at - 400 m in the drill-hole of the granitic site of AURIAT.

The test took place on the 16.12.1987. During it an inactive NaCl solution has been injected in a column containing Fontainebleau sand, then 36 samples could be taken. The whole operation has been controlled from the surface using a computer. The experiment developed itself in full conformity with the programme.

C2. Plans

The scientific programme starts at the onset of 1988 with the performance of several tests in AURIAT.

List of publications

PORCHERON J. Developpement et application d'un appareillage de mesure des propriétés de rétention du milieu géologique par traceurs radioactifs en forage (sonde FORALAB).

31.07.1987 FI 1W/ 065

PORCHERON J. Développement et application d'un appareillage de mesure des propriétés de rétention du milieu géologique par traceurs radioactifs en forage (sonde FORALAB).

31.12.1987 qualification de la sonde FI 1W/ 065

Title : Field verification of advanced transport models for radionuclides in heterogeneous soils.
Contractor : Delft Geotechnics
Contract number : FI1W/0083
Duration of contract: from 1987 to 1989
Period covered : upto February 1988
Project Leader : dr. M. Loxham

A. OBJECTIVES AND SCOPE.

The migration of leachate from the site into the surrounding geosphere is one of the key issues in the safety analysis of shallow burial low level radioactive waste sites. This migration is dominated by the balance of convective and adsorption processes, both of which are strongly influenced by soil macro-heterogenities. The overall objective of this program is to assess the importance of typical heterogenities found in shallow soils and to develop modelling techniques to relate structure information to the prediction of the movement of leachate through both the unsaturated and saturated zones.
Earlier programs conducted under community funding have lead to the development of the necessary predictive modelling techniques and their assessment in the laboratory. The scope of work of this particular contract is to use the field experimental results being gathered by the British Geological Survey in their Drigg study to attempt a field scale verification of the modelling techniques.
The results of this work will be especially important at the site assessment stage of a facility and in its safety analysis in that they will allow a proper balance to be found between the extent and detail of the soils information required, the sophistication of the models employed and the nature of the conclusions that can be drawn.

B WORK PROGRAM

The work program is as follows :-

1. Data collection and critical review. This item covers the import of data from the BGS study to this contract.
2. Predictive modelling of the field experiment
   a. Homogeneous models
   b. Stratification models.
   c. Determinate models.
3. Evaluation of the modelling exercise.
   a. Inter-model assessment
   b. Absolute assessment

C PROGRESS OF WORK AND OBTAINED RESULTS

At this point in time the data base is still being assembled from the results of the field assessment being made available by the BGS.

This data will be reported in the next progress report.

Title : *IN-SITU* STUDY OF RADIONUCLIDE DIFFUSION IN CLAYS BY MEANS OF THE AUTOLAB PROBE

Contractor : CEA/IPSN CEN CADARACHE
F 13108 St. Paul-lez-Durance

Contract No. : FI1W/0144

Working period : 30 months

Project Leader : J. PORCHERON

A. OBJECTIVES AND SCOPE

The storage of nuclear wastes in a deep geological formation calls for that a dependable knowledge of the site safety is gained. Significant data on the radionucléide diffusion throughout argillaceous materials should be acquired by *in-situ* observations and measurements in a drill-hole, provided that the conditions of the receptor environment are safeguarded.

In the field of the *in-situ* measurements, two families of instruments* presently exist or are under development :

a) Equipment making it possible a direct measurement of the environment characteristics, such as pH, Eh, Ca^{++} content, temperature, radio-activity, resistivity. Those probes make it possible to obtain a logging of the previously-mentioned parameters in a drill-hole. A drill-hole chomatography probe, for the indirect measurement of chemical elements present as traces in the drill-hole, is presently being developed.

b) The second class of probes is related to the experimentation in a drill-hole to obtain the velocity of radionuclide migration in the fourth barrier. The velocity of the water which is the vector of the radioactive pollution may vary in wide proportions.
First, there is the domain of the convection-dispersion which is that of the FORALAB probe presently used, second, the domain of the diffusion where the very slow progress of the phenomena requires that the *in-situ* experiment complies with special specifications.

* CEA/IPSN - Cadarache Centre.

c) Representativeness of the *in-situ* experiments

The representativeness of the *in-situ* tests is related to the drill-hole water characteristics because, as the hole is being drilled, water is used which is entirely foreign to the environment. Moreover, the hole may also fill itself with water from a higher-lying water table.

From the chemical point of view, however, as chemistry is the criterion for the radionuclide condition, an equilibrium is gradually gained between the foreign water and the geological environment with which it is in contact. There are two phases in the drill-hole, viz. the solid environment which is "in excess" and the water ; the equilibrium is reached by dissolution, the solid environment acting as a buffer.

B. WORK PROGRAM

B1. AUTOLAB is a probe designed for measuring the delay term of the radionuclide *in-situ* in the drill-hole clays.

B2. Specificity of the AUTOLAB probe

The probe is designed for diffusion measurements, which entails particular characteristics for grappling the slowliness of the phenomena.

The specification data required from the probe are as follows :

- operability in a drill-hole without time limitation (in practice, 6 months),
- complete autonomy, no supervision, no power feed,
- good exchange between the drill-hole water and the inside of the probe under static conditions (no pump operating),
- no pollution of the environment.

B3. Description of the probe (Fig. 1)

The probe is composed of a reaction chamber, of 5 l. capacity (65 mm dia., 1500 mm high), capable of containing 10 samples (approximately 10 mm dia., 50 mm high)..

The tracer is contained in a glass bulb which will be ruptured by a weight (messenger) sliding along the carrier cable.

The reaction chamber may be put in communcation with the drill-hole by windows (36 cm^2 surface) which may be actuated using the drill-hole pressure. It suffices for this to lower the probe by a few meters, which acts upon a hydraulic valve held closed by a spring set at a pressure corresponding to the drill-hole depth ; the valve, when opening, permits the action of the hole water on a piston opening or closing the windows.

B4. Experiment

The probe will be used for measuring the *in-situ* migration of radionuclides in clays.

a) Equilibrium stage

In a first stage the argillaceous material samples (in 10 mm dia., 50 mm high tubes) are left to come into an equilibrium with the drill-hole water. The water diffuses into the material ; a diffusive front of equilibrium is formed and will slowly progress for several months.

b) Experimental stage

When the foregoing stage is completed, the windows get closed, the tracer (double tritium-lanthanide or actinide marking) is released from the glass bulb using the messenger (this also puts an electric cell-driven agitator into action).

The tracers arediffused into the clay. A second diffusion front is formed, offset with respect to the first one and propagating in a zone already settled to a chemical balance with the drill-hole water.

B5. Tests planned

- Qualification of the probe on the AURIAT site.

Samples are selected with various sand contents and various natures of argillaceous materials.

The tracers will be Tritium and Europium.

The experiments will take place :

. in the granitic site of PARTENAY,

. in the saline site of GOERLEBEN,

. in the argillaceous site of MOL.

Use will be made of Tritium, of an actinide or, if unavailable, of a lanthanide.

The number and composition of the samples will be determined for each particular case. Filling materials may be usde, as necessary.

C. WORK PROGRESS AND RESULTS OBTAINED

The probe is partly manufactured ; the opening and closing system of the reaction chamber has been tested at depths varying from 200 m to 800 m and, after some modifications, has given satisfaction.
The contract beginning date is the 1st of January, 1988, and 1988 will make it possible tofully perform the development of the probe and also the in-laboratory development of measurement methods.

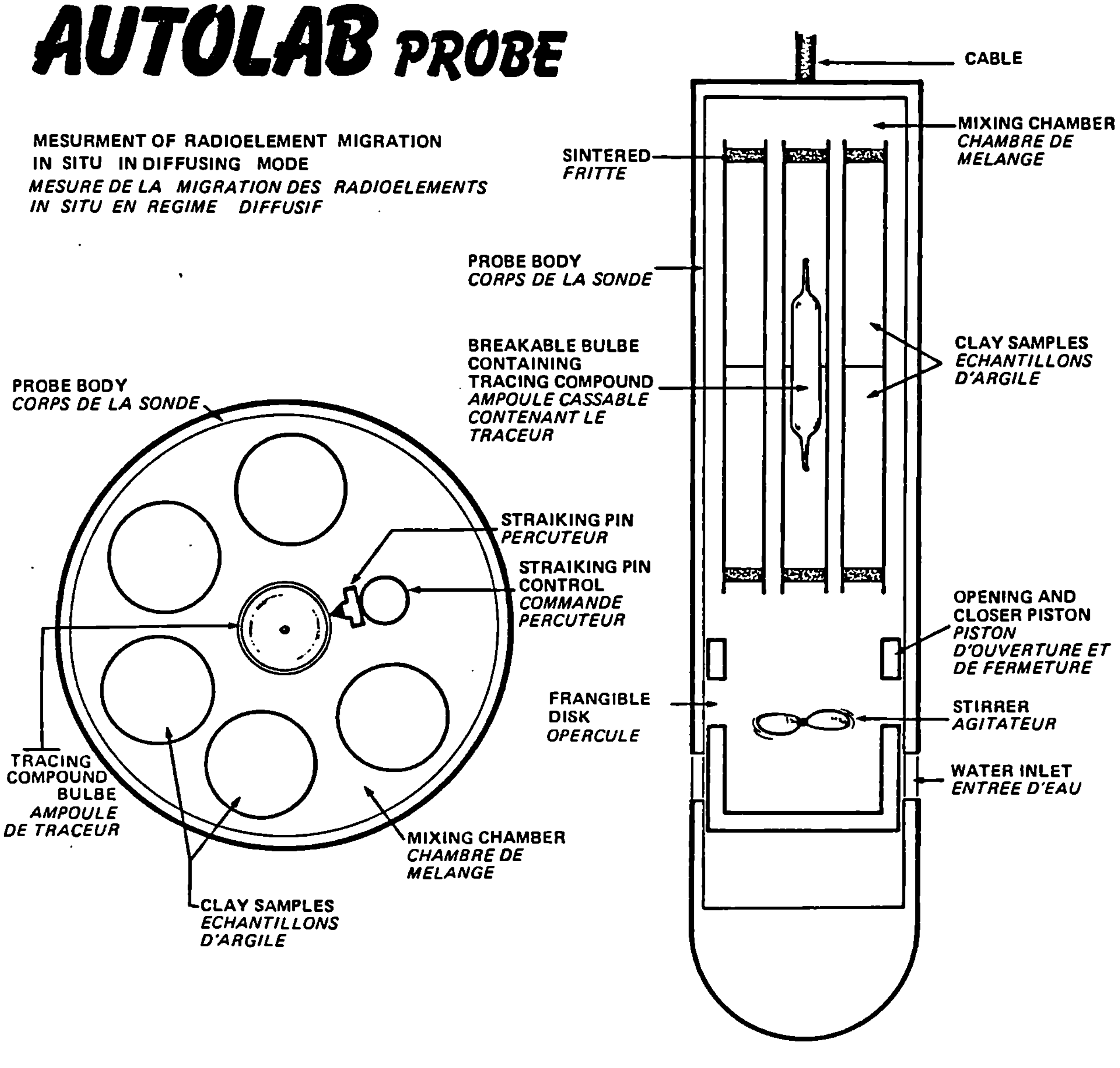

AUTOLAB PROBE
MESURMENT OF RADIOELEMENT MIGRATION
IN SITU IN DIFFUSING MODE
MESURE DE LA MIGRATION DES RADIOELEMENTS
IN SITU EN REGIME DIFFUSIF
PROBE BODY
CORPS DE LA SONDE
TRACING COMPOUND BULBE
AMPOULE DE TRACEUR
CLAY SAMPLES
ECHANTILLONS D'ARGILE
MIXING CHAMBER
CHAMBRE DE MELANGE
STRAIKING PIN
PERCUTEUR
STRAIKING PIN CONTROL
COMMANDE PERCUTEUR
CABLE
SINTERED
FRITTE
PROBE BODY
CORPS DE LA SONDE
BREAKABLE BULBE CONTAINING TRACING COMPOUND
AMPOULE CASSABLE CONTENANT LE TRACEUR
MIXING CHAMBER
CHAMBRE DE MELANGE
CLAY SAMPLES
ECHANTILLONS D'ARGILE
OPENING AND CLOSER PISTON
PISTON D'OUVERTURE ET DE FERMETURE
FRANGIBLE DISK
OPERCULE
STIRRER
AGITATEUR
WATER INLET
ENTREE D'EAU

Figure 1

In-situ determination of the macropermeability of a clay formation in view of assessing leakage and mass transfer in a deep argillaceous formation

Contractor : SCK/CEN, Mol (B)
Contract n° : FI1W/0145/B
Contract period : July 1987 - December 1989
Covered period : July 1987 - December 1987
Project leader : A.A. Bonne

A. OBJECTIVE AND SCOPE

The objective of the experiment is to determine "in situ" the permeability of a clay formation at the mesoscale, the overall permeability of an argillaceous host formation at that scale being an extremely important parameter for the long-term and short-term performances of a geological disposal concept. The experiment is of particular interest because it will be performed into the Boom clay formation. The permeability of this formation is determined on the regional scale as well as on the hand specimen scale, and it is expected that, from this macropermeability test, the relevance of possible heterogeneities and discontinuities will be detected.

B. WORK PROGRAMME

1. Detailed design of the experimental set-up and development of the appropriate research model for the optimisation of experimental set-up.
2. Purchase of the instrumentation and equipment.
3. Calibration, testing and mounting of the instrumentation and equipment.
4. Performance and follow-up of the experiment.
5. Further adaptation/development of the research model for the final interpretation of the experiment.
6. Termination of the experiment and reinstatement of the initial conditions.
7. Final interpretation.

C. PROGRESS AND RESULTS OBTAINED

State of advancement

According to the planning the first efforts for this experiment were devoted to the design and dimensioning of the in situ test, with the support of a research model.

Progress and results

A first concept that has been developed and evaluated concerns a metal tube, to be emplaced over a distance of 10 meters within the clay along a horizontal direction, in the bedding plan of the Boom clay. Only the most distant 5 metres of this tube should consist of a screen, in order to avoid not to "sample" the zone that has been frozen and thawed immediately around the URL. A screen surface of 5 m^2 is aimed at.

To be able to estimate an optimal emplacement of instrumentation the distribution of the potentiometric heads one can expect in the surroundings of such a drain has been simulated by the METIS-code, taking into account also the actual pressure field around the URL.

Several alternative simulations have been run by varying the permeability of the clay or the dimensions of the drain. It was calculated that, regardless of the configuration (i.e. dimensions of the drain, applied boundary conditions) or the admitted permeability, the pressure drop profile should almost completely be covered within 1.5 m around the drain.

Nevertheless, to measure also the pressures within the range 0-4 bars, pressure gauges should be installed at a distance of at least 0.05 m, with intervals of about 0.1 m. Previous experiences however, indicate that it is very difficult to get such an accuracy for the placement of devices at distance from the gallery in the clay.

On the other hand, permeability has a decisive influence on both the time needed to obtain a steady state regime and the expected total discharge rate (see table below).

Permeability (m/s)	transient regime time (d)	discharge rate Q (1/d)
10^{-10}	10	19.3
10^{-11}	120	4.9
$4x10^{-12}$	120	0.8

Influence of clay permeability on discharge rate and length of transient regime

For the evacuation of the drained fluid from the test tube two possibilities have been considered. A gentle ventilation system and a water collection system. Preference is being given to the last option because of the ease of control.

All the evaluations up to now assumed a homogeneous clay without fractures of joints. In the design work the examination has been launched on the importance of the hypothesis that the clay would be fractured and show a layered homogeneity at the "sampling" point.

Laboratory and field tests for radionuclide movement and fast flow paths in clay

Contractor: Harwell Laboratory
Contract No: FI1W/0154
Duration of contract: January 1988 to April 1989
Project Leader: P.J. Bourke

A. OBJECTIVES AND SCOPE

Some clays are rather homogeneous - others have silty or sandy layers and, if hard enough, fractures. These features may provide paths for flow and solute convection much faster than convection and diffusion through the bulk of the clay. Evidence for this is the common observation that flows from boreholes into some clays are much higher than predicted assuming them to have the permeabilities measured in the laboratory with intact samples - this discrepancy is probably due to the permeabilities of silts and sands being much higher than that of clay to the low resistance to flow through inter-connected fractures.

The rates, retardation and dispersion of radionuclide leakage through such paths will be very different from those predicted assuming the clay to be uniformly permeable and diffusive. hence the need to investigate and characterise these fast leakage paths. This type of investigation can only be carried out through field work.

The main objective of this work which will be done in the clay beneath the UKAEA site at Culham, is therefore to assess the extent to which flow occurs through these paths rather than by permeation throughout the bulk clay. A subsidiary objective is to measure the in-situ permeability of the silt and sand - laboratory measurements are sometimes in doubt because these materials may be too friable to allow undisturbed samples to be obtained. Also, if practical, field measurements of the permeability of clay between highly permeable layers and fractures will be made for comparison with laboratory measurements.

In a second part of the programme, in-situ measurements on radionuclide diffusion in clay will be carried out at the Underground Research Laboratory at Mol, for comparison with laboratory experiments.

Numerous laboratory measurements have been made in the past of the diffusivity of clay. These are usually done by allowing a solute to diffuse through the pore water in centimetre thicknesses of clay until a steady rate is obtained with constant solute concentrations at the faces of the sample, when the diffusivity may be easily calculated. The samples are disturbed as little as possible in obtaining them from the ground and are restressed to in-situ conditions in the laboratory test cells but some changes of the properties may have occurred.

B. WORK PROGRAMME

Planning permission for the fast flow path work at Culham from the South Oxfordshire District Council had been hoped for in January, but because the Oxfordshire County Council wish to take an oversight of the application, permission is not now expected until the spring. Access to the CEN/SCK Mol Underground Research Laboratory for the radionuclide diffusion experiment has been scheduled for October 1988. Hence no scientific progress to report.

4.3.C. Natural analogues

FIELD INVESTIGATION WITH REGARD TO THE IMPERMEABILITY OF CLAY FORMATIONS

Contractor: ENEA, CRE CASACCIA, ROME (ITALY)
CONTRACT No: FI1W/0063-I
Duration of contract: January 1987 - December 1988
Period covered: January 1987 - December 1987
Project leader: C. Polizzano

A. OBJECTIVES AND SCOPE.

The main aim of this work is to assess surficial methods for detecting the secondary permeability in clay and shale in sedimentary basins.
The proposed method is based on the detection of some noble gases in soil-gas as tracers of fractures, faults etc..
The chosen gases are helium 4 and radon-222. Both these gases are used from several years for locating ore, oil and geothermal fluids as well as earthquake precursors.
Helium and radon are members of the chemically inert noble gas family of elements. Naturally occurring helium is composed of two isotopes, helium-4 and the milion time less abundant helium-3. Helium-4 is continuously produced from alpha particles emitted during the radioactive decay of uranium-238, uranium-235 and thorium-232. It is a non radioactive atom with an atomic weight of 4. Naturally occurring radon is composed of three isotopes, Rn-222, -220 and-219, produced by alpha decay from a radium parent.
Radon is also monoatomic but unlike helium is radiaoctive with half-lives 3.8 days for Rn-222, 56 seconds for radon-220, and 4 seconds for radon-219.
In this first report only helium will be discussed. The helium in the atmosphere is a mixture of helium of different origin: radiogenic helium mainly from the metamorphic basement, with a helium-3/helium-4 ratio of about 1×10^{-8}; primordial helium from the mantle, with helium-3/helium-4 ratio of about 1×10^{-5}. The mole fraction in the atmosphere is only 5.2×10^{-4} (5.24 ppm v/v). The rate at which helium escape from the crust is lower than the rate of its production so that the crust itself may represent an accumulation zone for this elemet.
Helium reaches the surface using fratures and faults as preferential routes for escaping. The choice of this element for detecting fractures relay on:

-it is a chemically fully inert element;
-its atomic radius is very small, comparable whith that one of hydrogen.

These characteristics make helium one of the most mobile element and therefore it can behave as an excellent tracer of geological discontinuities as well as of the primary permeability of the rocks. This report will discuss the results of the survey done in Val d'Era (Tuscany).

B. WORK PROGRAMME The programme is based on the following steps:

-preliminary survey of helium in soil-gas at a regional scale in sedimentary basins characterized by distensive tectonics and, for comparison, by compressive ones;
-surveys of both gases in soil-gas in selected areas.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

A regional survey for helium was carried out in Val d'Era. About 1000 soil-gas sample were collected and analyzed. A second helium regional survey is now in progress in an Adriatic basin characterized by compressive stress, where a similar amount of sampleswere collected.

PROGRESS AND RESULTS

1. The Val d'Era is a sedimentary basin hosted in a graben of miocenic age, oriented NW-SE. It is located in central western Italy. It covers an area of about 600 square kilometers.

The sedimentary terrains, under study, are formed by:

-pleistocenic mostly sandy and comglomeratic sediments with some clay levels;

-lower and medium pliocenic clay displaying a thickness of about 1000 m;

-upper Miocen formed by conglomerates and sandstones interbedded with gypsum levels.

The soil gas samples were collected by means of hollow probe inserted in the soil to a depth of about 50 cm, extracting the gas by a hypodermic syringe. The sample was then transferred to evacuated glass containers for laboratory analyses. The measurements were conducted on a DUPONT SS A 120 modified mass spectrometer, fitted with a constant pressure inlet system and connected to a chart recorder. The helium concentration is expressed as the differences in ppb between the content in the sample and the content in the atmosphere used as reference standard (5240 ppb). The sensibility limit of the instrument is of the order of 20-30 ppb. The sample were collected on an almost regular grid with an average density of 1.5 sample per square kilometer. A total of 919 samples were collected. Particular care was taken in selecting the sampling point as gas extraction from unhomogeneous soil may be affected by air dilution. In Fig. 1 a frequency histogram of helium-4 values is reported. The most representative values are included between 100 and 350 ppb above the atmosperic level; it means between the mean value +/- the standard deviation. The obtained values show an enrichment of helium, compared to the atmosphere, in a range between 0 and 12%.

As the analytical sensitivity is +/- 30 ppb, only values exceeding four times this value may be considered anomalies (positive or negative), while values from -120 to +120 ppb are considered equal to zero.

In the following discussion about the regional distribution of helium values, only helium contents higher than the atmospheric one are considered as positive anomalies. In this case the observed enrichment may be a clear sign of the presence of deep origin helium.

A comparison with the results obtained in helium surveys done in other Italian zones shows that the heliumleakage in the studied area is not very high. This corresponds to the fact that most of the clayey terrains outcropping in the

Val d'Era are very poorly permeable to this gas. Still positive anomalies, with enrichment ranging from 7% to 12% were found in several places.
Anomalies were particularly found to correspond to different geological situations:
-several of them are related to the outcropping of pliocenic trachytic intrusions near Montecatini and Orciatico;
-other ones were found across the valley itself according to N-S, E-W and NE-SW directions, that correspond to some of the main fault systems of the appenninic chain;
-only few anomalies were found aligned according to NW-SE direction, that correspond to the trend of the graben itself.
At this stage of the research it seems possible to observe:
-the helium anomalies are not directly related to specific lithological complex;
-the anomalies are related to fracture systems;
-the more recent (and probably still active) fracture systems present higher level anomalies;
-several zones within clayey basin appear to be impermeable to this gas,may be because of the lack of fractures or for self-sealing phenomena.
As an example of the study done,fig.2 reports the distribution map on regional scale. If these first results will be confirmed, it seems that the proposed method may be an usefull tool for studying the real permeability state due to the tectonic stress in clayey formations. It is important to evidence that this data may be obtained by means of simple and direct field investigations.

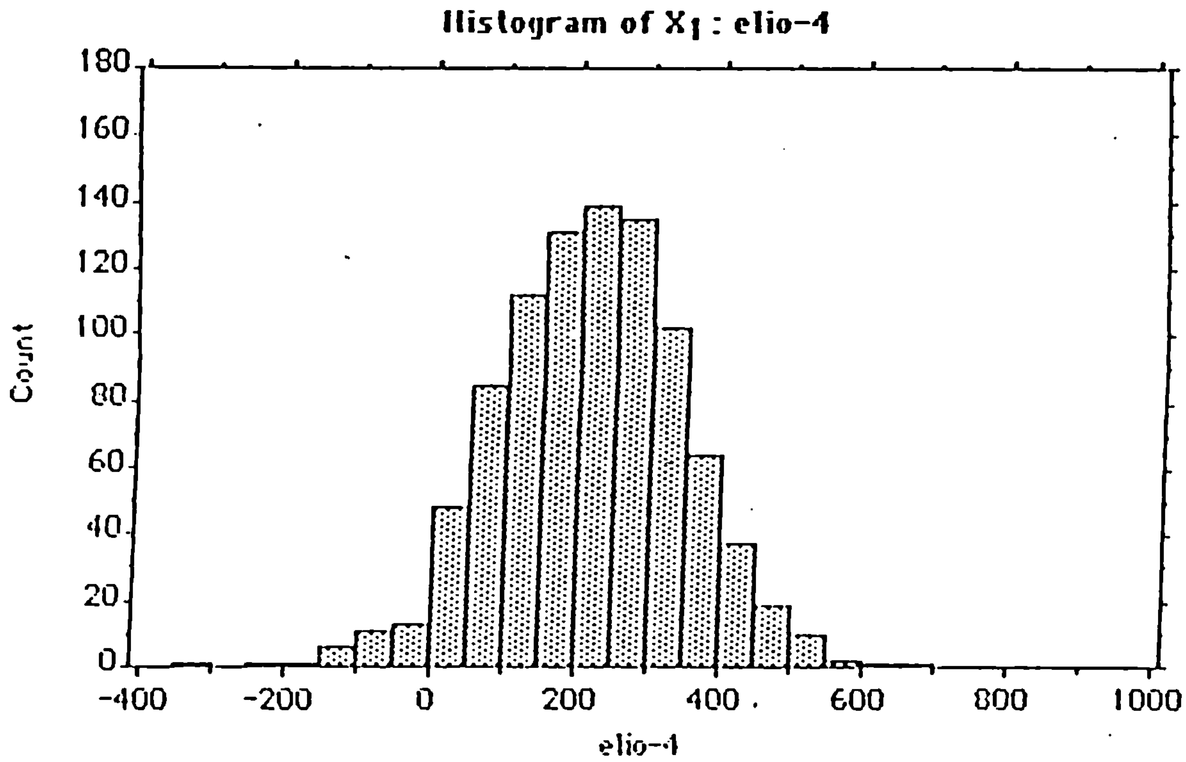


FIG. 1 - Frequency hystogram of helium contents, expressed as differences (ppb) with regard to helium content in the atmosphere. The values are homogeneously distributed. Most of them furthermore display weak enrichment with regard to the helium concentration in the at_ mosphere (zero reference).

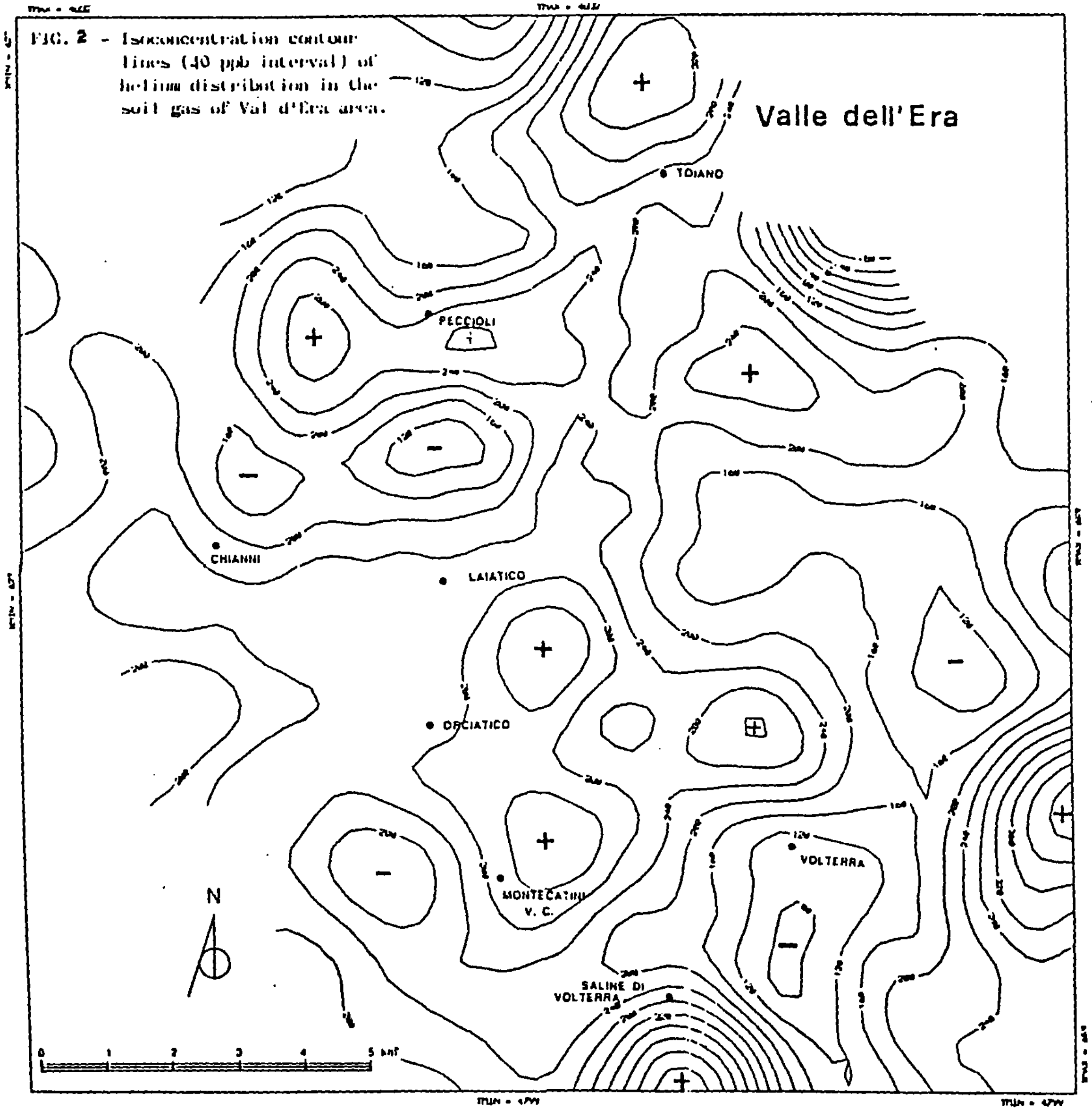


FIG. 2 - Isoconcentration contour lines (40 ppb interval) of helium distribution in the soil gas of Val d'Era area.

MODELLING OF RADIONUCLIDE MIGRATION IN THE GEOSPHERE : NATURAL ANALOGUE STUDIES

Contractor : Centre d'Etude Nucléaires de Fontenay-aux-Roses, CEA/IPNS/DAS/SAED - FRANCE

Contract n° : FI1W/0070

Duration of contract : January 1987 - December 1988

Period covered : January 1987 - December 1987

Project leader : P. Escalier des Orres

A. OBJECTIVES AND SCOPE

The study of the migration processes of elements in the geosphere through natural analogues is one of the best way to validate the calculation tools developped to predict radionuclides transfers on long time periods.

It has for objective to quantify these phenomena with slow kinetics, to show the thoroughness of the mechanisms taken into account in the models, or to permit their modification, if necessary.

The present study is based on the interpretation of the data obtained by the British Geological Survey on different "natural analogues" sites in the U.K.

B. WORK PROGRAMME

1. Modelisation of the elements transfers in the argillaceous sediments from Loch Lomond.

2. Pre-modelisation of natural analogues sites on the first sets of data gathered by the BGS.

3. Interpretation through models of the complete data sets : transfer in cristalline rocks (matrix diffusion), transfer in clay quaternary sediments, for example.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Work already done concerns transfers in silts, clays and peat sediments of a natural analogue site in Great Britain, Needle's Eye, near Dalbeattie, in southern Scotland.

It results from a cooperation between the BGS (Keyworth), which is in charge of the investigations on site and the Paris School of Mines (Fontainebleau), which does the modelisation of the transfers.

Two uraniferous veins, containing pitchblende, are the known primary ore. In order to reconstitute the radionuclide migrations, we need to be able to characterize the source term and the current distribution of the radionuclides in the quaternary sediments. These sediments can be dated and give us a chronology frame-work.

In 1987, the BGS has organized two campaigns of sampling, followed by analyses of the collected material. Many of these measurements are not finished, but should be available within the next six months.

In august 87, members of CEA and Ecole des Mines visited, with the BGS, Needle's Eye and two other analogue sites in U.K., in order to determine the state of the field investigations and discuss the possible use of these sites as natural analogues.

In october, a mission to the BGS allowed to collect the existing data and get much information from the investigations. It became possible, therefore, to interprete these data and build a model that shows what can be done. Many measurements and analysis are still necessary to get a reliable modelisation.

A report, written at the end of 1987 (1), presents the data and an interpretation, with the possible simulations and the propositions for further investigations. These points will be discussed with P. HOOKER (BGS) and G. MACKENZIE (SURRC) at a meeting on January the 29 th : a new investigation program will be defined from the conclusions of this first report.

With a considerable effort on sampling and analysis, it is possible to assume that defendible and valuable results can be obtained through a numeric simulation of Needle's Eye analogue site.

(1) R. SOUBEYRAN, E. LEDOUX, G. de MARSILY, Modelisation du transfert d'"analogues" naturels; Rapport d'avancement au 31.12.1987, LHM/RD/88/11

STUDY OF MIGRATION PROCESSES IN CLAY FORMATIONS OCCURRING IN NATURE.

Contractor: ENEA, CRE CASACCIA, ROME (ITALY)
Contract No: FI1W/0071
Duration of contract: January 1987 - December 1988
Period covered: January 1987 - December 1987
Project leader: A. Brondi

A. OBJECTIVES AND SCOPE

The permeability state of clay may be affected by tectonic events. Fractures and faults may indeed give rise to a secondary permeability within argillaceous rocks.Ochraceous bands aside from the fracture planes evidence circulation of meteoric water within fractures systems in clay. The penetration depth of these water in clay should reveal the thickness of clay affected by tectonic secondary permeability due to tectonics. The present work is aimed at ascertaining the real influence of tectonics on a clay formation in the Siena basin in central western Italy. The tectonics of the basin, a typical graben, is well defined.

B. WORK PROGRAMME

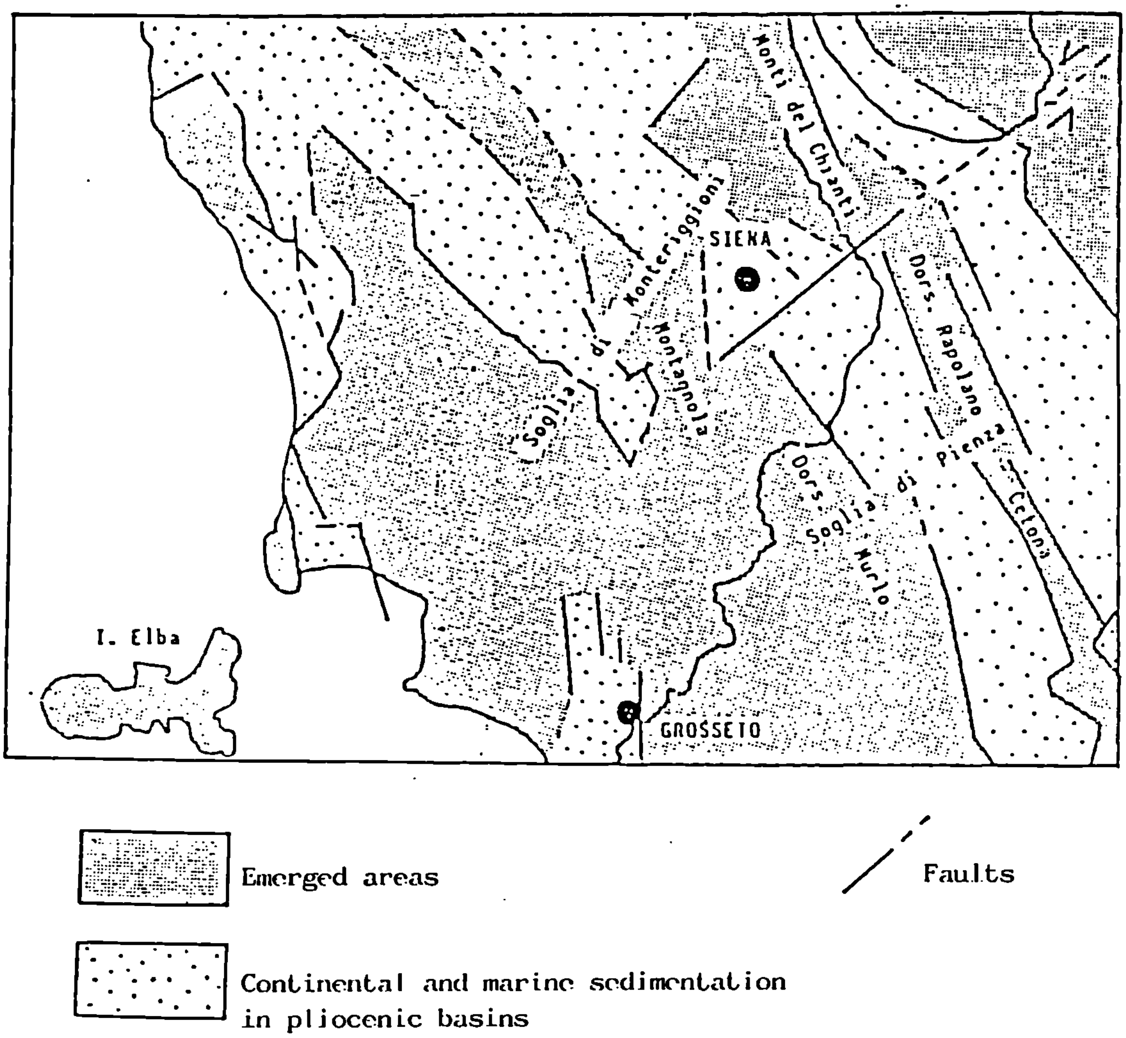
Three main lines have been envisaged:

- Selection of the most appropriate situations referred to the general tectonic frame;
- Studies on the variations of the geochemical system of clay because of the penetration of the meteoric water;
- Investigation on the extent and causes of the secondary permeability of clay and their importance with regard to the stability of clay formation.

C. <u>PROGRESS AND RESULTS</u>

Field investigations have been conducted on pliocenic clay of an area of 900 square kilometers. The most important fault systems have been mapped. A geological interpretation of landforms by means of aerial photographs was completed.

Fig.1 - DISTRIBUTION OF THE MAIN QUATERNARY AND PLIOCENIC BASINS IN SOUTHERN TUSCANY



Natural analogues of radionuclide migration in granitic rocks through the study of palaeo-hydrothermal alteration

Contractor : BRGM - Orléans, France
Contract no. : FI 1W/0072/F
Working period : August 1986 to August 1988
Project leader : P. Peaudecerf

A. OBJECTIVES AND SCOPE

Mineralized zones in granitic rocks which have been influenced by hot water (hydrothermal activity) over long geologic periods may be considered as useful natural analogues of the conditions occurring around a heat-producing repository in granite. Study of these zones gives valuable information about the migration and retention of elements analogous to the radionuclides present in the repository.

Development of research on one or more sites of former hydrothermal activity in a granite environment will enable an approach to the problems of migration and retention of elements such as the rare earths, uranium and thorium which are themselves analogous to the radionuclides in their geochemical behaviour. The time scale will be that of the geologic environment of 0.1 to 1 million years. The volumes considered will take into account the far field (pervasive alteration) and near field (vein alteration) phenomena. The final aims of this programme are :

1. To define the physicochemical conditions of the alteration examined and the mineralogical carriers of the elements analogous to the radionuclides
2. To test on existing programmes (PATH) or on those being developed, the data supplied by the direct approach (validation of thermodynamic parameters, assessment of the reaction kinetics on natural examples).

B. WORK PROGRAMME

B.1. Petrographic and mineralogical investigation of the various events which have affected the system.

B.2. Analysis of the analogue element carriers in two parts :

- B.2.1. Separation of the primary and secondary phases developed by the alteration and quantitative analysis of the analogue elements in the separated phases and in rock samples ;
- B.2.2. Location of analogue elements by nuclear methods. From these data the mass balance and the distribution and mobility of the analogue elements during the palaeo-alteration will be established.

B.3. An indirect approach by using mass transfer codes on major trace and analogue elements to mobilize the geochemical behaviour of the alteration systems.

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

Following the signing of contract FI1W/0072/F in October, it was decided to proceed to selection of an additional site for the study of palaeo-hydrothermal alteration enabling the continuous two- or three-dimensional analysis of a system. This selection was made after a period of exploration during which thirty or so sites were visited in Brittany and the Massif Central.

Once the selection of the Fombillou site in the Massif Central was made, an inter-disciplinary field programme, involving mineralogists and geochemists, was undertaken. Work progress is as follows:

B.1. is virtually completed.

B.2. is nearly completed; B.2.1. is in progress and B.2.2 is completed.

B.3. is under way.

PROGRESS AND RESULTS

B.1. Petrographic and mineralogical investigation of various events which have affected the system

The main results obtained show that the hydrothermal system of Fombillou is polyphase and underwent at least two major hydrothermal processes as well as supergene alteration especially on the wall rocks of the main hydrothermal system.

The first hydrothermal cycle which has affected the site took place at temperatures ranging from 400 to 200°C. It developed throughout the exposed zone investigated with accompanying alteration of biotites generating the association chlorite-phengite-orthose, phengitisation of muscovites and plagioclases and recrystallisation of orthose. This cycle occurs with Sn, W and B anomalies in the walls of the veined zone.

The second cycle has only affected the walls of the main vein over 1 m and the walls of satellite veinlets over a few centimeters. This phase developed clay alteration with occurrence of illite, Ro-type randomly interstratified materials and kaolite rocks. Clay alteration is increasingly intense near the vein to the point of removing preexisting minerals. The paragenesis suggests a temperature of about 100°C. Sulphide mineralisation occurs in the vein and developed an As, Pb and Cu anomaly in the host rock.

Following the above work, computations, based on Gresens' equations and an isocon diagram, were performed to evaluate changes in volume and in composition. This resulted in a better characterisation of transfers which took place in whole rock during clay alteration. In the distant selvage environment (1 m to 0.5 m or so), mineralogical alterations occurred at constant SiO_2 and Al_2O_3 and constant volume (Fig. 1a).

In the near selvage environment (less than 0.5 m) only Al_2O_3 remains constant and the volume increases to 24 % ($fv\ Al_2O_3 = 1.24$) (Fig. 1b). The main negative variations in the elements (depletion) are controlled by major phenomena that dominate the alteration processes: (1) removal of biotite, and (2) alteration of plagioclases with losses of Mg, Mn, Li, and of Na, (Ba), Sr, Ca respectively.

Stoichiometric computations of reactions from microprobe analysed minerals are under way. They will enable a comparison betweeen data obtained from evaluations made on whole rock and evaluations of mineralogical reactions described in the hydrothermal system.

Investigation on fluid inclusions in the various quartz generations of the lode filling has identified, as already established by previous data, two major hydrothermal phases marked by : (1) a first generation of inclusions with low salinity fluids which have evolved towards domains of temperature ranging from 400° to 110°C; (2) a second generation of late inclusions displaying high salinity fluids (NaCl equiv.) and a strong Ca_{2+} signature developed at temperatures of about 100°C.

Study of the thermal signature of the main vein by the study of sealing of fission tracks in apatite has provided a curve of relative age around the vein. This gave an image of the geothermal gradient induced by hydrothermal solutions. An age of 70 m.y. obtained for the most proximal sample corresponds to the last thermal activity of the vein system at temperature above 100°C.

A plateau age of 240 m.y. corresponding to the last cooling phase of granite at temperature below 130°C was obtained for the most distal sample collected 15 m of the vein.

B2. Analysis of the analogue element carriers in two parts:
B.2.1. Separation of the primary and secondary phases developed by alteration and quantitative analysis of the analogue elements in the separated phases and rock samples.

This part is under way but is hindered by the nature of the alteration which renders obtention of fine phases difficult.

B.2.2. Location of analogue elements by nuclear methods

The results obtained through mapping of uranium and study of induced fission tracks show a good correlation between the development of the alteration phases and the distribution of uranium, the value of which increases near the vein. But the support of these concentrations, mainly iron oxides, suggests late reworking of this element in supergene environment controlled by hydrothermal alteration induced porosity.

Study of the disequilibriums in the family of uranium 238 in the main vein environment (Fig. 2) provides some pieces of information to the questions raised by mapping of the distribution of total uranium.

The most plausible evolutionary model for the Fombillou site is as follows:

- during the emplacement of mineralisation , several million years ago, a first disequilibrium occurred in the system releasing uranium in some crystalline phases. Then in the course of time, a new ^{238}U ·· 1 equilibrium was achieved in alteration phases which probably had not the same characteristics as the crystalline phases of granites and no nuclear recoil generating $^{234}U/^{238}U$ disequilibrium (hydrated iron oxides ?);
- a more recent or present-day alteration phase has reworked or is reworking the "free" uranium from the host rock towards the wall rocks of the vein accounting for $^{234}U/^{230}Th$ disequilibriums.

B.3. Indirect approach by using mass transfer codes

Acquisition and formatting of softwares and thermodynamic data took us one year of work. The first computations on the alteration parageneses of Fombillou are currently being performed.

List of publications

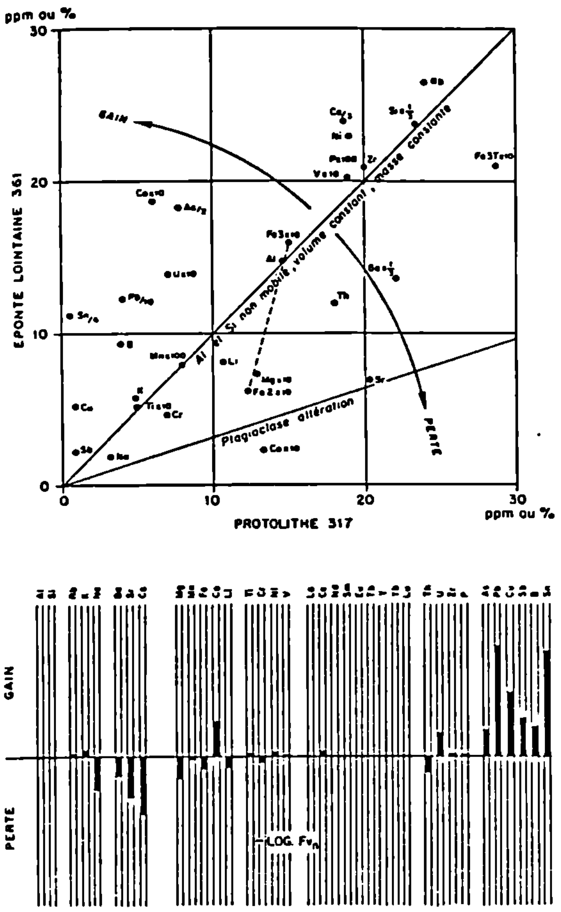
/1/ Publishing of Miss Griffault's thesis, Evaluation and transfers of major and rare earth elements during hydrothermal alterations of granites. An example: Granite of the Ballon d'Alsace (The Southern Vosges).

/2/ Griffault, L., Jebrak, M., Lemiere B., Piantone, P., and Sureau, J.F., Hydrothermal alteration systems as analogues of nuclear waste repositories in granitic rocks. An example: The Langenberg hydrothermal system. (Presentation to the EEC Congress in Brussels, April 28 to April 30, 1987).

Figure captions

Fig. 1 - Isocon diagram and diagram showing calculated enrichment/ depletion of elements in distant selvage environment (about 1 to 0.5 m of mineralized vein) (a) and in near selvage environment (about 0.5 to 0 m of mineralized vein)(b).

Fig. 2 - Ternary diagram with relative ^{238}U, ^{234}U and ^{230}Th activities. The inserted triangle represents the different processes leading to isotopic disequilibrium. Samples are 317 about 15 m from the vein, 315 about 12 m, 360 about 8 m, 305 about 3 m amd 361 less than 1 m.


ppm ou %
EPONTE LOINTAINE 361
PROTOLITHE 317
ppm ou %
GAIN
PERTE
Al ni Si non mobile, volume constant, masse constante
Plagioclase altération
GAIN
PERTE
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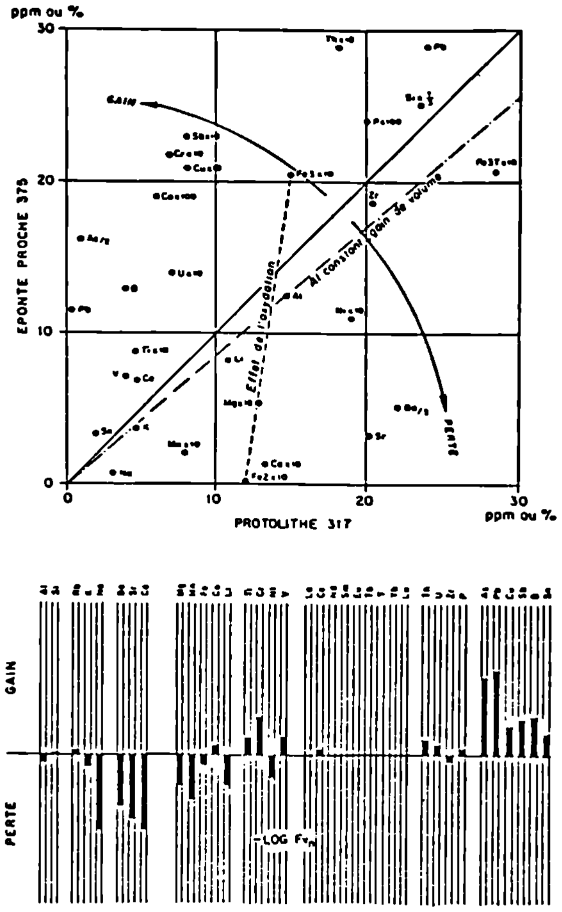
1 A


ppm ou %
EPONTE PROCHE 375
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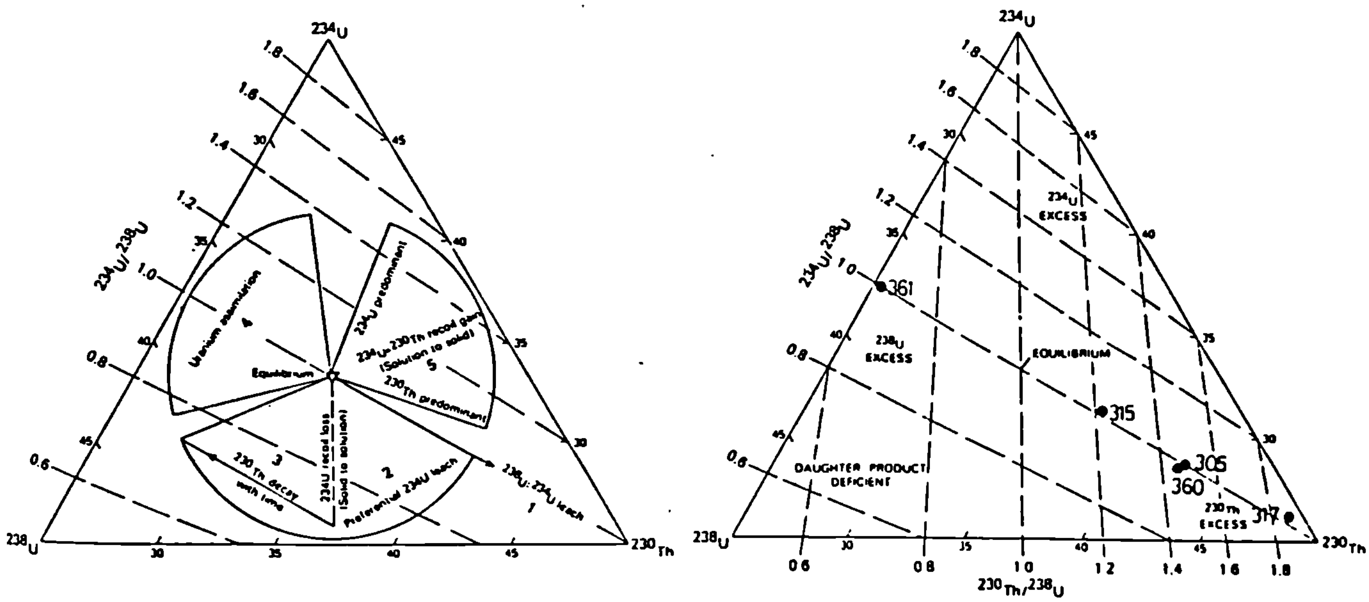
234U
238U
230Th
234U/238U
Uranium accumulation
234U predominant
234U-230Th recoil gain (Solution to solid)
230Th predominant
Equilibrium
230 Th decay with time
234U recoil loss (Solid to solution)
Preferential 234U leach
234U:234U leach
234U EXCESS
238U EXCESS
EQUILIBRIUM
DAUGHTER PRODUCT DEFICIENT
230Th EXCESS
361
315
305
360
317
230Th/238U
Fig. 2

Natural Analogue Studies of Radionuclide Migration

Contractor: British Geological Survey/NERC, Keyworth, Nottingham, UK
Contract No: FI1W/0073/UK
Duration of Contract: October 1986 - September 1989.
Project Leader: P J Hooker

A. OBJECTIVES AND SCOPE

It is important to be able to validate and support models of long-term predictions of radionuclide migration in the geosphere. The main aim of this research is to examine natural geochemical discontinuities and gradients as analogues of radionuclide transport in sediments. The mechanisms of processes of mobilisation, advection, diffusion and retardation for natural decay series elements and iodine and bromine will be addressed. This will entail some development of the techniques for measuring small concentrations and the speciations of these elements in both the solid and pore water phases. Analytical determinations by alpha spectrometry and neutron activation analysis will be carried out by SURRC (Dr A B MacKenzie) under subcontracts. Support in modelling will come from co-operation with Ecole des Mines de Paris, Fontainebleau.

B. WORK PROGRAMME

B.1. Phase 1986 - 1987.

B.1.1. Site investigations

B1.1.1. Collection of fresh Loch Lomond sediments; analysis of I and Br depth profiles; preliminary modelling for effective diffusion coefficients.

B.1.1.2. Pilot investigation I, Br, U and Th gradients across marl/clay boundaries in a well characterised sediment core from Lundin Castle, Fife, eastern Scotland.

B.1.2. A desk study of surface diffusion as a solute transport process for major cations through clays, with implications for trace radionuclide migration.

B.2. Phase 1988-1989.

B.2.1. Site investigations will be concentrated on measuring and modelling the speciation and mechanisms of distribution of I, Br, U and Th in the Loch Lomond and Lundin Castle sediments.

B.2.2. Application of the desk study conclusions to a field investigation of Ca and Na gradients in a mixed sediment sequence with reference to radionuclide migration.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

From previous work on Loch Lomond sediments it had been established that it was important to measure the I and Br concentration gradients more fully and to elucidate the chemical nature of the elements, especially in the mobile pore water phase. To meet this end, a sensitive working method for the separation of iodide from iodate from bromide has been developed by SURRC for application to new core material proposed to be collected in 1988. SURRC have also started on an improved method for Ra-226 analysis.

The collaborative modelling exercise with the Ecole des Mines de Paris, Fontainebleau, was begun through a field visit to the BGS analogue sites in Scotland in August. It was agreed that the hydrogeological and geochemical situation at the Needles Eye locality near Dalbeattie, southern Scotland, was suitable for the Ecole to model. The objective is to model the transport and distribution patterns of uranium in the post glacial sediments

PROGRESS AND RESULTS

1. Site investigations (B.1.1.)

B.1.1.1. Loch Lomond

The arrangments to collect fresh sediment core samples from Loch Lomond have been postponed to 1988. This is because the technique for measuring iodine and bromine was still under development at SURRC, East Kilbride, and because of substantial commitments to field investigations at the Needle's Eye analogue site on the coast near Dalbeattie in southern Scotland. The Needle's Eye site was visited by a group from the Ecole des Mines de Paris, and the CEA in early August 1987 when BGS and SURRC were carrying out field work there. It was agreed that the site was suitable for modelling collaboration to take place between BGS/SURRC and the Ecole, and the exercise is progressing well, with the emphasis on modelling the transport and distribution of uranium in the Needle's Eye sediments.

Previous results in the form of diffusion and concentration gradients obtained on Loch Lomond sediments have demonstrated the need to elucidate the chemical forms of the I and Br distributions in the pore waters and in the marine band deposits. The development of radiochemical methods has taken up a susbstantial part of the SURRC effort in the last six months. These studies have ben aimed at establishing techniques for investigation of halogen speciation in sediment interstitial waters for the Loch Lomond project, but work has also been started on development of a radiochemical method of radium analysis which would be of value to both the Loch Lomond study and the Needle's Eye project.

Short activation (about 1 minute) of samples in the UTR-300 reactor has previously been demonstrated to provide a sensitive technique for analysis of iodine and bromine at the levels observed in the Loch Lomond interstitial waters and recent efforts have been devoted to the separation of I^-, Br^- and IO_3^- species (BrO_3^- was also included although it would not be expected to be encountered in the samples). An extensive series of separation schemes has been investigated using anion exchange resin (AGl x 8) to concentrate the halogen species from solution followed by sequential elution of the different forms. The following scheme has been evolved to form the basis of a working method.

1. Irradiate 0.1ml of sample solution for 1 minute at a neutron flux of 3×10^{12} ncm^{-2} sec^{-1}.

2. Load the irradiated sample on to a 5cm x $1cm^2$ column of Bio-Rad AG1 x 8 resin in the-OH form using 0.1M NH_4OH and wash the column with 10ml 0.1M NH_4OH
3. Elute IO_3^- with 40ml 0.5M KOH and count the solution.
4. Elute Br^- with~14ml 2.5M HNO_3 and count the solution.
5. Slurry and count the resin for I^- (and BrO_3^-).

A slight interference of I^- and IO_3^- (less than 10%) has still to be solved. This may be a real effect or may be due to impurity problems and is being further investigated at present. Radiolysis effects were considered as a possible explanation but were discounted since the effect is insensitive to a fourfold variation in neutron fluence. Further refinement of the method, establishment of blanks etc is still required, but the method should be available for application to the samples from the proposed sampling in 1988.

Work has also been started on development of a method of radium analysis based upon radiochemcial separation, electrodepositon and alpha spectrometry. Radium is an element of direct interest in radioactive waste disposal and previous work at Loch Lomond and Needle's Eye suggest that useful information could be derived from accurate ^{226}Ra analysis. Two techniques are commonly employed for ^{226}Ra analyses namely sample dissolution followed by emanation, collection and counting of ^{222}Rn, the decay product of ^{226}Ra, or direct gamma counting of the solid sample. The former method suffers from a lack of chemical yield tracer and our experience indicates that significant loss of ^{226}Ra can occur, in particular in samples with a high Ba content, giving a systematic error on the results. Spectral interference, loss of ^{222}Rn gas and corrections for self absorption effects present problems in the direct gamma spectroscopy method. SURRC have therefore started a programme of investigation of radiochmical separation of radium At present , successful separation of ^{226}R from solution can be achieved using cation exchange resin and elution methods are now being investigated.

B.1.1.2. Lundin Castle

The results of the determinations reported earlier for the core of sediments from Lundin Castle have not been added to or interpreted yet.

2. Surface diffusion study (B.1.2.)

A number of key reports and papers on the surface diffusion phenomenon have been identified. It is clear that existing cation concentration data for interstitial waters in an 'impermeable' clay layer are difficult to invert in a way that would unequivocally demonstrate the significance of the mechanism in the overall transport process. The study continues, despite this fundamental difficulty.

Publications

HOOKER, P.J., CHAPMAN, N.A., MACKENZIE, A.B., SCOTT, R.D. and IVANOVICH, M. 1987. Natural analogues of radionuclide migration in sediments in Britain. IN Natural Analogues in Radioactive Waste Disposal (eds. B. Come & N A Chapman) CEC EUR 11037 EN, pp 104-115.

Long-term diffusion in rock: natural analogue

Contractor: Harwell Laboratory, UKAEA
Contract No: FI1W/0074
Duration of contract: July 1986 to July 1987
Project Leader: P.J. Bourke

A. OBJECTIVES AND SCOPE

Introduction

Aqueous phase diffusion into the matrix of fractured rocks is an important mechanism for retarding radionuclide migration. Therefore, it is important to quantify both the diffusivity and solute accessible porosity of various rock types. However, because of the low diffusivity of granite it has not been possible to obtain laboratory data for D_i and α on granite samples thicker than 5 cm. The object of this natural analogue study, therefore, was to identify larger specimens of granite which have been undergoing natural diffusion processes for longer, known, periods of time, in order to study diffusion over greater distances.

The principle of the experiment was to examine trace element profiles developed in a block of granite as a result of its immersion in sea water.

Solutes in the sea water will diffuse into the block and, conversely, solutes present at higher concentrations within the block will diffuse outwards. Anion profiles have been examined in this study, since these elements will be weakly-sorbed or non-sorbed and therefore will be most mobile.

B. WORK PROGRAMME

B.1. In 1956, a number of freshly blasted granite blocks were transported from a Cornish granite quarry and placed in front of the East Pier, Falmouth Docks, in order to act as wavebreaks. The blocks were entirely immersed in sea water, except at Spring low tides when their upper surfaces were exposed.

B.2. In February, 1987 two blocks of dimensions approximately 1.5 x 1.0 x 0.5 metres, were recovered. Petrological examination of the blocks confirmed that they were of the coarse-grained megacrystic biotite granite variety, from the Carnmenellis pluton.

B.3. Samples of fresh, unweathered granite of this variety were obtained in order to determine the levels of trace elements which can be leached from granite which has not been immersed in sea water.

B.4. Cores drilled through the granite blocks were sectioned and crushed to a particle size of 1cm. These samples were then contacted with AnalaR water for 50 days, after which time the solutions were analysed for Cl^-, Br^-, F^-, SO_4^{--} and NO_3^- using anion chromatography.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

This contract has now been concluded and a final report written. The report has been cleared for publication by the UK DoE, who jointly funded the work. This report will be published as Harwell Report AERE-R12744 in January 1988.

Solute diffusion profiles for Cl^-, Br^-, F^- and SO_4^{--} have been measured in a granite block which was immersed in the sea at Falmouth, Cornwall, for 30 years. The apparent diffusion coefficient and the solute accessible porosity have been estimated from the Cl^- and Br^- profiles, and these values have been compared with previously obtained laboratory data. SO_4^{--} and F^- are partially sorbed in the granite block, and their sorptivity is estimated from an analysis of their pore water concentration profiles.

PROGRESS AND RESULTS

The matrix properties which control solute transport in granitic rocks have previously been examined /1/. Laboratory experiments were performed to determine both the intrinsic diffusion coefficient (D_i) and the rock capacity factor (α) using through-diffusion techniques in which steady-state diffusion of a solute under a constant concentration gradient is established across a membrane of rock. D_i and α are defined as:

$$F = D_i \frac{dc}{dx} \qquad \text{.......... 1}$$

- where F is the steady-state flux per unit cross-sectional area of rock, and $\frac{dc}{dx}$ is the concentration gradient across the sample.

$$\alpha = \phi + \rho R_d \qquad \text{.......... 2}$$

- where ϕ is the solute-accessible porosity of the porous medium, ρ the density and R_d the distribution ratio.

The diffusion coefficient obtained from an analysis of the solute concentration profiles in the granite block is the apparent diffusion coefficient, D_a. This is the appropriate coefficient to use when the distance that a species has diffused is being considered /2/. It is related to the intrinsic diffusion coefficient, D_i, by:

$$D_a = \frac{D_i}{\alpha} \qquad \text{.......... 3}$$

The Cl^- and Br^- profiles within the block are flat, implying that equilibrium has been reached between the seawater and the granite porewater.

The concentrations of leachable Cl^- and Br^- are consistent with the model that the pore water has $[Cl^-]$ and $[Br^-]$ identical to that of sea water ($\sim$19000 µg/g and 67 µg/g respectively) and that $\alpha = 1.3 \times 10^{-3}$. This value of α is similar to the previous estimates of ϕ and suggests that Cl^- and Br^- are essentially non-sorbed in the granite. A minimum D_a can be calculated from these profiles and yields $D_a \geq 9 \times 10^{-11} m^2 s^{-1}$. The calculated D_i is, therefore, $\geq 10^{-13} m^2 s^{-1}$, at least a factor of 3 higher than that measured in the laboratory.

In contrast to the Cl^- and Br^- profiles, the concentration profiles for F^- and SO_4^{--} indicate that these elements have high concentrations at the margins of the block (to depths of up to 15 cm) and are in the process of diffusing outwards into the surrounding seawater. The initially high porewater concentrations of F^- and SO_4^{--} in the block are believed to result from weathering of the granite prior to its immersion in the sea, due to the breakdown of primary minerals such as pyrite and the micas. F^- and SO_4^{--} sorptivity has been estimated from an analysis of the porewater concentration profiles.

The values of D_i obtained from an analysis of pore water profiles in the granite block are equal to, or greater than, $10^{-13} m^2 s^{-1}$. This is a factor of at least 3 times greater than the 3 laboratory-generated D_i values previously reported for fresh Carnmenellis biotite granite. However, diffusion through fracture surfaces of Carnmenellis granite has also been investigated in the laboratory, and has demonstrated that D_i is enhanced in the rock adjacent to the fracture by up to 200 times /3/. It is possible, therefore, that the diffusivity of the granite block is higher than the original estimate of $3 \times 10^{-14} m^2 s^{-1}$. This could be examined further by laboratory through- diffusion experiments on samples taken at various distances from the faces of the granite block.

This preliminary experiment has demonstrated the potential for the measurement of solute migration in granite, as a result of the rock being immersed in sea water for a known period of time. Diffusion of Cl^- and Br^- from the sea water into the block has attained equilibrium, indicating a higher diffusivity for the granite than previously expected. In addition to solute diffusion from the sea water into the granite, there has also been out-diffusion of some solutes into the sea. It is believed that high concentrations of such solutes, eg F^- and SO_4^{--}, were generated at the margins of the block due to weathering processes.

Therefore, there is a potential for measuring out-diffusion of other partially sorbed nuclides which have been released from original mineral phases during weathering of the granite. However, this depends upon an understanding of the pore water profiles developed across a granite block which is undergoing progressive in-situ weathering in the near-surface environment.

List of Publications

Jefferies, N.L. 1987. Long term solute diffusion in a granite block immersed in sea water. Harwell Report AERE R12744.

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/1/ LEVER, D.A. and BRADBURY M.H. (1985). Rock-matrix diffusion and its implications for radionuclide migration. Mineralogical Magazine, 49 pp 245-254.

/2/ LEVER, D.A. Harwell Laboratory Report AERE R 12321 (1986). Some notes on experiments measuring diffusion of sorbed nuclides through porous media.

/3/ BRADBURY, M.H. Measurement of important parameters determining aqueous phase diffusion rates through crystalline rock matrices. Journal of Hydrology, 82 pp 39-55. (1985).

NATURAL ANALOGUE AND MICROSTRUCTURAL STUDIES IN RELATION TO RADIONUCLIDE RETARDATION BY ROCK MATRIX DIFFUSION IN GRANITE.

Contractors:	University of Oviedo, Spain University of Exeter, UK.
Contract No.:	FI1W-0143
Contract period:	1st October 1987 - 31st December 1989.
Reporting period:	1st October - 30th April 1988.
Project leaders:	M. Montoto (Oviedo); E. M. Durrance (Exeter)

Objectives of the study.

In most radionuclide transport models, it is assumed that radionuclides migrating in solution along fractures will diffuse into water held in pores within the rock matrix adjacent to fractures, and will thus be retarded relative to the flow of water; for many nuclides, this retardation will be enhanced by sorption onto the pore walls. In the retardation models developed by the Atomic Energy Research Establishment at Harwell, UK, for example, the main limit to diffusion of radionuclides into the rock adjacent to fractures is the fracture separation (S), the penetration depth of the nuclides being S/2 (Lever et al., 1982). Similarly, in the Swedish research programme, it is assumed that non-sorbing nuclides can diffuse into the rock matrix to the extent that they "saturate the rock sections between the fractures" (KBS, 1983). The possibility that there exists adjacent to fractures a zone to which diffusion might be restricted, or that the pores adjacent to fractures might be clogged by the products of alteration and/or mineralisation, do not seem to have been included in these models.

The experimental verification of diffusion models is normally based upon the determination of diffusion coefficients for samples of intact rock collected away from the influence of fractures, thus ignoring the possible effects of the fractures themselves on diffusion. Additionally, the properties (notably the porosity) of the samples used in such experiments will probably have been changed significantly by removal of the confining pressures to which they were subjected in the ground, thus rendering diffusion coefficients unreliable. The uncertainties of the diffusion concept, and the need for further experimental validation, are acknowledged in the Swiss research programme (NAGRA, 1985).

The objective of the study is to assess the effectiveness of diffusion as a mechanism for the retardation of radionuclides. The approach adopted involves examination of the microstructure of crystalline rock adjacent to and remote from fractures, and determinination of the extent to which the uranium-238 decay series is in equilibrium or disequilibrium in rock adjacent to fractures. The effect on porosity and potential diffusion of the fractures themselves will also be assessed, with particular regard to stress-relief effects and to pore-clogging by the products of alteration, mineralisation and precipitation.

This study will contribute to the Spanish programme of research into the suitability of crystalline rocks for the long term isolation of high level radioactive waste. It is hoped that the results of the study will help to resolve a major area of uncertainty in existing radionuclide retardation models.

Outline of Research.

The main purpose of the study is to establish whether or not the diffusion depth in rock adjacent to fractures is sufficiently limited to undermine the validity of existing diffusion models. The two main elements of the study are (a) an examination of the pore structure of rock adjacent to fractures, and (b) measurement of the extent to which the uranium-238 decay series has been disrupted by movement of water along fractures and by diffusion of members of the decay series into and out of the rock matrix adjacent to fractures. The work will include the following:

(1) Porosity and permeability determinations.

The porosity and permeability of intact rock samples adjacent to and remote from water-conducting fractures, and the permeability of fracture walls, will be determined in the laboratory. A non-steady state permeameter for the determination of intact rock permeabilities down to nanodarcy levels is being developed. The latter should be capable of determining the permeability of most granites that are likely to be encountered (Brace, 1980).

(2) Microstructural analysis: digital image processing.

Thin sections will be studied by optical (including transmission, reflected light and fluorescence) microscopy and scanning electron microscopy, the microstructure of the rock adjacent to fractures and the availability of pores for diffusion being analysed using digital image processing techniques and multi-image analysis. Particular attention will be paid to the interconnectivity of pores and to their nature adjacent to fractures. The applicability of acoustic microscopy to the study will be investigated.

(3) Mineralogical studies.

The mineralogy (primary and alteration) of granite samples, and of fracture and microfracture linings and infillings, will be studied by optical and scanning electron microscopy and other techniques (such as X-ray diffraction) as necessary. The potential for sorption on fracture and microfracture surfaces will be assessed.

(4) Uranium series disequilibrium studies.

The penetration of modern waters (the last million years) into the rock adjacent to fractures will be investigated by measuring the state of radioactive disequilibrium in the uranium-238 decay series. Alpha spectrometry will be employed following separation of uranium and thorium by ion exchange techniques. An existing method employed in work on the granites of south west England is being modified, with particular regard to the choice of spike added before separation of uranium and thorium to determine recovery. The modifications are aimed at reducing the need for complex corrections, which are required when using spikes of short half-life, and to reduce contamination of detector surfaces by alpha recoil mechanisms. From each of the fractured cores or blocks studied, 'slices' of rock at increasing distance from the fracture surface will be collected for analysis, allowing the construction of disequilibrium profiles from fracture faces into the rock matrix.

(5) Mossbauer studies.

The state of oxidation of iron in rock adjacent to fractures will be determined using Mossbauer spectroscopy. This will provide additional evidence for interaction between water in fractures and the rock adjacent to fractures.

(6) In situ stress determinations.

It is hoped to obtain in situ stress data for at least some of the sample sites. Such data will contribute to an understanding of the stress history of the site and of the development and activity of the fractures present. At some sites, these data will already be available. At any new Spanish site studied, in situ stress determinations will be carried out using overcoring techniques.

These studies will be supported by geochemical analysis of representative rock samples (adjacent to and remote from fractures) and of groundwaters, the latter including the determination of uranium series isotopic signatures. To enable successful interpretation of the data obtained in the study, samples will be collected from sites which are thoroughly characterised in terms of their structure (including fracture characteristics), petrography, stress history (including present-day stress field), hydrogeology and groundwater geochemistry.

It is the main objective of the study to collect samples from the Hercynian granite massifs of Spain, allowing syn-tectonic and post-tectonic, altered and unaltered, and high fracture density and low fracture density granites to be compared. It was originally intended to collect samples from the underground laboratory planned for the Duero valley (Project IPES), supplementing these samples from elsewhere in Spain and from other countries where possible. The postponement of Project IPES has placed greater importance on samples from other countries. Samples have already been collected from Stripa, Sweden, and others are being made available to the project from the Underground Research Laboratory at Whiteshell, Canada. It is hoped to obtain further samples from granite massifs in other countries, and from other sites in Spain, in the near future.

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Smellie, J. A. T., MacKenzie, A. B. and Scott, R. D., 1986. An analogue validation study of natural radionuclide migration in crystalline rocks using uranium-series disequilibrium studies. Chem. Geol., 55, 233-254.

MIGRATION OF URANIUM DAUGHTER RADIONUCLIDES IN NATURAL SEDIMENTS

Contractor: Natural Environment Research Council of the United Kingdom
Contract No. : FI1W.0146.UK
Duration of contract : 1 December 1987 to 31 May 1990
Period covered : 1 July 1987 to 31 December 1987
Project leaders : Dr. J. Thomson

A. OBJECTIVES AND SCOPE

This project utilises a characteristic uranium profile shape developed in deep-sea turbidite sediments to examine the behaviour of uranium and its daughter isotopes over time-scales desired for the isolation of radioactive waste. The geochemical background is that homogenous organic-rich turbidites, emplaced in the deep-sea, experience oxidation from the top downwards by bottom water. Uranium redistributes in the turbidite in response to the oxidation front, but this redistribution ceases when the turbidite is isolated from bottom water on emplacement of the next turbidite. Two long cores (MD24 and MD10) are available from a 1985 NEA cruise with several such units up to 750 ky old preserved. Good stratigraphic, geochemical and geotechnical data are available, and pore water advection in the cores is believed to be negligible.

The goals of the project are:
Determination of uranium and its longer-lived daughter radionuclides in individual turbidite units with ages between 250 and 750 ky to compare the observed profiles with those predicted by radioactive ingrowth systematics.
Utilisation of the experimental data to estimate effective diffusion coefficients of the different elements for modelling purposes. Such data will be relevant to the in-situ geochemical and conditions of the sediments over the long time scales indicated.

B. WORK PROGRAMME

2.1 Development and verification of a radiochemical analytical scheme for the analysis of uranium-238, uranium-234, thorium-232, thorium-230, protactinium-231, radium-226 and polonium-210.
2.2 Determination of activity versus depth profiles of the above radionuclides for different turbidites of different ages (250-750 ky) in core MD24.
2.3 Determination of a gross uranium profile for core MD10 to guide sampling and comparison of corresponding turbidite unit profiles with those of core MD24.
2.4 Chemical partitioning studies of selected samples (if necessary).
2.5 Model data obtained.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Radioanalytical development for the sample type involved in the project has been a major aspect in this initial period. The aim was to include analysis steps for radium-226 and polonium-210 into the established laboratory scheme for the natural alpha-emitting uranium and thorium isotopes. Good progress has been made with polonium-210 but it appears that a separate analysis will be required for radium-226.

In the meantime 18 samples of turbidite t from core MD24 have been analysed for the uranium and thorium isotopes and work has begun on samples from turbidite w. An initial interpretation of these data is given below.

PROGRESS AND RESULTS

2.1 Development of radiochemical scheme.

The total dissolution scheme used in this laboratory is based on potassium fluoride and potassium/sodium pyrosulphate fusions of sediment samples with calibrated spikes added for isotope dilution alpha spectrometry. A method has been developed to plate polonium isotopes from a dilute hydrochloric acid solution of the fusion cake to give a silver counting plate suitable for alpha spectrometry. The solution derived from the fusion procedure was unsuitable for radium-226 analysis by the radon-222 emanation method, however, due to occlusion of radium-226 into a slow-forming precipitate. Alternative separate dissolutions for radium-226 analysis are therefore being tested, based on lithium metaborate fusion and hydrofluoric acid/perchloric acid digestion. This work continues: when complete the new overall method will be tested on uraninite samples known to be at secular equilibrium.

2.2 Uranium and thorium analysis of core MD24.

The profiles of uranium-238, uranium-234 and thorium-230 versus depth in turbidite t of core MD24 are shown in Figure 1. It is evident that a very high degree of radiochemical closure exists in this sedimentary unit, which is inferred to have been continuously in a weakly reducing pore water environment for 600 ky. An in-situ effective diffusion coefficient $<10^{-12} cm^2.sec^{-1}$ is required to maintain the uranium-238 profile shape observed. Several previous studies of deep-sea sediments have observed an unequivocal preferential mobility of uranium-234 relative to uranium-238 which is not the case here. The mean uranium-234/uranium-238 activity ratio obtained from the 18 analyses is 0.999 +/- 0.005, and that for the thorium-230/uranium-234 activity ratio is 1.005 +/- 0.008. The remarkable immobility observed here in the decay sequence uranium-238 - uranium-234 - thorium-230 is further illustrated by the thorium-230/thorium-232 activity ratio versus uranium-238/thorium-232 activity ratio plot (Figure 2). The data of Figure 2 define a slope indistinguishable from 0.45, the value required for secular equilibrium in the uranium-238 - thorium-230 decay chain. Similar data appear to be obtained for turbidite w, but that profile is not yet complete.

Figure 1: Activity versus depth profiles for turbidite t in core MD24, showing uranium-238 (crosses), uranium-234 (circles) and thorium-230 (triangles)

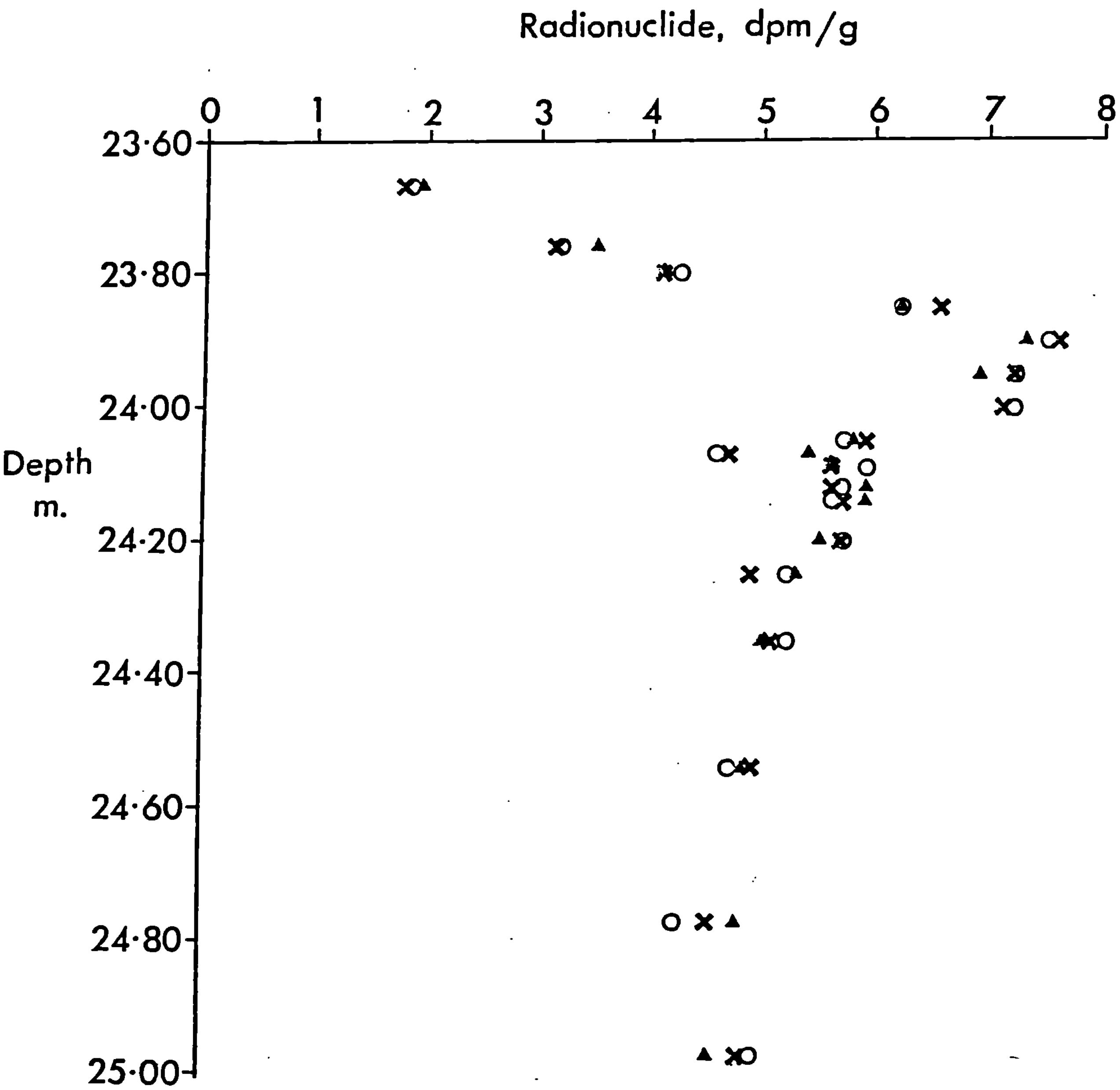
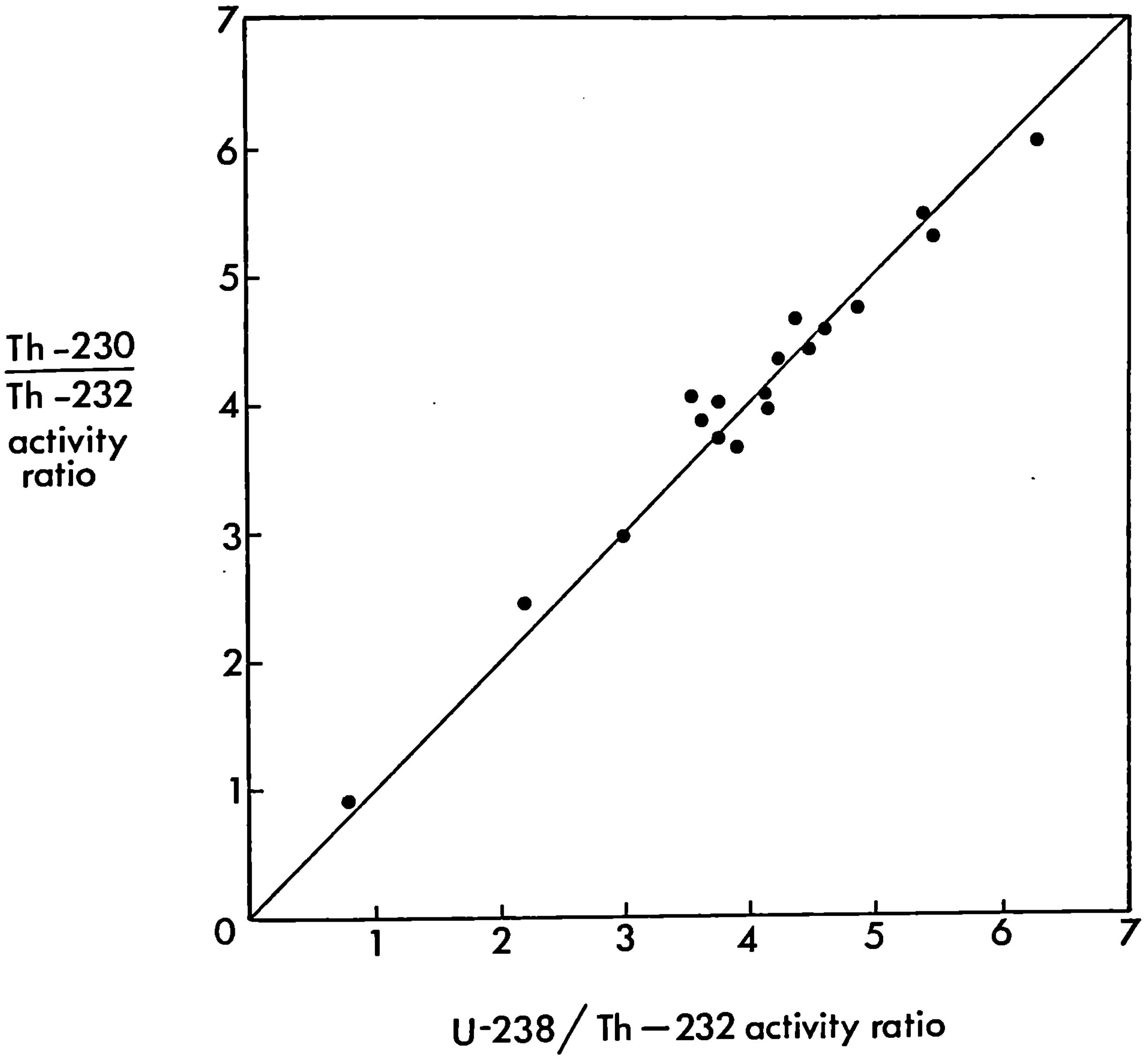


Figure 2: Thorium-230/thorium-232 activity ratio versus uranium-238/thorium-232 activity ratio plot for turbidite t in core MD24. This presentation yields a line of gradient 0.45 only if secular equilibrium obtains in the uranium-238 decay sequence.



STUDY OF THE MIGRATION OF U, TH AND REE IN AN INTRAGRANITIC URANIUM DEPOSIT

Contractor: CEA-IRDI/DRDD/SESD/SCPCS/LECALT - Fontenay-aux-Roses - FRANCE
Contrat n°: FI1W/0149
Duration of contract: from December 1987 to December 1989
Period covered: December 1987
Project Leader: J.C. PETIT - M.T. MENAGER

A. OBJECTIVES AND SCOPES

The intragranitic uranium deposit of the Jalerys (granite de Grury-Morvan-France) is considered in this study as a natural analogue of a high level radioactive waste repository realized in a similar geological formation. The physico-chemical processes of transport for some trace elements of interest are being investigated mainly in the near field.

More specifically, the aims of this investigation are:

- to obtain information on the elemental mobilisations of U, Th, and REE through surrounding argillaceous and granitic barriers from a particularly highly concentrated source term,

- to determine the geochemical mechanisms involved during the transport of radionuclides and to evaluate, as far as possible, their migration rates,

- to establish the relationship between experimental data on the geochemical behaviours of transuranic elements and those of their "natural analogues",

- to characterize, on the basis of all the available data, the retention capacity of a repository, which relies either on the properties of the near field only or on those of the overall geological formation,

- finally, to model the interaction between the granite, the fluid and the ore body by means of a geochemical code (EQ3/6).

A collaboration with COGEMA and CREGU is planned on this subject.

B. WORK PROGRAMME

B.1. Sampling of the Grury granite intruded by uraniferous mineralizations (the Jalerys mine and the Jacquot open quarry)
B.1.1. Samples are taken at regular intervals along a direction roughly perpendicular to the vein, from the mineralized body to the fresh granite.

B.2. Mineralogical studies at the laboratory
B.2.1. Petrographical and mineralogical works on primary and secondary parageneses, specially on U-Th-REE-rich ones, with optical and electron microscopy (scanning and transmission coupled with X-rays analysis) as well as fission track micromapping.

B.2.2. Study of the geochemical properties of the granite and of their evolution during alteration (major and trace elements analysis by ICP and neutron activation analysis).
B.2.3. Determination of the physico-chemical properties of fluids responsible for the alteration by the study of fluid inclusions (microthermometry, Raman microprobe).
B.2.4. Evaluation of temperatures active during the functioning of the system by the study of the thermal annealing of fission tracks registered in appropriate minerals.

B.3. Isotopic studies at the laboratory
B.3.1. Study of radionuclide mobilizations using uranium and thorium-series disequilibria for dating the last opening of the system (α and γ spectrometries, ion microprobe).
B.3.2. Dating of alteration minerals, whenever feasible.
B.3.3. Evaluation of the sorption efficiencies for U, Th and REE of granite-forming minerals for various degrees of alteration corresponding to different surface states (Rutherford backscattering, specific nuclear reaction analysis).

B.4. Modelling
B.4.1. Modelling of interactions between solid/solution by means of the EQ3/6 geochemical code and comparison with data of the natural system.
B.4.2. Simulation with this code of the evolution with time of a high level radioactive waste intragranitic repository.

C. PROGRESS OF WORK AND RESULTS OBTAINED

During December 1987, the sampling of the Jalerys mine, the preparation of polished thin sections for petrographic and fisson track analysis, as well as the crushing of samples for major and trace element analysis were performed.

LIST OF PUBLICATIONS

As this programme started only one month ago, no publishable data are available yet. We give here recent publications on a relevant subject, illustrating our methodology.

DRAN, J.C., DELLA MEA, G., PACCAGNELLA, A., PETIT, J.C., MENAGER, M.T., Sorption of actinides analogues on granite minerals studied by MeV ion beam techniques. Radiochimica Acta (in press).

MENAGER, M.T., PARNEIX, J.C., PETIT, J.C., DRAN, J.C., Migration of U, Th and REE in a fossil intragranitic geothermal system: implications for the mobility of actinides around a radwaste disposal. Radiochimica Acta (in press).

PARNEIX, J.C., MENAGER, M.T., TROTIGNON, L., PETIT, J.C., Hydrothermal alteration in the Auriat granite (Massif Central, France): analogy with a radwaste disposal. CEC Report n° EUR 11037 EN (1987) 13pp.

4.3.D. Development of calculation tools for the description of radionuclide migration

Modelling of migration phenomena in the Boom clay and of heat dissipation from a HLW repository in the multi-layered hydrogeological systems surrounding the Boom clay

Contractor : SCK/CEN, Mol (B)
Contract n° : FI1W/0055/B
Duration of contract : October 1986 to December 1989
Period covered : January 1987 - December 1987
Project leader : A.A. Bonne

A. OBJECTIVES AND SCOPE

For a correct understanding of the near-field phenomena induced by the presence of HLW in a clay formation a good prediction capability of the migration of radionuclides near to the sources is to prime importance, especially in view of assessing the possible impact of radiolysis due to the presence of released radionuclides in the near-field. As well the migration of ionizing radionuclides as the hydrogen produced by physico-chemical conditions determining the corrosion, leaching, sorption, etc. in the near-field.

Experimental results from radionuclide diffusion tests in clay urge to implement the radionuclide migration model in order to take into account diffusion as well in the stagnant porosity as in the cinematic porosity of a clay medium.

The thermal loading of the Boom clay formation has been calculated previously assuming a set of hypothese which need to be verified. One of the hypotheses is that the heat dissipation is only be conduction and the permeable strate in top of the host formation were assumed to present the same characteristics with regard to heat dissipation as the clay itself. A numerical modelling of the thermo-convective multi-layered system around such a repository has to confirm the validity of these hypotheses and to yield a more realistic assessment of the heat dissipation in the overburding aquifereous layers.

B. WORK PROGRAMME

1. Implementation and adaptation of the analytical code MICOF
2. Evaluation of the thermal impact due to HLW disposal into a stratified clay formation in a multi-layered aquifer system (Mol site)

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The MICOF-code is systematically and continuously implemented in more detail and for the specific hypotheses. The modelling study for the evaluation of the thermal impact due to HLW-disposal into the multi-layered sequence of permeable and impermeable strata is completed before schedule.

Progress and results

1. Implementation and adaptation of the analytical code MICOF

The analytical code MICOF has been further developed for the calculation of gamma-radiation yielded by a HLW-canister and of the alpha/beta-doses due to released radionuclides and as a result the impact of the radiation exposure in the clay can be assessed. The main conclusion of these calculations is that on the very long term (10 E6 years) only a very limited volume of clay surrounding a stack of HLW-canisters will be altered by an increased oxidation. According to the calculations figures of 3.5 m to 4 m were obtained for the radius of the altered volume around the stacks.

2. Evaluation of the thermal impact due to HLW-disposal into a stratified clay formation in a multi-layered aquifer system (Mol site)

In order to assess the modifications by the thermal loading HLW-repository, on the flow pattern inside the clay formation and in the adjacent aquifers and to assess the impact of the groundwater flow on the temperature distribution inside the clay, a numerical analysis of the coupled heat and flow movement around a repository has been performed in cooperation with the Centre d'Informatique Géologique (Paris).

Previous calculations on the heat transfer in Boom clay, pointing out that heat conduction is the dominant transfer process, have been confirmed. Heat transfer by thermoconvection is to be neglected. It was also found that, irrespective of the thermal density in the repository thermoconvective circulations will be induced in the neogene sands overlying it. Taking also into account the regional groundwater flow and the varying lithostratigraphy of the neogene formations, the simulations show that thermoconvective cells can be developed only between 30 and 160 m depth, where the intrinsic permeability amounts to at least 10 E-12 m2. It was also concluded that the temperature profile in this stratified medium behaves in a very similar way as the profile obtained for pure conductive heat transfer.

COUPLING BETWEEN A GEOCHEMICAL MODEL AND A TRANSPORT MODEL OF DISSOLVED ELEMENTS .

Contractor: Centre d'Etudes Nucléaires de Fontenay-aux-Roses
IPSN/DAS/SAED-FRANCE

Contract N° : FI1W/0075

Duration of contract : from december 1986 - to june 1988

Period covered : January 1987 - December 1987

Project leader : J. JACQUIER.

A. OBJECTIVES AND SCOPE

In order to assess the safety analysis of an underground repository, we have to model the transport of radioelements in groundwater and their interactions with the geological medium. So the objective of this study is the elaboration and experimental validation of the coupling of a geochemical model with a transport model of dissolved element.
In this case, it is necessary to link a work of mathematical modelisation on simple laboratory experiments where geochemical phenomena are well identified ; that is the goal of the present study.

B. WORK PROGRAMME

2 . 1 Dimensioning of a laboratory experiment, on the basis of a simple modelisation of the transport and geochemical phenomena.

2 . 2 Flow-through experiments on crushed limestone.

2.2.1 Influence of the variation of temperature of the water : 40° or 25°C.

2.2.2 Influence of the presence of a pollutant like strontium chlorure at different concentrations.

2.2.3 Influence of the preestablished, equilibrium between water and crushed limestone.

2 . 3 Interpretation of the results of the experiences in the perspective of the modelisation developed in item 2.1.

.../...

C - PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The item 2.1 (dimensioning of the experiment), is developed in the report/1/. A laboratory experiment was chosen to be developed at Saint-Paul-les-Durance (Centre d'Etudes Nucléaires de Cadarache - IPSN/DERS/LESS) on crushed limestone. In this report, theoretical simulations are presented to predict, on the basis of flow-through experiments, the chemical evolution of the solution, by variation of the temperature (e.g , in terms of dissolution-precipitation of calcium-carbonate (figure 1).

Progress and results

2.2 Flow-through experiments were conducted this year. Some experimental difficulties were encountered like the thermal isolation of the column (notably the implantation of the thermal collectors) or the determination of the right rate of flow through the column in accordance with kinetic consideration. Eleven experiences were realised as shown in table I.

2.3 A first interpretation of the results of these flow-through experiments is now under investigation /2/. At this moment, the experiments with strontium chlorure and distilled water, at room temperature, are examined, from some results of chemical analysis (figures 2,3,4).
The general shape of the curves looks regular ; strontium has a noticeable behaviour, its concentration increases quickly after the 50 th. hour to 70 hours ; at this state it does not seem to have reached a stable state (figure 3(b)). On the other hand, we notice that calcium concentration is higher when there is more strontium (figure 4).

With the geochemical model CHIMERE, some calculations have been made, notably to examine the state of equilibrium of water with respect to minerals.
For this purpose, a speciation calculation is done and it appears that the electroneutrality condition is not respected, and the residual balance appears to be significantly different from zero. Moreover, the saturation indexes with respect to calcite, aragonite (another crystalline shape of calcium carbonate) and dolomite indicate that the solutions are largely oversatured. This problem is perhaps linked to the previous. A possible explanation is that, before analysis, water samples were not filtered : in this way, components of small solid particles are taken into account in water analysis.
So, it will be perhaps necessary to effect some corrections, because electroneutrality is not respected and there is no filtration.

Development of models

A coupled model is now in development, named STELE. It is the result of the coupling between a geochemical model, CHIMERE and the code METIS /3/.

The objective is to predict the evolution in space and time of the chemical composition of the solution and to evaluate the spacial distribution of dissolved, precipitated, or degased amounts of each mineral or gas /4/. The method of resolution is in two step procedure.

The coupled model STELE will require some adjustments to simulate the flow-through experiments.

/1/ COUDRAIN-RIBSTEIN A. (1986) - Elaboration et validation expérimentale d'une méthode de résolution du couplage entre un modèle géochimique et un modèle de transport d'éléments en solution. Rapport annuel CIG, LHM/RD/86/114.

/2/ VINSOT A.-JAMET P. - COUDRAIN-RIBSTEIN A. (1987) - Elaboration et validation expérimentale d'une méthode de résolution du couplage entre un modèle géochimique et un modèle de transport d'éléments en solution. Rapport annuel CIG, LHM/RD/88/5 (to be transmitted).

/3/ GOBLET P. (1986) - Développement du code METIS.
Rapport final METIS 2. Rapport CIG/ENSMP,LHM/RD/86/77.

/4/ COUDRAIN-RIBSTEIN A. - MOREL F.M.M. (1987)- Modélisation du transfert d'éléments majeurs réactifs dans un champ de température variable : méthodologie et exemples simples. Bull. Soc. Géol. France, (8), t III, n°5, p 1009 - 1017.

TABLE I - SUMMAR Y OF THE REALIZED

FLOW-THROUGH EXPERIMENTS

TEMPERATURE WATER	ROOM TEMPERATURE	38 OR 40°C
DISTILLED	• FLOW RATE : 20 ml/h • FLOW RATE : 100 ml/h	•
DISTILLED + STRONTIUM CHLORURE	• CONCENTRATION = 10^{-3} M/L • CONC. = 10^{-1} M/L	• CONC. = 10^{-3} M/L • CONC. = 10^{-1} M/L
EQUILIBRATED	•	•
EQUILIBRATED + STRONTIUM CHLORURE	• CONC. = 10^{-1} M/L	• CONC. = 10^{-1} M/L

FLOW RATE = 100 ml/h WITHOUT PRECISION

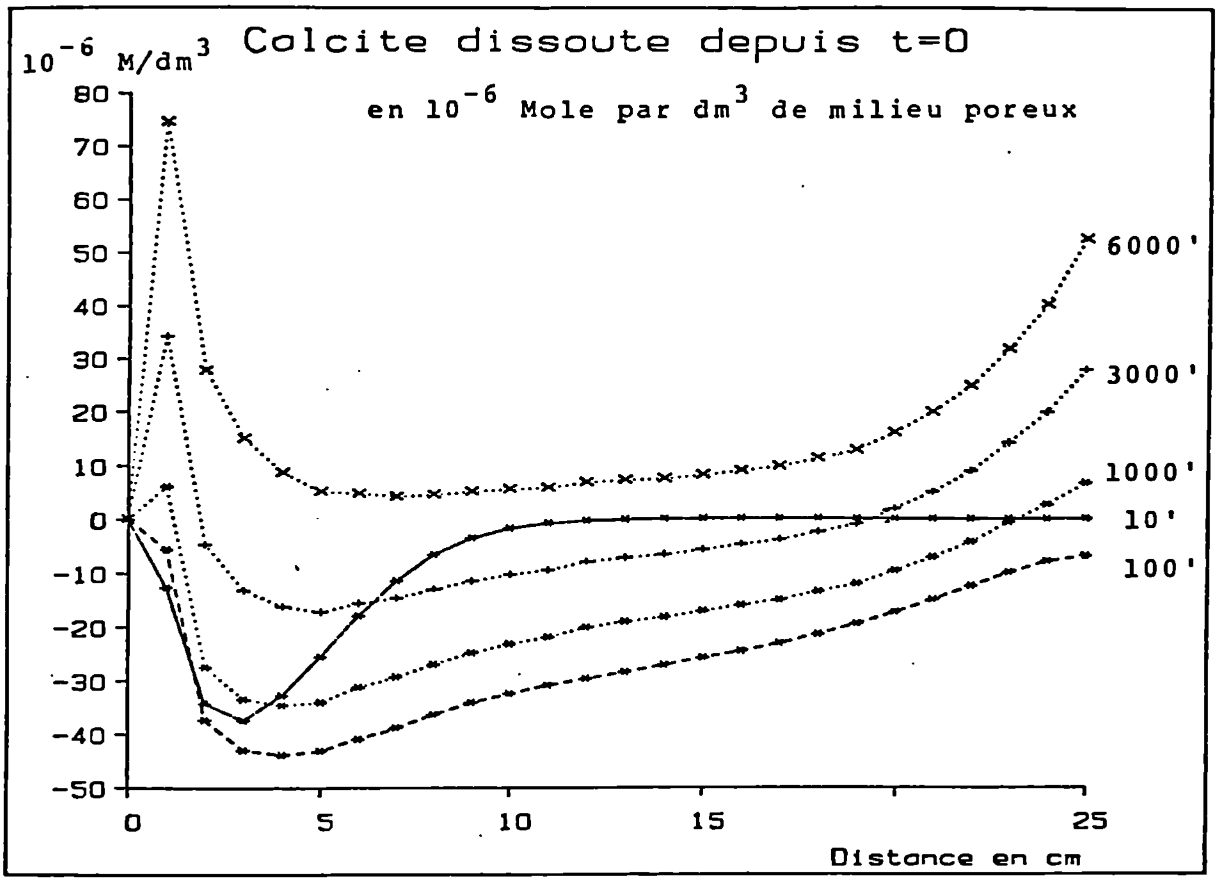
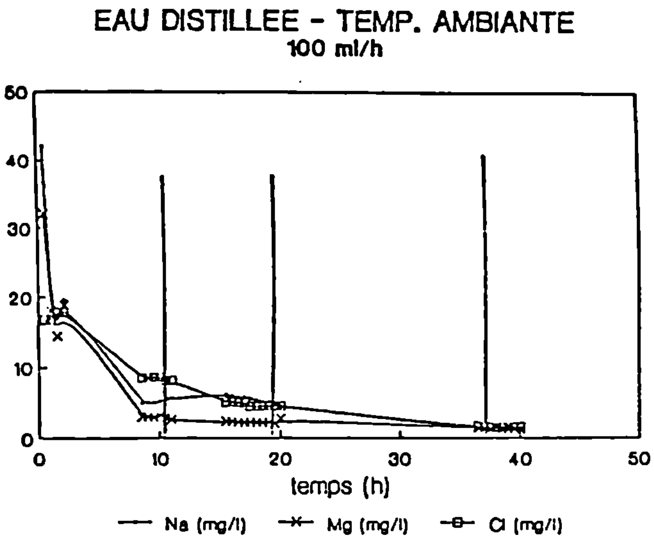
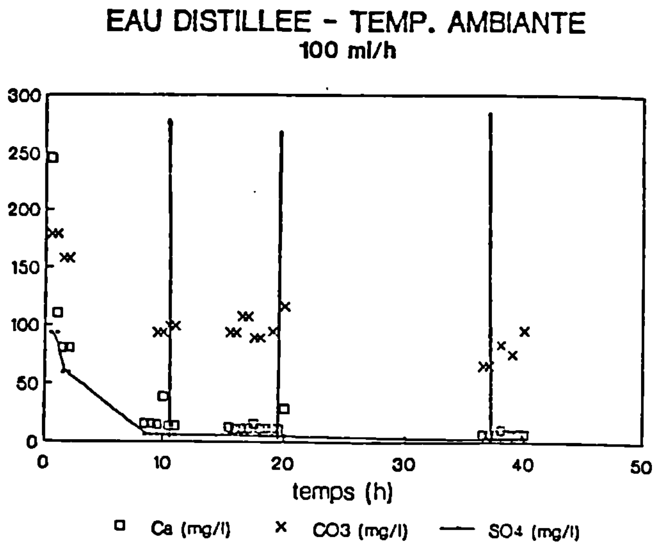


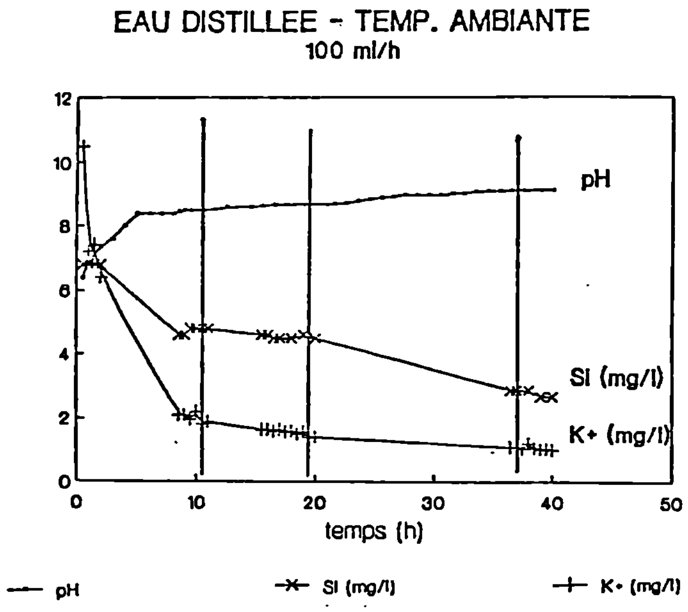
Figure 1 : Balance of dissolved calcite (>0)
or precipitated (<0) from starting time



2 (a)

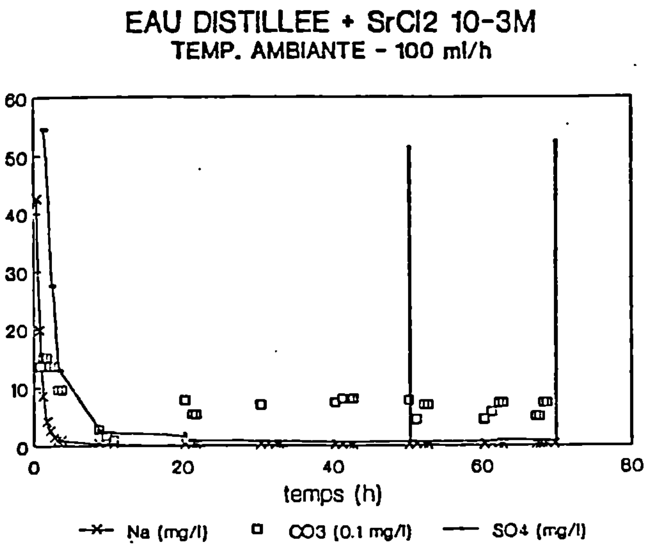


2 (b)

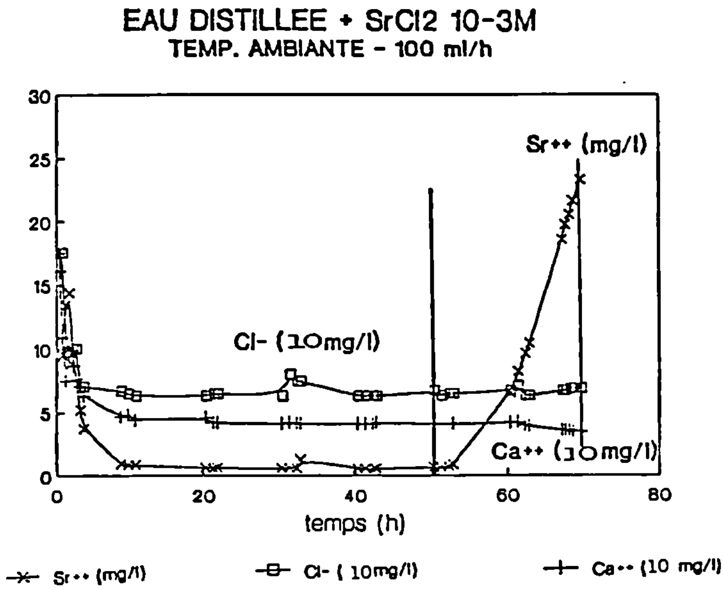


2.(c)

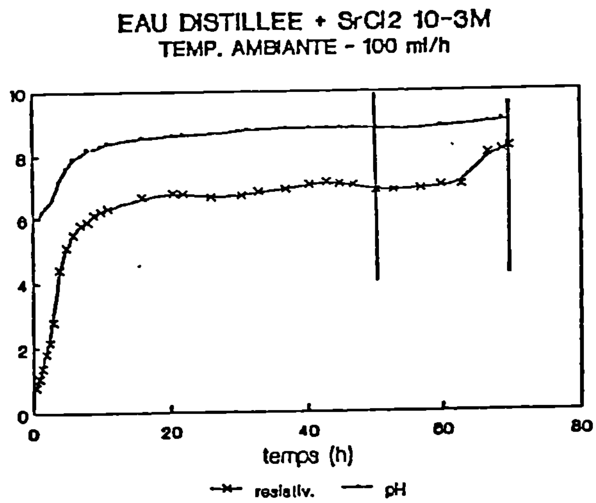
Figure 2 (a, b, c) : Distilled water - Room temperature
100 ml/h



3(a)



3(b)



3(c)

<u>Figure 3 (a, b, c)</u> : Distilled water + $SrCl_2 10^{-3}M$
Room temperature - 100 ml/h

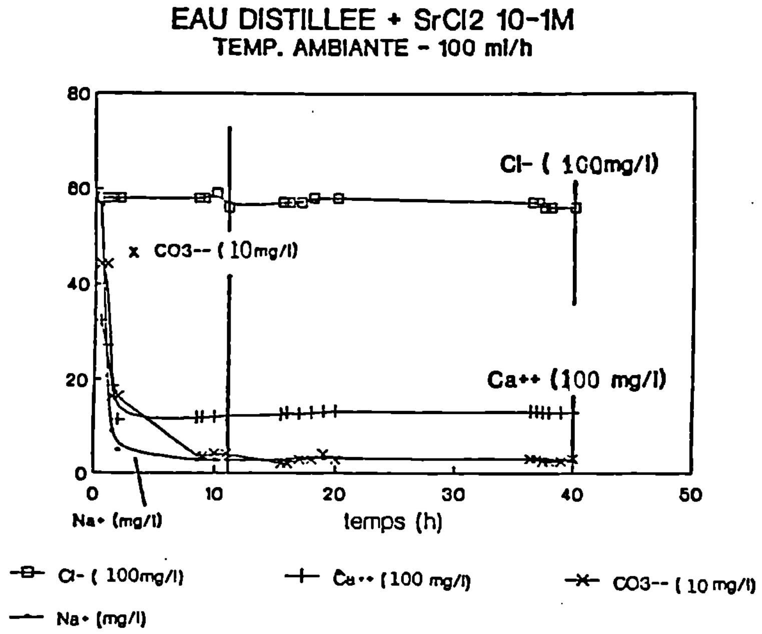


Figure 4 : Distilled water + $SrCl_2$ 10^{-1}M
Room temperature - 100 ml/h
(missing results for Sr)

INTERCOMPARISON OF PREDICTIVE COMPUTER PROGRAMS FOR RADIONUCLIDE MIGRATION IN THE GEOSPHERE

Contractor:	W.S. Atkins Engineering Sciences, Epsom, U.K.
Contract No:	FIIW/0077
Duration of Contract:	February 1987 - January 1990
Period Covered:	February 1987 - December 1987
Project Leaders:	T W Broyd, D Read

A. OBJECTIVES AND SCOPE

Prediction of the transport of radionuclides through the geosphere requires detailed knowledge of aqueous geochemistry, host-rock mineralogy and the specific mechanisms of solid-solution interaction. Such knowledge often needs to be obtained using computer models and associated databases, which must be shown to provide accurate results, i.e. are validated for use. International code verification and proving exercises have become accepted as an important means of assisting the validation process.

This contract will establish an international project called CHEMVAL, aimed at reviewing current progress and establishing research needs in the areas of chemical and chemical transport modelling. The objectives of CHEMVAL are as follows:

i) to produce the best possible overall thermodynamic database for use with aqueous speciation and coupled chemical transport codes, consistent with project resources and time-scales.

ii) to apply aqueous speciation computer models to a range of realistic waste disposal situations, and hence to establish and/or confirm areas of research requirement.

iii) to provide validation both for aqueous speciation models and coupled chemical transport codes.

B. WORK PROGRAMME

1. Comparison, sensitivity and extension of databases. The results of other parts of the work will be used in determining the most appropriate course of action.
2. The application of available aqueous speciation programs and databases to a range of hypothetical, though realistic, waste disposal situations.
3. The application of available programs coupling chemistry and waste transport to a range of test cases.
4. Validation of aqueous speciation and coupled codes by comparison, where possible, with a) experiments, b) field tests and c) natural analogues.

The exact scope and nature of work will be as agreed at plenary meetings of CHEMVAL participants, to be held throughout the duration of the project.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

During 1987 the overall structure of CHEMVAL has been established, both in terms of organisations involved and an outline schedule of work for the duration of the project. Certain stages of the work are well advanced, but no single item of the work programme (section B) has yet been completed.

PROGRESS AND RESULTS

i) Structure of CHEMVAL

The organisation structure is shown in Figure 1. The work is being co-ordinated by Atkins ES with Riso National Laboratory providing critical peer review and ensuring overall compatibility with other MIRAGE2 activities. That part of CHEMVAL concerned with model application and validation currently has sixteen participating organisations, all within Europe. Thermodynamic database work is being undertaken by the University of Wales Institute of Science and Technology (UWIST) and the University of Manchester (UM), both under sub-contract to Atkins ES. Of these, UWIST are broadly responsible for the provision and maintenance of a standard "CHEMVAL" thermodynamic database, with UM being responsible for its critical review and extension.

Work on the thermodynamic database will continue throughout the duration of the project. Verification and validation aspects may be separated into four components, as follows:

STAGE 1 application of aqueous speciation codes to a range of realistic cement water and groundwater compositions.

STAGE 2 validation of aqueous speciation codes against experimental field and laboratory data

STAGE 3 verification of coupled chemical transport codes

STAGE 4 validation of coupled codes against experimental data

The anticipated timescale of each topic is given in Figure 2. Whilst the ultimate aim is validation of the chemical models, stages 1) and 3) will provide significant information on the level of agreement between different research organisations, as well as highlighting deficiences in the databases used.

A three tier system of project meetings has been established (Figure 2) to chart progress in each of the main project areas. This has been designed to accommodate both CHEMVAL and MIRAGE2 work schedules. The results of each of the above stages will be reported, individually, during the project. Additionally, summary reports will be issued on specific aspects of database development.

ii) Verification of aqueous speciation codes

Verification cases have been constructed to reflect, as far as possible, the various disposal options envisaged by member countries. They incorporate a cementitious leachate, to test the application of models to solutions at pH12, and two alternative far-field situations; a clay aquitard and sandstone aquifer or a granite host-rock and limestone aquifer. Roughly six separate simulations are performed on each of the five main geochemical systems, ranging from relatively simple base case problems of aqueous speciation to increasingly complex reaction path calculations involving considerable judgement and experience on the part of the analyst. Radioelements included were those identified as being important during previous radiological assessment programmes, namely; americium, plutonium, uranium and technetium plus caesium, strontium and cobalt. The chemical processes modelled for each cement leachate or groundwater system are summarised in Table 1. Results are obtained using both the participants' "in-house" databases and also using the standard CHEMVAL database, to enable differences caused by the use of different databases to be established.

iii) Reports

A report on Stage 1 of the work is in preparation. In addition, reports from the University of Manchester on a comparison of databases in common use, and a review of the CHEMVAL database, will be produced shortly.

iv) Publications

"Verification and validation of predictive computer programs describing near and far-field chemistry of radioactive waste disposal systems", by D Read and T W Broyd.

Intl. Conf. on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Munich, September 1987.

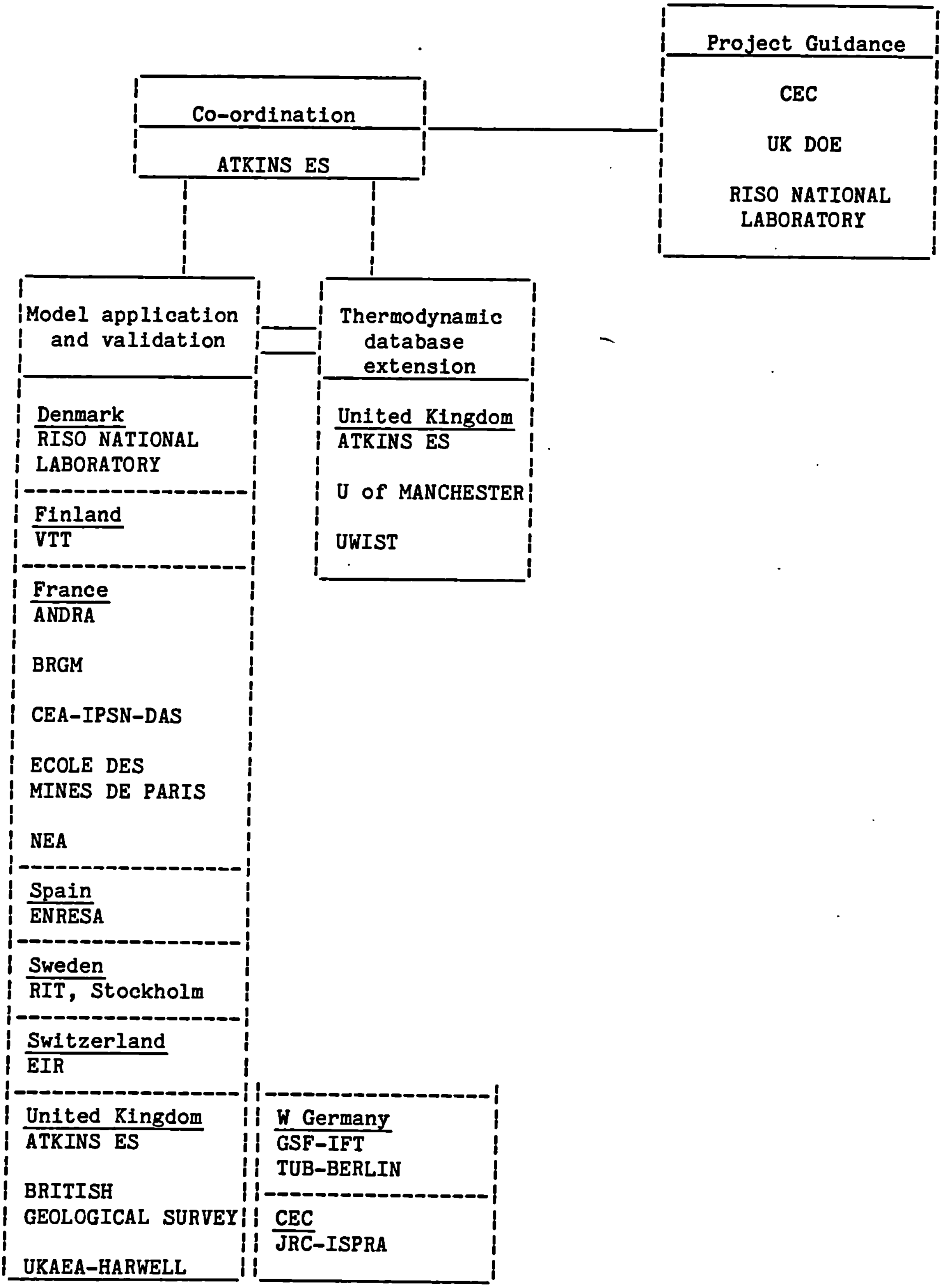


FIGURE I ORGANISATION OF CHEMVAL

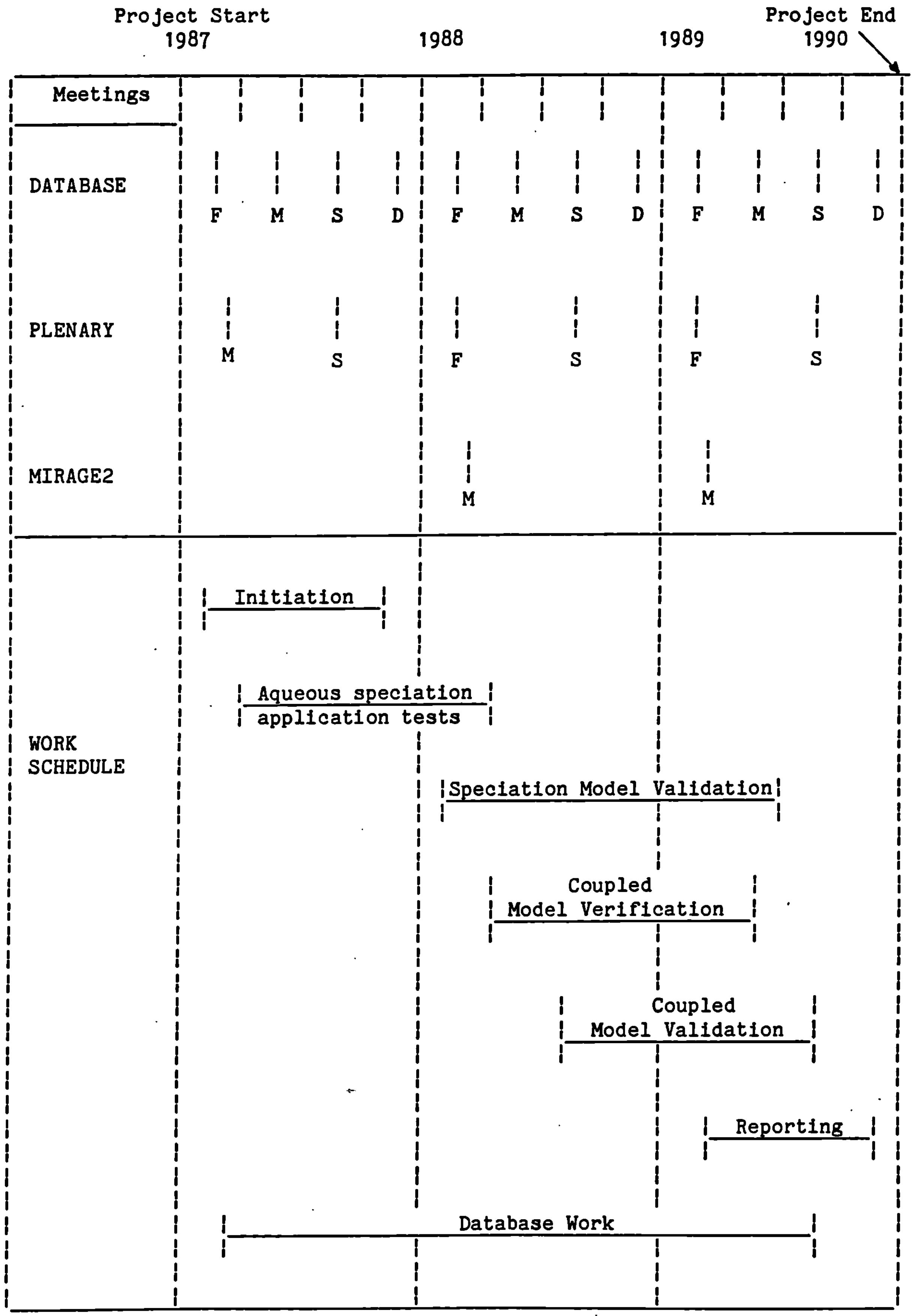


FIGURE 2 OUTLINE SCHEDULE OF CHEMVAL

	SYSTEM				
PROCESSES	CEMENT Am,Pu, Cs,Sr	CLAY Am,Sr	SANDSTONE Am,Pu,Sr, Co	GRANITE U,Tc,Sr	LIMESTONE U,Sr
AQUEOUS SPECIATION	*	*	*	*	*
PRECIPITATION - DISSOLUTION	*	*	*	*	*
pH BUFFERING	*	*	*	*	*
AQUEOUS REDOX EQUILIBRIA	*	*	*	*	*
IRREVERSIBLE OXIDATION/REDUCTION	*	*	*		
ORGANIC COMPLEXATION	*	*			*
TEMPERATURE VARIATION				*	
SALINITY EFFECTS		*	*		*
SOLUTION MIXING		*	*	*	*
SILICATE HYDROLYSIS				*	
pCO_2 VARIATION				*	*

TABLE 1 - ATTRIBUTES OF AQUEOUS SPECIATION TEST CASES

FAR-FIELD MODELLING OF RADIONUCLIDE MIGRATION

Contractor : Harwell Laboratory, United Kingdom
Contract No. : FI1W/0078
Duration of contract : January 1987 - December 1989
Period covered : January 1987 - December 1987
Project leader : M.J. Norgett

A. OBJECTIVES AND SCOPE

Numerical simulation of groundwater flow and solute transport is an essential element of any assessment of the performance of a proposed repository for nuclear waste. The accuracy and realism of such simulations must be clearly demonstrable and also defensible against critical public scrutiny. Detailed simulations are expensive so any increased computational efficiency offers the opportunity for more extensive sensitivity analysis as part of a comprehensive repository assessment.

The project aims to improve the capability, efficiency and realism of the NAMMU code, which simulates groundwater flow and solute transport through a porous medium. Our detailed objectives are to discover and exploit superior methods for solving significantly non-linear problems; to introduce into the code a capability for modelling chemical reactions; to identify and test improved techniques for simulating the progress of sharp fronts in solute concentration; and to identify better-founded representations of solute dispersion. The last two topics will be covered by sub-contracts placed at Universities in the United Kingdom.

The NAPSAC code presently calculates flow through a three-dimensional network of fractures. Our aim is to decide upon and implement the most appropriate method for calculating solute transport through a three-dimensional network, so NAPSAC could be used to investigate radionuclide migration from a repository in hard fractured rock.

B. WORK PROGRAMME

1. Improved methods for solving significantly non-linear groundwater-flow problems will be implemented in NAMMU because those currently available, although robust, are expensive.
2. The NAMMU code will be enhanced to provide a means of modelling the impact of chemical reactions on solute transport in a porous medium.
3. Methods will be assessed and tested that offer prospects of simulating efficiently the advance of sharp fronts in solute concentration, without spurious dispersion.
4. Models of inhomogeneous materials will be explored to provide better understanding and descriptions of solute dispersion.
5. The NAPSAC fracture-network code will be enhanced by incorporating a judiciously chosen technique for calculating solute transport.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

In late Spring, once full funding for the project was available, University staff with relevant experience were invited to tender for sub-contracts covering topics 3 and 4. Various proposals were received advocating different approaches to the problem of simulating efficiently and accurately the advance of sharp fronts in solute concentration. In our judgement, the proposal from Professor Roe of Cranfield Institute of Technology offered the best prospect of immediate progress. Professor O'Connell of Newcastle University offered the only proposal dealing with solute dispersion. The recruitment of research assistants to undertake both tasks has proved tedious and time-consuming, but now both Professors Roe and O'Connell have secured suitably experienced staff. The research to be undertaken will begin towards the beginning of 1988 and the sub-contracts are for one year.

Progress at Harwell on the remaining topics was hindered by resignations so it was possible to make a start on enhancing NAMMU only in October when an additional member of staff began work. He has started by examining how to interface NAMMU with an existing chemical equilibrium code. Once this task has been assessed, it will be possible to review methods for solving non-linear problems. The development of the NAPSAC code will begin on schedule at the beginning of 1988.

Progress and Results

Incorporating chemical reactions in the NAMMU code (Task 2)

The resources in the NAMMU code provided for modelling solute transport in one, two or three dimensions have been reviewed and a number of detailed improvements implemented. The code has been enhanced so that the sorption of one solute can depend on the concentration in solution of a second species. Data exist to validate this simple but significant chemical interplay within a porous medium. To provide a more general capability, NAMMU will be coupled with a code capable of determining equilibrium amongst various chemical species. PHREEQ /1/ seems best suited for this latter task. We anticipate that NAMMU and PHREEQ will be invoked in turn, the first to calculate the transport of fixed amounts of each species, the latter to re-equilibriate the mixture at the end of each timestep. This strategy has been exploited successfully in the CHEQMATE /2/ code, but NAMMU provides wider opportunities for calculating solute transport.

Developing numerical methods to simulate the advance of sharp fronts in solute concentration (Task 3)

Five proposals addressing this topic were submitted and assessed. Two advocated the adoption of moving and adaptable finite-element grids. This approach undoubtedly offers substantial benefits but is cumbersome to implement in two and particularly in three dimensions. Lagrange-Galerkin finite-element methods were also recommended and have evident potential, but are dealt with in another project that will enhance the NAMMU code. Particle methods are also attractive as a means of modelling dominantly advective transport, but have already been implemented within the family of codes to which NAMMU belongs.

Professor Roe's proposal, and one other, stressed the capability of the so-called flux-limiter approach /3/. Roe has originated, developed and exploited this method primarily for calculating aerodynamic flows.

However, there are evident parallels between the equations describing shock waves and sharp fronts in solute concentration. We therefore concluded that the flux-limiter approach can be adapted conveniently to modelling the advance of such sharp fronts, with good prospects of substantially reducing the impact of spurious dispersion.

Improving understanding and representation of dispersion (Task 4)

Professor O'Connell submitted the only proposal dealing with this topic. Dispersion would be investigated by calculating solute transport through portions of a randomly heterogeneous medium, which is specified by the distribution and spatial correlation of permeability. The code needed for such calculations already exists. The present project will focus primarily on statistical techniques and analysis.

References

/1/ PARKHURST, D.L., THORSTENSON, D.C. and PLUMMER, L.N., U.S. Geol. Surv. Water Resource Investigations, NTIS Tech. Rep. P1381 - 167801 (Revised), pp 80-96 (1985).

/2/ SHARLAND, S.M., TASKER, P.W. and TWEED, C.J., Proc. 10th Int. Symp. on the Scientific Basis for Nuclear Waste Management, Boston, December 1986, eds. J. Bates and W. Seefelt, (Materials Research Society, Pittsburgh, 1986), p 683.

/3/ ROE, P.L., Ann. Rev. Fluid Mech. (1986).

GEOCHEMICAL MODELLING

Contractor: Risø National Laboratory, Denmark
Contract No.: FI1W/0079
Duration of contract: August 1986 - December 1989
Period covered: August 1986 - December 1987
Project leader: B. Skytte Jensen

A. OBJECTIVES AND SCOPE

In order to predict long-term behaviour of radionuclides in the environment, existing computer programs need to be improved and modified such that they can handle realistic problems with ease. Some of these changes will be introduced when rewriting the previously constructed computer programs WHATIF-AQ and WHATIF-PW.

The improvements comprise the following points:

1.1 The inclusion of algorithms which realistically model phenomena like ion-exchange, coprecipitation reactions and the formation of solid solutions. These processes can with advantage be handled by mass-transfer programs like WHATIF-PW, EQ6, etc., but not with the speciation programs like WHATIF-AQ, EQ3 or PHREQUE.

1.2 The development of a new design which increases the versatility of the WHATIF program series as well as improving their user-friendliness and speed of computation. The existing programs have been written in BASIC and will in the revision be translated into PASCAL, with a resulting increase in speed of up to 20 times. The new design will in addition allow the user to choose among several options of envisaged processes as well as of conditions imposed on the system being studied.

1.3 The database, containing the relevant thermodynamic data characterising the formation of complex species and solid phases, will simultaneously undergo a revision with regard to its internal structure such that revised or new data may be introduced without simultaneously revising the computer-programs. This work will be closely coordinated with the work going on in the CHEMVAL group and naturally with the work being done within the contract No. FI1W/0080, GEOCHEMICAL DATABASES.

B. WORK PROGRAMME

2.1 To develop a quantitative formulation for ion-exchange and coprecipitations and for the formation of solid solutions, which are convenient for inclusion in the geochemical mass-transfer programs.

2.2 To select the options to be included in the programs which are envisaged as mimicing realistic processes and/or conditions being encountered in natural systems, and to design a program structure where these options are selected with ease. This work will run parallel with the translation of the programs into PASCAL.

2.3 To develop a database system which offers the user freedom of choice of species to be included into the calculations, depending on conditions or actual observations.

C. PROGRESS OF WORK AND OBTAINED RESULTS

The translation of the WHATIF-AQ program into PASCAL is in principle finished. Additional refinements have improved speed such that a speciation calculation, where up to 150 species are considered, takes only a few seconds.

Options for choosing fixed or floating values of pH or/and pE(Eh,P-O_2) are available as well for fixed or floating (P-CO_2). The program does likewise offer the option to neglect equilibria which may be considered too slow to be established under the conditions being studied. Typically it could be to question if the sulphate/sulphide equilibrium is active.

Although algorithms for the direct determination of amounts of solid phases after a speciation calculation are available, they are all too slow and a combination of the WHATIF-AQ and the WHATIF-PW programs is chosen as the most promising and versatile approach for the modelling of geochemical changes in the environment. This is mainly because the mass-transfer program may be used to model differential processes like those which occur when ion-exchange and coprecipitation processes proceed.

Minor algorithms for handling these processes have been constructed and tested and are ready for incorporation into the final program.

The translation of the mass-transfer program WHATIF-PW into PASCAL is in principle straightforward, but at present thoughts are given to possible improvements which may be introduced simultaneously with the revision.

Before these improvements will be implemented the structure of the database has to be ajusted to the new program structure. This work, which is not considering the content of the database, is at present going on in the way that different possibilities are tried on a minor test program, WHATIF-exp.

The construction of convenient input- and output schemes is also considered. The input should allow for an easy choice of options and ease of entering data. The output will in addition to presenting computed concentrations for all the macro species also write the distribution of trace elements on their possible soluble species as percent of total. The extra time for the calculation needed is negligible.

The development of the combined programs is expected to be finalised within the present contract.

GEOCHEMICAL DATABASES

Contractor: Risø National Laboratory, Denmark
Contract No.: FI1W/0080
Duration of contract: August 1986 - December 1989
Period covered: August 1986 - December 1987
Project leader: B. Skytte Jensen

A. OBJECTIVES AND SCOPE

The input to a geochemical database is derived from experimental data published in literature. In the computation the program will correct for variations in conditions as for example temperature, ionic strength etc. To do this properly and in a simple manner all experimental data need to be reduced to the standard conditions i.e. 25°C, 1 bar and zero ionic strength, whereafter these data are used as a basis in the computations. Available physico-chemical knowledge tells how to do this reduction, but in practice this can often only be handled by more or less precise approximations and in other cases is the needed experimental information not available. These complications are considered in the CHEMVAL group, by NEA and the CODATA groups and recommendations from these groups will be taken into account when presenting the final database. To offer a possibility for future users of the database it will contain the original literature data as well as information about the experimental conditions under which they have been obtained etc. so that other reduction schemes may be used if wanted.

Geochemical calculations as done today look for the final equilibrium in a thermodynamic sense and are not able to take kinetic factors, which may hinder the formation of a solid, into account. These calculations do therefore often find equilibrium assemblages of minerals which seldom if ever are encountered in nature. It is therefore needed to find some remedy whereby one can bypass the purely thermodynamic arguments without violating them. The clue to the discrepancy between observations and theory is no doubt of kinetic origin and if additional kinetic arguments may be quantified simply they may be used to ajust the computations to observations.

One approach is to classify minerals according to field observations, simultaneously relating these observations to existing conditions. Another approach which is attempted is to operate with the concept of supersaturation needed before a nucleation starts.

B. WORK PROGRAMME

2.1 To select a database valid within the temperature range 10-90°C, which is internally consistent and as complete as possible.

To handle chemical equilibria at higher temperatures a separate database is needed because very few experimental data are available and predictions will be based on hypotheses and/or theory. A database developed by US-geological survey seems for such cases to be the best available.

A computer program will be developed which allows a data selection to be ajusted such that it is internally consistent. This work will mainly be done by Joe Pearson Jr., formerly at INTERA. The work of compiling data will closely follow the work being done within the CHEMVAL group, NEA, CODATA a.o.

2.2 It is attempted to include in the database information (or data) which allow the user to make empirical predictions on the probability of formation of solids under given conditions. This information will be based on the experience of field workers and on information in the geological and mineralogical literature. Another approach being tested is based on the idea that the rate of nucleation is the factor determining which of possible precipitates actually are formed.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The study of existing geochemical databases with regard to their content, structure and layout is continuing with the aim to select an optimal structure.

Different methods of reducing the experimental data to standard conditions are evaluated and the merits of the different methods are compared.

It has been decided to establish two separate databases valid at moderate temperatures, i.e. 10-100°C, one for use in aqueous speciation calculations containing only data for soluble species, and the second containing data for solid phases. A further extension may be to establish a set of databases for use at elevated temperatures.

The databases compiled will present the original experimental data available and the conditions under which they have been determined. In addition suggestions for subroutines useful for reduction of data to standard conditions will be mentioned.

With this compilation the original data are always available for the user and he/she is offered the possibility to apply other preferred methods for data reduction if wished.

For different applications the user may extract selected sets of either equilibrium constants or free-energy data for use in diverse application programs.

PROGRESS AND RESULTS

2.1 Several databases have been collected including the one developed by the CHEMVAL group.

The design of the program securing internal consistency within a dataset is in progress. The fundamentals are already available in the WHATIF-G>K program, which is used in connection with the existing WHATIF programs.

2.2 The empirical approach using "probabilities of observation" as a criterion for the formation of solid phases under given conditions has been implemented in the existing WHATIF-PW program and found to perform well. The main problem is to secure an accepted classification of minerals into groups according to their possible observation and not to any computational difficulties.

In the present version of the WHATIF database, the insertation of new data or their revision is rather time-consuming, but these problems will be avoided in the new versions.

The quantitative approach using supersaturation indices (or rates of nucleation) as measures for the probability of formation of solids has been used with success on the calcite, magnesite, dolomite-problem in a WHATIF-PW calculation.

The rate of nucleation, which is related to the supersaturation allowed before precipitation starts, is believed to be dependent of the size and complexity of the unit cell in a crystalline solid. The larger the unit cell the more difficult it will be to form a nucleus in solution and a larger supersaturation is allowed before precipitation starts. These conditions may be condensed in a semitheoretical expression, which will in addition also include estimates of temperature effects on limits for precipitation.

The work is expected to be finalised within the present contract.

MIGRATION OF RADIONUCLIDES BY HIGH-DENSITY BRINES: FINALISATION OF THE METROPOL CODE

Contractor: RIVM, Bilthoven, The Netherlands
Contract No.: FI 1W/0081
Duration of contract: October 1986 - October 1988
Period covered: January 1987 - December 1987
Project Leaders: P.Glasbergen, F.Sauter

A. OBJECTIVES AND SCOPE

Transport of radionuclides, possibly released from a salt dome repository in the surrounding aquifers, is a key problem in the safety analysis of waste disposal in salt. For the numerical solution of the set of equations (Darcy's, Fick's law and extensions of these laws for high density brines) which describe the transport, a family of computer codes, called METROPOL, has been developed.

So far METROPOL-1, 2 and 3 have been developed, dealing with, respectively, steady state 3D flow, transient 3D flow and transient 3D flow of fluid with high density differences.

The objective of the present contract is to complete the development of the computer code METROPOL-4, which simulates the transport of low concentration dissolved species, including such processes as adsorption and decay.

In order to make METROPOL easily accessible to other users documentation will have to be written, whereas for an easy interpretation of calculated results much effort will have to be put into the development of post-processing facilities.

B. WORK PROGRAMME

1. Inclusion of physico-chemical processes, such as dispersion, diffusion, adsorption, desorption, decay, dissolution/precipitation of salt, chemical reactions, in the METROPOL-code.
2. Inclusion of thermal effects.
3. Code development. New numerical techniques should be studied for the solving of large sets of linear equations as well as for the integration in time (adaptive time integration scheme).
4. Testing and validating the METROPOL-3 code in the case of the flow of high-density brine.
5. Preparing user manuals for METROPOL.
6. Development of post-processing facilities such as particle tracking, contour plotting.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

METROPOL-3 has been tested in several cases, going from relatively easy 1D cases to rather complex 3D problems. The code is also being used in the international model intercomparison study Hydrocoin.

Many problems were encountered in the testing phase; these difficulties are due to the strong coupling of the flow and transportequation in high density flow. Especially in 2D and 3D flow, problems occurred due to the inconsistency of the boundary conditions for the pressure and the salt mass fraction. It proved to be necessary to implement the code on a CRAY-supercomputer, since solving these coupled equations in 3 dimensions is not feasible on a scalar computer. Implementation on a CRAY-XMP in Bracknell (UK) has been completed and tested.

METROPOL-4, which simulates the transport of low concentration species, has been developed and is in a testing phase now.

User manuals for METROPOL-1, 2 and 3 and several post-processing facilities (particle tracking, plotting) are available.

PROGRESS AND RESULTS

1. Inclusion of physico-chemical processes.
   In METROPOL-4 the transport of low concentration species by groundwater is simulated. The code METROPOL-4 now includes the processes of advection, diffusion, dispersion, adsorption and decay. The transport of several dissolved species, which are members of a decay-chain can be computed.
   METROPOL-4 is now in a testing phase; first results calculated with METROPOL-4 are compared with analytical solutions.
   No attempt has yet been made to include chemical reactions in the METROPOL-code or to couple it with a chemical model.

2. Inclusion of thermal effects.
   No work has been done on thermal effects since it seemed more important to get a good understanding of the density effects, due to dissolved salt, first.

4./3. TESTING METROPOL-3; CODE DEVELOPMENT

During the testing phase for METROPOL-3 many problems arose due to the strong coupling of the equation for flow and for salt-transport. The fluid-density differences play an important role in the numerical behaviour of the model; if these are large, small timesteps are necessary. Since the solving of this set of coupled equations was not feasible on a scalar computer, at least not for large 3D-problems, it was decided that METROPOL-3 should be implemented on a supercomputer. To make optimal use of the capabilities of such a computer, several parts of the program had to be rewritten.

Furthermore it was necessary to reflect on the numerical techniques used in the code. The Picard iteration scheme, which is used to linearise the equations, will possibly be replaced by a method where the two equations are solved simultaneously.

The implementation of an adaptive time integration scheme has proved to work well in METROPOL-2 (transient fresh water flow), but was not yet implemented in METROPOL-3.

An iterative method, the so-called Conjugate Gradient method, has been chosen for the solving of the large set of linear equations, which arises from the discretisations in time and space. For the non-symmetric system in the case of transport equation the Conjugate Gradient Squared method /1/ has been implemented.

The influence of the boundary conditions in complex 2D or 3D situations can be of crucial importance. In fluid flow and transport of low concentration species, there are in general no problems defining the boundary conditions. In high-density flow, however, the combination of an inflow boundary, together with a noflow boundary for the diffusive/dispersive flux, resulted in instable behaviour of METROPOL-3. It seems that, also on physical grounds, not all types of boundary conditions for pressure can be combined with any type of boundary condition for the salt mass fraction. Further research is needed on this subject.

5. DOCUMENTATION

User manuals for METROPOL-1, 2 and 3 are published now. These manuals give a mathematical description of the theory on which these models are based; the basic equations solved are given, as well as techniques used to solve them.

Input descriptions are also included in these manuals. For METROPOL-3 the theory and input-description given are preliminary since the METROPOL-3 code is still in development.

6. POST-PROCESSING

Several post-processing facilities are ready; the most important are:

- particle tracking; with the help of a relatively accurate scheme, with automatic step control, pathlines of a fluid particle in a given velocity field can be calculated.
- mesh plotting.
  The 3D mesh used in the finite element method can be plotted (2D cuts or 3D plots).
- contour plotting.
  Contours of, for instance, pressure or salt mass-fraction can be plotted in 2D cuts through the domain.
- trajectorie plotting.
  The calculated trajectories (particle tracking) can be plotted as projections on a 2D surface or in a 3D plot.

REFERENCES

/1/ SONNEVELD, P., CGS, a fast lanczos type solver for non-symmetric linear systems, Report no. 84-16, Department of Mathematics and Informatics, University of Technology Delft (1984)

/2/ SAUTER, F.J., User's manual METROPOL, a mathematical description, Interim report nr. 728514002, RIVM, Bilthoven, The Netherlands (1987)

STUDY OF THE COUPLED THERMO-HYDRO-MECHANICAL EFFECTS ON A HLW REPOSITORY IN A GRANITE GEOLOGICAL FORMATION

Contractor: ANDRA - Paris (F)
Contract n°: FI1W/0148
Contract period: 01.10.87 - 31.03.89
Project leader: J.M. Perez

N.B. No progress report made available.

TRANSFER MECHANISMS OF RADIONUCLIDES IN THE GEOSPHERE

Contractor : Centre d'Etudes Nucléaires de Fontenay-aux-Roses, CEA/IPSN/DAS/SAED-FRANCE

Contract n° :FI1W/0167

Duration of contract : october 1987 - March 1989

Period covered : January 1987 - December 1987

Project leader : A. CERNES

A. OBJECTIVES AND SCOPE

It is generally agreed that the main processes governing solute transport in the geosphere are : convection, hydrodynamic dispersion, molecular diffusion (Fick's law) and interaction with the rock matrix (adsorption - desorption). In most cases, when mathematical models are designed to take into account only these physical phenomena, or even just a few of them, they will give a true representation of reality.

In the science of non-equilibrium thermodynamics, which describes the evolution of the systems caused by thermodynamic forces, this method does away with non-diagonal couplings of the forces and fluxes. However, this simplification is only valid if one can be sure that the effect of the couplings is negligible, and it is probable that the special conditions prevailing in the vicinity of radioactive waste, in particular the high temperature gradients, exclude the use of the simplified approach.

The objective of this study is therefore to investigate the effects of these physical phenomena and to express them mathematically as well as to evaluate the importance of their role in the aforementioned special conditions.

B. WORK PROGRAMME

1. Theoretic research. This phase makes a review of the principal phenomena likely to play a part in the transfers occuring in natural media and to extract and adapt their mathematical expressions.

2. Bibliographic study. The bibliography,as extensive as possible, is undertaken on these phenomena, in order mainly to have an idea of the scale of the parameters involved.

3. Applications. The results obtained will be applied to the radionuclides transfer in a geological medium, particulary to a porous medium. Calculations will be made (1D or 2D) to show the relative importance of the different transfers, specially regarding the thermal effect of the disposal.

.../...

C. PROGRESS OF WORK AND OBTAINED RESULTS

The two organisations conducting this study are the Paris School of Mines (Centre d'Information Géologique and Centre de Physique de l'Irréversibilité) and the Atomic Energy Commissariat (IPSN/DAS).

To begin with, a wide-ranging review was made of already published theories and articles. The formulation of the phenomenological equations of non-equilibrium thermodynamics is particularly complex, at least when one attempts to find an analytical solution to them. The available literature sometimes contains incoherences which make it difficult not only to understand the phenomena but still more to quantify them. Nevertheless, it was possible to extract and adapt the mathematical expressions for the principal phenomena likely to play a non-negligible part in natural media, except for the electrical ones, which are considerably more complex than the others. The phenomena in question are principally : chemical sedimentation, the Soret effect and its corollary the thermogravitational effect.

From a rational point of view it seemed preferable to consider these phenomena separately and in their presumed order of importance. The efforts were therefore primarily concentrated on the thermogravitational effect, which is the cause of impressive overconcentrations in porous media subjected to laboratory constraints. This thermogravitational phenomenon is the result of the combination of the Soret effect and natural convection induced by a horizontal or sloped thermal gradient. It was given particular attention between 1939 and 1955 as a method for separating isotopes. The magnitude of the overconcentration depends on the establishement of the appropriate relation between the Soret flux and the velocity of the fluid, and the porous medium is useful as a means of adjusting this velocity. The research into earlier publications yielded a number of studies of the thermogravitational effect in porous media, in particular those by SCHOTT and COSTESEQUE of the laboratory of mineralogy and crystallography at the University of Toulouse. Their work contains valuable reports of experiments that show the magnitude of the phenomenon under high temperature gradients of the type prevailing in the vicinity of radioactive waste repositories. Furthermore, such experiments made with radionuclides, especially uranyle nitrates, show that these compounds are among the most sensitive to the Soret effect.

Since the phenomenology of the thermogravitational effect and the experimental results were known, we concentrated on solving the phenomenon numerically. It then became apparent that the particular formulation of the equations made it possible, at least as far as the abovementioned experiments were concerned, and after minor adjustments, to include the phenomenon in the existing models. Thus, attempts were made to validate the METIS + SORET effect model using the experiments by P. COSTESEQUE, and the preliminary results are very encouraging for the qualitative and even for the quantitative representation of the effect.

.../...

Considering the work to date, it seems probable that it will be possible to include the Soret effect in the mathematical models in the not too distant future. The next stage will be the study of chemical sedimentation, a phenomenon negligible on the scale of the laboratory but significant on that of the thickness of an aquifer. The mathematical expression of this sedimentation effect is, however, extremely complex (on the face of it, it does not seem possible to disregard entropy and chemical potentials) and there are few publications on this subject. For all these reasons, the validation of a hypothetical numerical model will prove quite difficult.

4.4. SHALLOW LAND BURIAL

N.B. Research action will start only mid 1988

CHAPTER 5

TASK No 5

Safety of geological disposal

CHAPTER 5

TASK No. 5 : SAFETY OF GEOLOGICAL DISPOSAL

A. Objective

Assessment of the performance of isolation systems for radioactive waste and of the corresponding radiological impact.

B. Research performed under the 1980-1984 programme

Initiation and implementation of the first phase of the PAGIS (Performance Assessment of Geological Isolation Systems) project, the purpose of which is to assess the capacities offered by the various geological disposal options (salt, clay, granite and marine sediments) for the containment of high-level waste.

C. 1985-1989 programme

The studies to be conducted concern :

a) Continuation and completion of the PAGIS project, in accordance with the plans and procedure adopted during the previous programme

b) Initiation and implementation of the PACOMA project (Performance Assessment of COnfinements for Medium-Level or Alpha bearing waste : Safety assessment of alpha contaminated disposal systems for alpha contaminated radioactive waste and for medium-level waste buried into geological formations (clay, granite and salt); evaluation of the corresponding radiological impact

c) Support activities to PAGIS and PACOMA

D. Implementation of the programme

Fifteen contracts have been signed in the framework of the Third Programme of which eight for PACOMA. The available information is listed hereafter.

5.1. PAGIS Project

Performance evaluation of HLW-waste disposal in geological formations - PAGIS 2 project : clay option

Contractor : SCK/CEN, Mol, Belgium
Contract No. : FI1W/0001-B
Duration of Contract : January 1985 - March 1987
Period covered : January 1987 - March 1987
Project leader : A. Bonne

A. OBJECTIVE AND SCOPE

The essential objective of the PAGIS project is an evaluation of the capability of selected geological formations and of the associated engineered barriers to confine vitrified high level waste. During phase 1 of PAGIS a methodology has been set up and scenarios, data and models have been selected. In phase 2 various models are combined to enable realistic assessments of the repository system performance. As well deterministic "best estimate" calculations as probabilistic calculations, allowing for sensitivity and uncertainty analyses, are performed. For the clay option, calculations are made for the reference site at Mol (Belgium) and for the variant site at Harwell (U.K.).

B. WORK PROGRAMME

B.1. Performance assessments for the reference site at Mol.
B.1.1. Preliminary best estimate evaluation of doses and risks to individuals and populations.
B.1.2. Estimation of the probability of occurrence for all relevant scenarios.
B.1.3. Definition and selection of parameters for sensitivity and uncertainty analyses.
B.1.4. Sensitivity analysis.
B.1.5. Uncertainty analysis.
B.1.6. Final assessment.
B.2. Performance assessments for the variant site at Harwell.
B.2.1. Best estimate calculations.
B.2.2. Uncertainty and sensitivity analyses.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The calculations performed for the reference site at Mol were completed. Many results had to be recalculated in order to adapt them to a recent I.C.R.P. recommendation /2/ to lower the ingestion dose factor of Np with a factor 10.

For the variant site at Harwell as well deterministic as probabilistic calculations have been elaborated by applying the computer codes developed for the reference site.

A variant site at Val d'Era has been considered during the first phase of PAGIS. However because of the unavailability of information on the regional hydrology it was not possible to make significant assessments for this site.

PROGRESS AND RESULTS

Reference site at Mol

The radiological consequences in the case of a normal evolution scenario and of natural river pathways to man, are estimated with the BIOS code /1/. This code calculates as well individual annual doses as collective doses. The BIOS code allows to consider many biosphere compartments such as rivers (Nete, Rupel, Scheldt), an estuary (Scheldt), a local sea (southern part of the North Sea), oceans, sediments and soils. Among the pathways considered, the fresh water compartment of the river Nete yields the highest individual dose rates. These doses are compared with the doses calculated for a water well pathway in Table I. The results obtained illustrate the importance of a water well pathway within the normal evolution scenario.

Since the second phase of PAGIS is terminated, an overview of the most important results can be given now. At the same occasion the results reported previously are adapted to the International Commission on Radiological Protection (ICRP) recommendations /2/ to decrease the dose factor for ^{237}Np with a factor 10. The doses estimated for the different considered scenarios are shown in Figure 1 together with the dose due to natural background radiations, which is about 1 mSv/y for northern Belgium. The doses estimated with deterministic best estimate calculations are at least four orders of magnitude lower than the dose due to natural background radiations.

The estimated risks are shown in Figure 2 and they can be compared with the total risk limits of 10^{-5} per year recommended by the ICRP /3/ for application in the case of waste disposal. Figure 2 shows that the risks estimated with probabilistic calculations which take into account the considerable uncertainties on the model parameters, are always more than two orders of magnitude below the total risk limit.

The sensitivity analysis selects the following influential parameters :

- the retention factor of Np in clay ;
- the effective thickness of the clay layer ;
- the Darcy velocity in the aquifer.

These results confirm the paramount importance of the radionuclide transport through the clay layer. Other important phenomena are the dilution processes which take place in the aquifer system.

Variant site at Harwell

As for the reference site two pathways to man are considered within the normal evolution scenario : a natural rivers pathway and a water well pathway. The dose rates calculated for both pathways are given in

Table II. Again the water well pathway yields dose rates which are a few orders of magnitude higher than those calculated for river pathways. The results obtained from the probabilistic calculations are comparable with the results obtained for the reference site.

REFERENCES

/1/ LAWSON, G. and SMITH, G.M., National Radiological Protection Board, Report NRPB-R169 (1985)

/2/ International Commission on Radiological Protection, Publication 48, Annals of the I.C.R.P. 16(2/3), (1986)

/3/ International Commission on Radiological protection, Publication 46, Annals of the I.C.R.P. 15(4), (1985)

LIST OF PUBLICATIONS

J. MARIVOET, A. SALTELLI and N. CADELLI
Uncertainty analysis techniques
CEC, Report EUR 10934 EN (1987)

TABLE I: REFERENCE SITE AT MOL ; CALCULATED INDIVIDUAL MAXIMUM DOSE RATES FOR RIVER PATHWAYS AND FOR A WATER WELL IN THE CASE OF A NORMAL EVOLUTION SCENARIO (*)

Radionucl.	River pathways		Water well	
	time of occurr. (y)	max. dose rate (Sv/y)	time of occurr. (y)	max. dose rate (Sv/y)
Tc-99	1 10^{6}	1.1 10^{-11}	1 10^{6}	1.2 10^{-8}
Cs-135	13 10^{6}	1.7 10^{-12}	7 10^{6}	3.3 10^{-8}
Np-237	11 10^{6}	3.4 10^{-12}	11 10^{6}	7.0 10^{-8}
U-233	11 10^{6}	4.8 10^{-13}	11 10^{6}	1.6 10^{-9}
Th-229	11 10^{6}	2.8 10^{-12}	11 10^{6}	1.3 10^{-10}

TABLE II: VARIANT SITE AT HARWELL ; CALCULATED INDIVIDUAL MAXIMUM DOSE RATES FOR RIVER PATHWAYS AND FOR A WATER WELL IN THE CASE OF A NORMAL EVOLUTION SCENARIO (*)

Radionucl.	River pathways		Water well	
	time of occurr. (y)	max. dose rate (Sv/y)	time of occurr. (y)	max. dose rate (Sv/y)
Tc-99	1.0 10^{6}	1.4 10^{-6}	0.9 10^{6}	5.5 10^{-5}
Cs-135	118 10^{6}	5.0 10^{-20}	50 10^{6}	1.7 10^{-11}
Np-237	18 10^{6}	5.6 10^{-9}	16 10^{6}	7.9 10^{-7}

(*) The doses from the river and well pathways concern two different population groups. Therefore, the individual dose rates can not be added.

Performance Evaluation of HLW Waste Disposal in Geological Formations - PAGIS 2 Project: Salt Rock Option

Contractor:	GSF - IfT Braunschweig, FRG
Contract No.:	FI1W/0002-D
Duration of Contract:	July 1984 - April 1987
Period covered:	January 1987 - April 1987
Project Leader:	R. Storck

A. OJECTIVES AND SCOPE

The concerted action PAGIS has been started by the CEC to collect and assess the experience gained in the various countries of the EC in the field of HLW disposal. Based on the data, parameters, and models selected and the methodology developed in phase 1, the repository performance is under investigation in the current phase 2. In the assessment best estimate and uncertainty calculations are performed for the combined system of repository, overburden, and biosphere. Doses to man resulting from the release of radioactivity from the repository are obtained. The sensitivity to numerical and system parameters has been studied. Among others it shows how far appropriate choices of the repository design parameters can improve the performance of the whole system. This is done for a selected reference site and the main release scenarios. Also variant sites are considered. Simultaneously to this study on salt rocks, the geological formation clay is considered in Belgium, granite in France and the sub-seabed option in the UK.

B. WORK PROGRAMME

B.1. Best estimate calculations
B.4. Sensitivity study
B.5. Uncertainty analysis
B.6. Final assessment
B.7. Final report

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Final best estimate calculations for the anhydrite and human intrusion scenario as well as sensitivity studies have been performed. For the anhydrite scenario there is no release of radioactivity in the best estimate case. Variation of the time of brine intrusion to t = 0 years gives release of radionuclides, which has been used as a source term for the overburden performance for reference as well as variant site. With this souce term for the variant site bedded salt in France a best estimate calculation for the transport of radionuclides through the overburden has been finished.

Final uncertainty and global sensitivity analysis have been performed.

A draft version of the comprehensive final report has been distributed. Editorial work on the final version is completed during 1987.

Progress and results

B.1. Best estimate calculations

For the altered evolution scenario of water intrusion through the main anhydrite extended by a limited intrusion from an undetected brine pocket in the vicinity of the repository final best estimate calculations, parameter variations of numerical and system parameters have been performed with the code EMOS.

There is no release of radioactivity from the repository in the best estimate case. This is due to the high creep rate of salt rock at the elevated temperature of the HLW field leading to rapid closure of the voids.

A 3-d calculation with the code SWIFT of the hydrogeological situation of the reference site has previously been performed with a sweet water model. Pathways to the biosphere have been determined by particle tracking. Transport equations for these pathways have then been solved with the 1-d code TROUGH which is implemented in EMOS.

For the variant site with bedded salt in France 2-d hydrogeological calculations have previously been performed with the code CFEST. Pathways between repository and biosphere have been found by particle tracking. For the common source term for the reference and variant site the migration of radionuclides through the overburden has been calculated with the 1-d code TROUGH.

A final best estimate calculation for a human intrusion scenario of a solution mined cavern has been performed and probabilities of occurence have been discussed. The transport of radionuclides released into the overburden has been treated the same way as for the anhydrite scenario.

Dose conversion factors have been generated with the biosphere code ECOSYS. Individual doses to man are obtained from these factors and radionuclide concentrations in ground-water near the surface.

In all scenarios it was found that convection processes induced by temperature gradients and flow of gas do not contribute significantly to the transport of radionuclides out of the repository.

B.4., B.5. Sensitivity study, uncertainty analysis

Tests of the numerical stability of the code have been improved by variation of the parameters which determine the length of the time steps. In addition standard release calculation are performed with a more refined division of the repository into geometric compartments (sections).

There is no perceptable change of the result using smaller time steps or a more detailed devision of the repository into sections.

Local sensitivity studies to parameters have been performed, whose ranges of variability were previously determined. Parameters determining the flow of brine in the repository turned out to be most important for the near field. These are convergence rates as driving forces and permeabilities of various resistances in the repository. Depending on the attained values, a few parameters have the potential of switching on and off the release of radioactivity from the repository. For the overburden Kd-values play an important role.

Statistical routines have been prepared in close cooperation with the other contractors. The Latin hypercube sampling technique has been used for the generation of data sets for each run from the frequency distributions supplied.

The main problem encountered is the large variability of the system parameters during the Monte Carlo simulation. Long computation times per run which partly result from lacking optimization do not allow to run the desired large size statistical ensembles. The need for refinements of parameters and distribution functions caused some delay. The global sensitivity studies and final uncertainty analysis could be completed during January and February of the reference year. The calculations were completed by 300 MONTE CARLO runs where about 50% give a release of radionuclides.

B.6., B.7. Final assessment, final report

All calculations, additional variations of parameters and final MONTE CARLO runs were completed in March 1987.

A draft version of Parts II and III (modelling and results) of the comprehensive final report could be distributed end of April 1987. A complete draft version has been finished until July with some delay due to the neccessity of a revision of the Part I of the PAGIS report (PAGIS I).

Editorial work on the final report has been completed during the reference year.

PERFORMANCE EVALUATION OF HLW DISPOSAL IN GEOLOGICAL FORMATIONS - PAGIS PHASE 2 : GRANITE OPTION

Contractor : Commissariat à l'Energie Atomique, Paris
Contract No. : 427-84-9-WAS-F
Duration of contract : January 1985 - June 1987
Period covered : 1.1.1987 - 30.06.1987
Project leaders : J. LEWI (IPSN) and F. VAN KOTE (ANDRA)

A. OBJECTIVES AND SCOPE

The second phase of the PAGIS action is devoted to the evaluation of performances of repository systems in geological formations for high level vitrified wastes.
For the granite option the approach consisted of :

- on the one hand, studying each sub-system (near-field, far-field and biosphere) in detail. The corresponding calculations are performed by ANDRA.
- on the other hand, performing global assessment of radiological consequences with the MELODIE code. The corresponding calculations are performed by IPSN.

B. WORK PROGRAMME 1987

B.1. ANDRA :

B.1.1. Parametric studies for subsystems : the influence of discrete fracture zone location in two dimensional groundwater flow calculation.

B.1.2. Reviewing final report of PAGIS action-phase 2.

B.2. IPSN :

B.2.1. Deterministic calculations on :

First variant : United Kingdom site (normal evolution scenario, A and B disposal concepts).
Second variant: Barfleur site (normal evolution scenario, A and B disposal concepts).

B.2.2. Global sensitivity studies on reference case (Auriat site, normal evolution scenario and case A).

B.2.3. Uncertainty analysis on reference case (Auriat site, normal evolution scenario and case A).

B.2.4. Reviewing final report of PAGIS action phase 2.

C. PROGRESS OF WORK AND OBTAINED RESULTS

C.1. Subsystem studies : ANDRA

The carrying out of sensitivity studies in the far field has allowed to complete the results obtained during the year 1986 concerning the importance of fracture zone in the near field.

For the radionuclide migration calculations, the influence of parameters (location of the fracture zone, kf/Km and $(\varepsilon R)f/(\varepsilon R)m$) is studied :

Kf : hydraulic conductivity for the fracture zone
Km : hydraulic conductivity for the rock matrix
ε : porosity
R : global retardation term.

When $(\varepsilon R)f/(\varepsilon R)m=1$ the surface flux shows the evolution as a function of Kf/Km, with a saturation for Kf/Km >100 (figure 1). As far as the migration is concerned, the parameter $(\varepsilon R)f/(\varepsilon R)m$ is much more important than the ratio of fracture to host rock permeabilities. This is well illustrated on figure 2 where the percentage of the source term reaching the surface at $t = 5\ 10^4$ years is represented as a function of $(\varepsilon R)f/(\varepsilon R)m$ and Kf/Km.

C.2. IPSN

C.2.1. Deterministic calculations

1. First variant : United Kingdom site (granite under sedimentary cover). The regional groundwater flow study has allowed to identify the main discharge zones and to get a reduced cut, where the transfer simulations have been realized. The repository was located at 980 meters of relative depth (300 meters under the top of the granite formation).

   The calculations have been carried out for two cases :

   Case 1 : the whole of the domain has been considered as a granite formation.

   Case 2 : the sedimentary cover has been taken into account.

   The results are presented, for the main discharge zone, in table 1 and figure 3.

   Transfer calculations have shown the very strong dependency of the results on the retention properties of the cover.

2. Second variant : Barfleur site (coastal granite) : Barfleur site represents an example of a granite coastal site. The repository has been located in the fresh water zone at a depth of 500 meters. The repository location leads to a release of radioactivity in two different biosphere compartments :
   one terrestrial : "la Saire" and "Ruisseau de Barfleur";
   one marine : "l'Estran".

The main results are presented in table 1 and figure 4.

The dose rate values show the importance of the dilution capacity of the sea.

3. Main conclusions of deterministic calculations of normal evolution scenario (Auriat, Barfleur and United Kingdom site)

a) The delay provided by the geological environment in the vicinity of the disposal prevents the radionuclides released out of the source to be evacuated instantaneously.

In the MELODIE code, this fact has been modelled by coupling the source model with the geosphere model. In the case of Cs-135 and the normal evolution scenario of Auriat site, the activity attenuation factor with regard to the no coupling case is equal to 10 (case A) and to 15 (case B).

b) The transfer calculations have shown that the peak of total dose rate occurs after about 1 million years (cf. table 2).

c) The calculation results have shown a difference between the time of occurrence of the peak dose rate in case B with regard to case A (cf. table 3). In case B the delay pointed out gives way to a peak dose rate smaller than that computed in case A.

d) The radionuclides, the contribution of which to the peak dose rate is the most important, are a function of the site (cf. table 2).

C.2.2. Sensitivity to model parameters analysis for normal evolution scenario of the reference site (Auriat)

A sensitivity analysis algorithm has been provided by the JRC of ISPRA. This algorithm is based upon the latin hypercube sampling technique and a statistical analysis of the response surface. The transfer computations involve a reduced representation of the geosphere (1D) the physical characteristics of which are obtained from deterministic calculations.

Cs-135 and Np-237 have been selected for the analysis. This has shown the sensitivity of the results with the variability of the retardation factor in the granite, the permeability of the region nearest the repository and the dispersivity coefficient.

In the case of Np-237, the solubility limit and the diffusion coefficient in the bentonite are also important.

In the case of Cs-135 the bentonite thickness and retardation factor play a significant role.

C.2.3. Uncertainty to model parameters analysis for normal evolution scenario of Auriat site

The uncertainty is computed from calculated dose rates mean (200 runs) and the 95% confidence limit using Tchebycheff's theorem.

The uncertainty on model parameters for Cs-135 and Np-237 is about the mean value ($\Delta Y \sim 2,3$ 10-5 Sv/y (Np-237); $\Delta Y \sim 2,6$ 10-6 Sv/y (Cs-135).

It must be stressed that the statistical distribution assigned to model parameters (cf. table 4) has not been the subject of deep research work specific to site conditions; the results obtained should be interpreted with some caution.

		UNITED KINGDOM SITE			
		CASE 1 (Without sedimentary cover)		CASE 2 (With sedimentary cover)	
Repository concept	Radionu clide	Time of occurrence of the peak value (years)	Peak value for individual dose rate (Sv/y)	Time of occurrence of the peak value (years)	Peak value for indivi dual dose rate (Sv/y)
A	Tc^{99}	147 000	$0,38\ 10^{-6}$	147 000	$0,38\ 10^{-6}$
	Cs^{135}	1 320 000	$0,23\ 10^{-5}$	4 050 000	$0,48\ 10^{-7}$
	Np^{237}	1 050 000	$0,31\ 10^{-4}$	2 850 000	$0,21\ 10^{-5}$
	U^{233}	1 040 000	$0,10\ 10^{-6}$	2 800 000	$0,67\ 10^{-8}$
	Th^{229}	1 040 000	$0,60\ 10^{-5}$	2 800 000	$0,23\ 10^{-6}$

		BARFLEUR SITE			
		TERRESTRIAL BIOSPHERE (Ruisseau de Barfleur)		MARINE BIOSPHERE (l'Estran)	
Repository concept	radionu clide	Time of occurrence of the peak value (years)	Peak value for indivi dual dose rate (Sv/y)	Time of occurrence of the peak value (years)	Peak value for indivi dual dose rate (Sv/y)
A	Tc^{99}	351 000	$0,45\ 10^{-6}$	566 000	$0,79\ 10^{-10}$
	Se^{79}	393 000	$0,10\ 10^{-8}$	843 000	$0,30\ 10^{-13}$
	Cs^{135}	4 720 000	$0,52\ 10^{-6}$	7 870 000	$0,21\ 10^{-12}$
	Np^{237}	2 720 000	$0,64\ 10^{-4}$	4 850 000	$0,77\ 10^{-9}$
	U^{233}	2 660 000	$0,11\ 10^{-5}$	4 800 000	$0,31\ 10^{-11}$
	Th^{229}	2 660 000	$0,74\ 10^{-4}$	4 730 000	$0,38\ 10^{-8}$

TABLE 1 - Main results for normal evolution scenario, repository concept A for United Kingdom and Barfleur sites.

	AURIAT		UNITED KINGDOM				BARFLEUR			
	"LES PALLANDS"		CASE 1 (discharge zone 2)		CASE 2 (discharge zone 2)		TERRESTRIAL BIOSPHERE (R. de BARFLEUR)		MARINE BIOSPHERE (L'ESTRAN)	
	Case A	Case B	Case A	Case B	Case A	Case B	Case A	Case B	Case A	Case B
Peak value for the activity rate (Bq/y)	$6,5\ 10^{9}$	$4,6\ 10^{8}$	$2,5\ 10^{10}$	$4,3\ 10^{9}$	$2,5\ 10^{10}$	$4,3\ 10^{9}$	$2,2\ 10^{9}$	$2,0\ 10^{8}$	$2,0\ 10^{8}$	$1,7\ 10^{7}$
Time of occurrence of the peak value (years)	3.10^{6}	6.10^{6}	$1,1\ 10^{6}$	$1,7\ 10^{6}$	$2,8\ 10^{6}$	$3,4\ 10^{6}$	$2,7\ 10^{6}$	$6,5\ 10^{6}$	$4,7\ 10^{6}$	$9,9\ 10^{6}$
Peak value for individual total dose rate (Sv/y)	$3,0\ 10^{-5}$	$6,4\ 10^{-6}$	$4,0\ 10^{-5}$	$2,0\ 10^{-5}$	$2,8\ 10^{-6}$	$1,4\ 10^{-6}$	$1,4\ 10^{-4}$	$3,4\ 10^{-5}$	$4,7\ 10^{-9}$	$1,4\ 10^{-9}$
Main radionuclides	N_p^{237}	N_p^{237}	N_p^{237} Th^{229}	N_p^{237}	N_p^{237} T_c^{99}	Th^{229} T_c^{99}	Th^{229} N_p^{237}	Th^{229} N_p^{237}	Th^{229} N_p^{237}	N_p^{237}
Radionuclide contribution (%)	100	100	76 15	100	75 14	93 5	53 45	67 33	81 16	92 8

Table 2 - Main results of global assessment of radiological consequences.

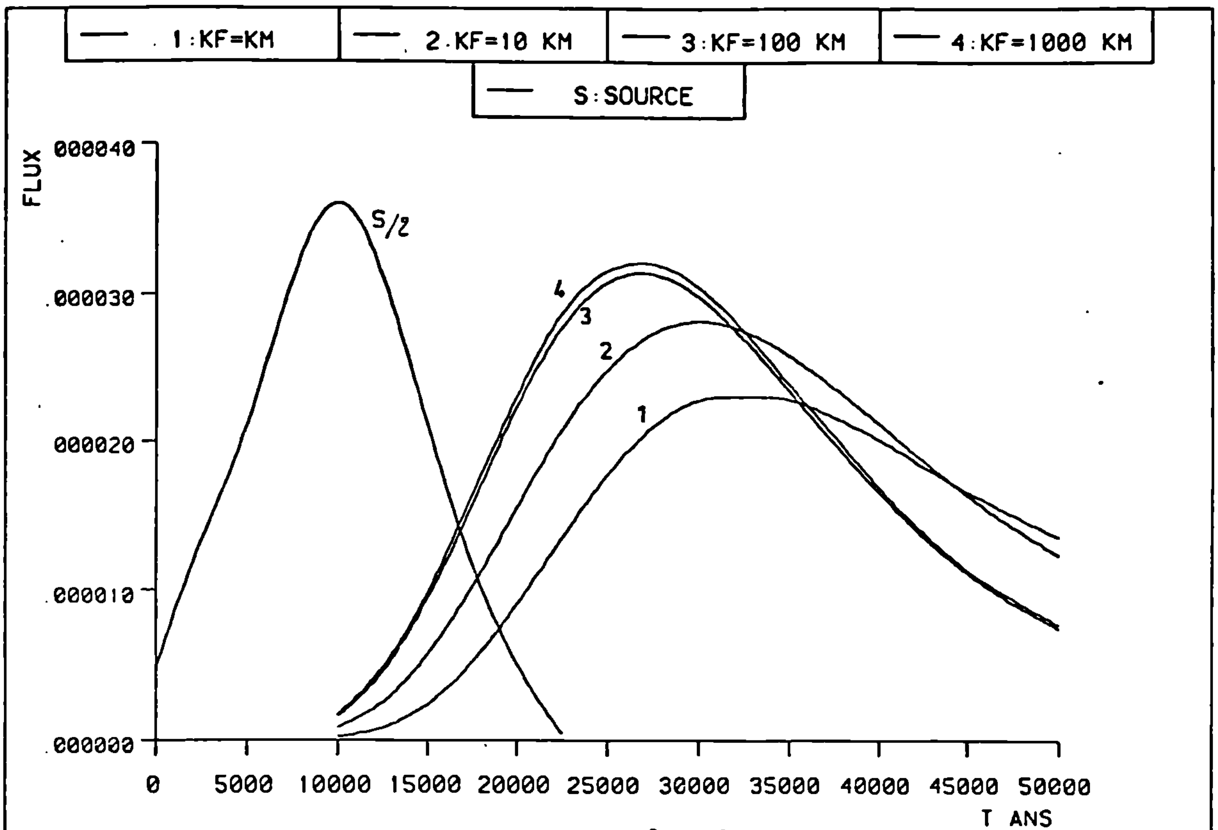


FIGURE 1 : Surface flux versustime for $\varepsilon Rf/\varepsilon Rm$ = 1

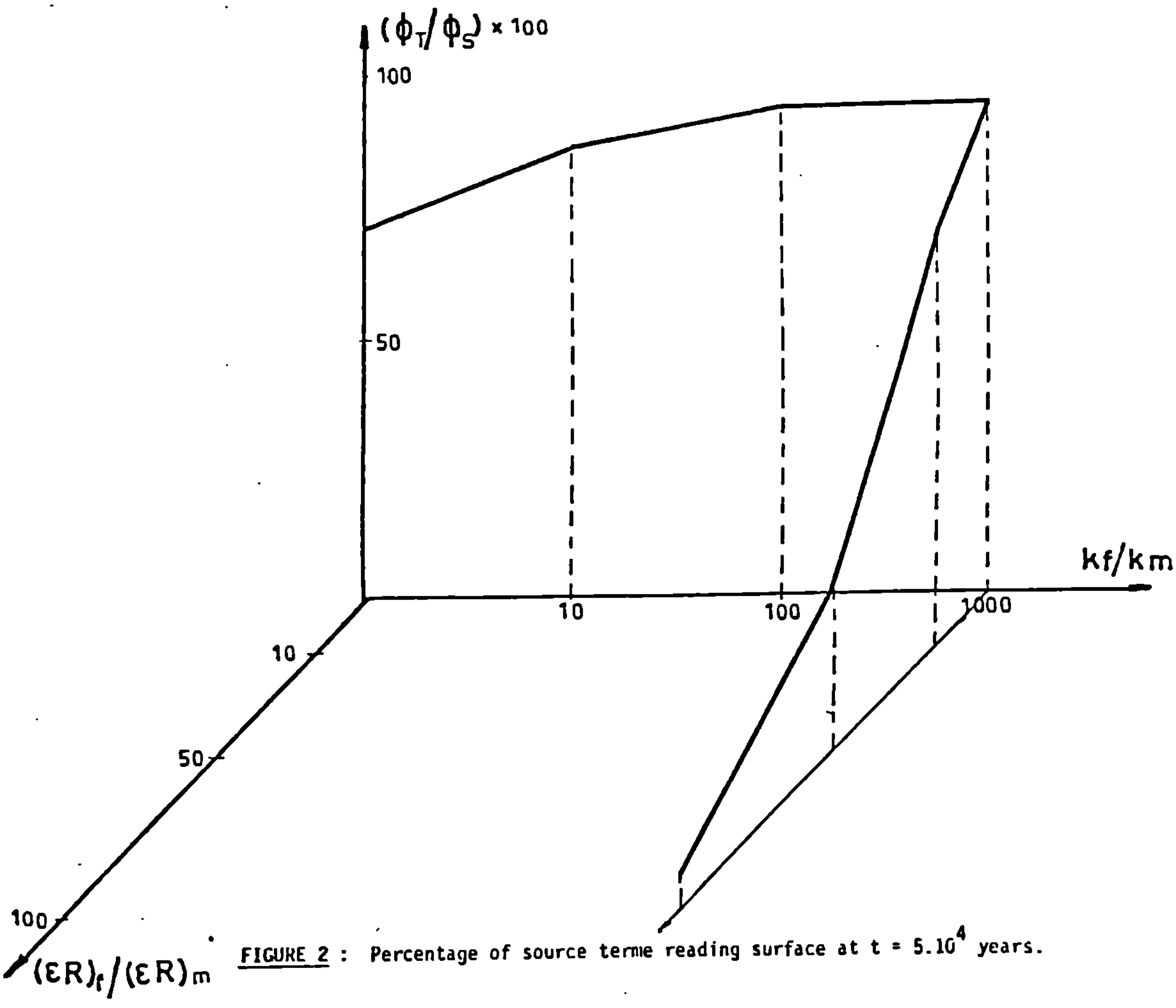


FIGURE 2 : Percentage of source terme reading surface at t = 5.10^4 years.

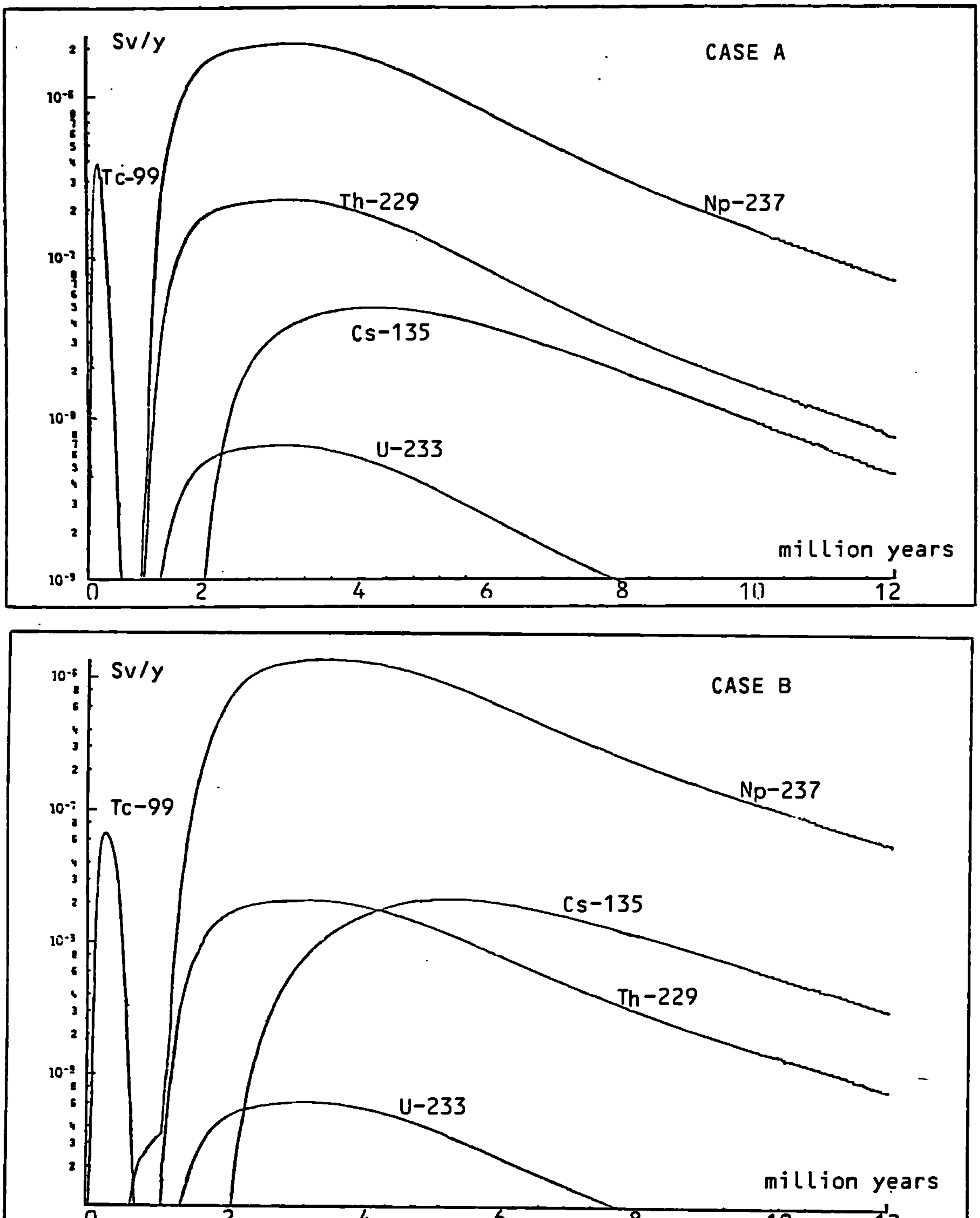


Figure 3 - Individual dose rate as function of the time (United Kingdom site, main discharge zone and disposal concepts A and B)

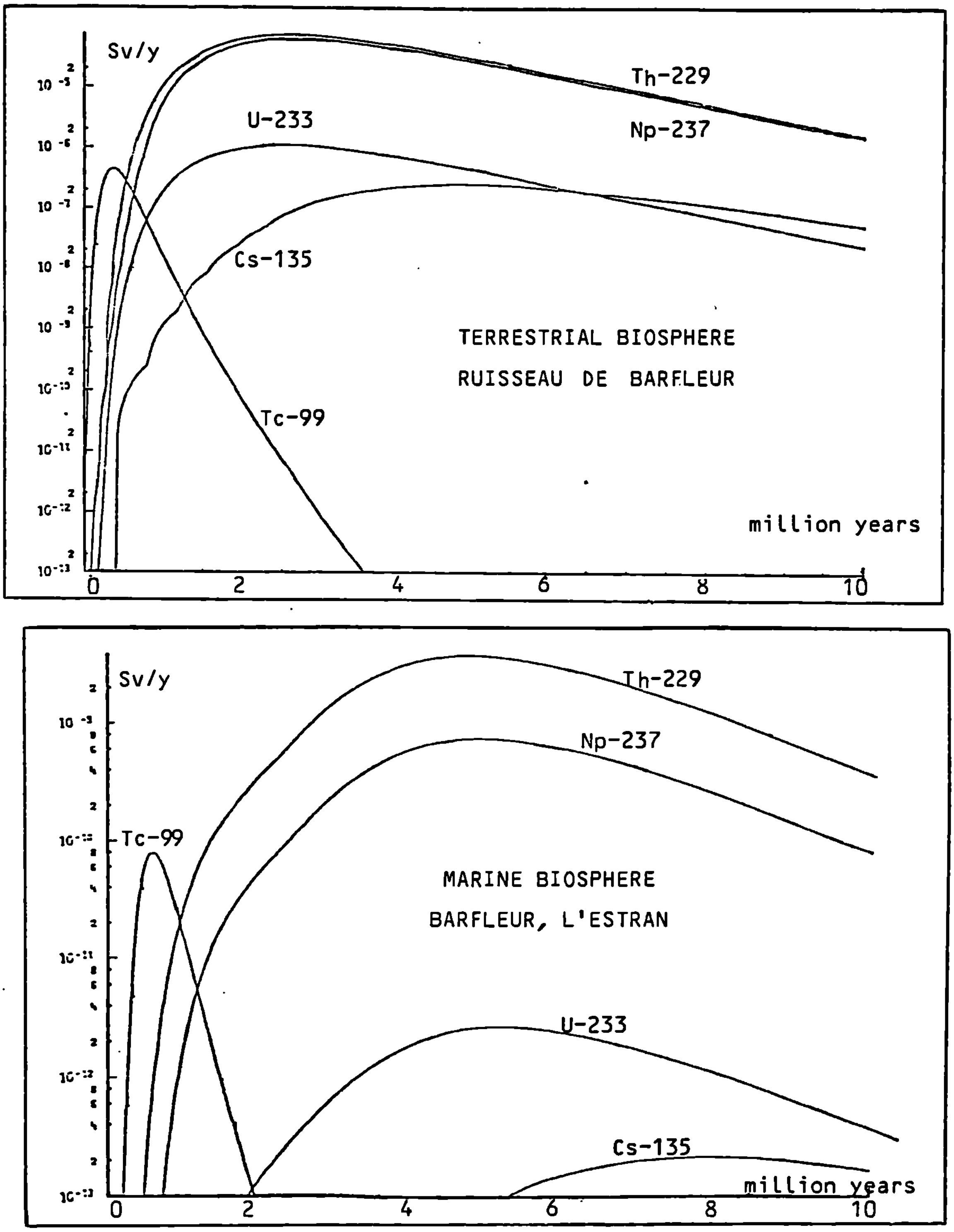


Figure 4 - Individual dose rate as function of the time at the Barfleur site for the two discharge zones and the diposal concept A.

Performance Evaluation of HLW Waste Disposal in Geological Formations - PAGIS 2 Project: Sub-Seabed Option

Contractor: NRPB, Chilton, UK
Contract No.: WAS-430-84-9-UK (H)
Duration of Contract: Part 1 of Phase 2 : 1 July 1984 - 31 December 1984
Part 2 of Phase 2 : 1 July 1985 - 31 March 1987
Period covered: January 1987 - March 1987
Project Leader: Ms M D Hill

A. Objectives and Scope

The main objective of PAGIS is to evaluate the capacity of various geological formations to act as repositories for vitrified high-level radioactive waste, using common assessment methodologies where possible. This contract is concerned with the sub-seabed disposal option; others are assessing disposal in clay, granite and salt formations on land.

In Phase 1 of PAGIS, which was completed in June 1984, the sites and waste emplacement techniques to be considered were selected. The reference site is at Great Meteor East (GME) and two variant sites were selected - one in the Cape Verde Plateau (CV) and the other in the Southern Nares Abyssal plain (SNAP). All these sites are in the Atlantic Ocean, and have been investigated in international studies of the feasibility of sub-seabed disposal.

The scope of Phase 2 is i) to perform a preliminary radiological assessment using the models and data chosen in Phase 1 ii) to undertake sensitivity and uncertainty analyses iii) to reappraise the data and models and to perform an improved assessment of potential doses and risks to individuals and populations.

B. Work Programme

B.1. Preliminary 'best estimates' of doses and risks to individuals and populations.
B.2. Estimates of the probabilities of occurrence as a function of time of various scenarios.
B.3. Definition and selection of parameters for sensitivity and uncertainty analyses.
B.4. Investigation of the sensitivity of the model results to variations in the values of parameters.
B.5. Quantification of the uncertainty in the model output.
B.6. Improved assessment using the best available models and data which have been selected considering results from B.2.-B.5.

C. Progress of Work and Obtained Results

State of advancement

In the previous year (ending December 1986) the calculations of the radiological impact of subseabed disposal of vitrified high level waste were completed and the first draft of the models and data report was started. In the reference year the draft report was completed and the remaining seven contract reports describing the results and conclusions were drafted and supplementary calculations were made. In addition, contributions were made to a series of drafts of the summary report for PAGIS phase 1 and 2.

Progress and Results

1. Final contract reports (B.2, B.3, B.4, B.5, B.6)

The final contract report consists of a series of 8 topical reports, bound into two volumes. The first volume is the models and data report (Topical Report 1) and a complete draft has been produced. Comments have been received from CEC and a revised draft is being prepared. The second volume contains the results and conclusions and consists of the remaining seven topical reports. Topical Report 2 (Best estimate results for the reference case) has been completed and comments received from CEC have been incorporated. Following a discussion at the October PAGIS steering committee meeting two extra calculations were made and the report was revised to include these. A final version was submitted in December.

Topical Report 3 (Best estimate results for variant cases) has been drafted and comments have been received from CEC. A revised version is being produced.

Topical Report 4 (Altered evolution scenarios) has been drafted and comments from CEC have been incorporated. Following a discussion at the October PAGIS steering committee meeting it was decided to reduce the number of altered evolution scenarios and to present the others as sensitivity studies. This decision was taken to ensure harmonisation between the four options in PAGIS. The revised draft is under preparation.

Topical Report 5 (Global Sensitivity studies) has been completed and comments received from CEC have been incorporated. This was submitted to CEC in December.

Topical Report 6 (Uncertainty analysis) has been drafted and a revised version is under preparation.

Topical Report 7 (Local Sensitivity studies) has been drafted and comments received from CEC have been incorporated. A revised version is under preparation following the discussion at the October PAGIS steering committee meeting which resulted in some of the altered evolution scenarios being redefined as sensitivity studies.

Topical Report 8 (Summary and Conclusions) has been completed and updated following the additional calculations and the redefinition of the altered evolution scenarios. This has been submitted to CEC.

2. Contributions to summary report

A summary report of the work done within PAGIS phase 1 and 2 is being prepared by Associated Nuclear Services (ANS) and covers all four options. A number of meetings have been held with ANS and with ANS, CEC and the other contractors to discuss the content of the report and its layout. Significant contributions have been made to the section discussing the subseabed option and to the general introductory and conclusions chapters.

SUMMARY AND REVIEW OF PAGIS - PHASE 2

Contractor: Associated Nuclear Services, UK
Contract No.: FI1W/0104-UK(H1)
Duration of contract: September 1986 to March 1988
Period covered: January to December 1987
Project Leader: T.J. Sumerling

A. OBJECTIVES AND SCOPE

The objectives of the work are;

- to prepare a summary of the results and conclusions of the performance assessments of the repositories for HLW in deep geological formations covering four options (clay, granite, salt and the sub-seabed); and
- to review criticality the basis, methods, models and data used for the performance assessments and to prepare a report setting out comments and suggestions relevant to further actions of the PAGIS project.

The 'Summary' report is intended for wide distribution and is to be written in relatively simple terms. The 'Comments and suggestions' report is for use by the Commission and the PAGIS secretaries.

B. WORK PROGRAMME

1. Discussions with the nominated representatives of the CEC and agreement of the study basis, including identification of the reference project reports.
2. Collation and initial review of the PAGIS phase I, and as they became available, phase II documents and supporting material.
3. Discussions with PAGIS secretaries and other relevant organisations, with the aims of assessing background and clarifying published material.
4. Preparation of a draft 'Summary' report of 200 to 250 pages, giving comprehensive coverage of the results and conclusions of the performance assessments for the four geological options.
5. Detailed critical review of the approach, the methodologies, models and data, and preparation of a draft 'Comments and suggestions' report.
6. Collation with the PAGIS secretaries and the CEC representatives to produce final versions of the two reports.
7. Production of master copies of the final reports.

C. PROGRESS OF WORK AND OBTAINED RESULTS

SUMMARY

Over one hundred documents concerning work carried out in Phase 2 of PAGIS have been received and considered by ANS. Reports from the Secretaries have been subject to revision and additions, some information is still outstanding. Discussion meetings were held with each of the four Option Secretaries. A preliminary draft Summary Report was prepared and submitted to the CEC and the PAGIS Steering Committee. A change in Report structure was agreed and second drafts of material covering each of the Options submitted to the CEC and Option Secretaries. A third draft, with greater standardisation of Figures and Tables and some simplification, is now being prepared in collaboration with the CEC.

PROGRESS AND RESULTS

1,2 Study basis and collation of reports

Over one hundred documents have been received by ANS from the CEC and PAGIS Secretaries concerning work carried out in Phase 2 of PAGIS. This includes general papers, topical reports draft sections from unified reports for each option, and redrafts of these. Although a substantial body of reports was available to ANS by June 1987 additional material and revised material related to the unified reports was received throughout the later part of the year. Major items still outstanding are presentation of the reworking of stochastic calculation for the Clay Option, results from the variant Salt Option site in the Netherlands and a concluding section for the Salt Option. Complete unified reports are still not available for any option.

3. Discussion with PAGIS Secretaries

One day discussion meetings were held with each of the Option Secretaries during March (Sub-seabed Option), April (Clay and Salt Options) and July (Granite Option). Each of these was timed to occur after a substantial proportion of drafts of the expected topical reports had been received. The meetings provided ANS with a clearer understanding of the overall approach adopted by each Secretary, enabled clarification of detailed matters related to the reports received by ANS, and enabled the Option Secretaries to present an overview of reports still to be produced and their schedule for doing so.

A two day discussion meeting was held with representatives of CEC and each Secretary to discuss the 2nd Draft Summary Report (see below), in December 1987. Final clarification of detailed points, some additional information and assistance with improvements to Figures, is being sought from each Option Secretary by written enquiry.

4,6 Preparation of draft Summary Report

A preliminary draft Summary Report was prepared to an 'Outline Contents Guide' which was presented at the 5th and 6th PAGIS Steering

Committee Meetings (PSCM). This was based on the structure employed in the PAGIS Phase 1 Summary Report, intended to stress coherence of treatment of options, and anticipated the following Chapters:

A. Introduction
B. Basis
C. Methodology
D. Modelling
E. Results
F Conclusions

Chapters B to F consisting of 5 sections each, 1 concerning 'General Aspects' and 1 concerning each Option - Clay, Granite, Salt, Sub-seabed. This draft was issued by ANS to the CEC and members of the Pagis Steering Committee in September 1987; it was discussed at the 7th PSCM in October 1987. This preliminary draft had some omissions due to late or non- receipt of reports and had not been fully checked for consistency between Options.

The view of the CEC, endorsed by the PSC, was that the Report was too complex in structure and a revised plan was adopted in which the following chapters were anticipated:

A. Introduction
B. Common Basis
C. The Four Options
D. Conclusions

In this, Chapter C formed the main body of the report and was subdivided into four sections, 1 for each Option. The CEC undertook to prepare drafts of Chapters A and B incorporating much of the material from Chapter A and the 'General Aspect' sections of the previous draft, ANS undertook to prepare a draft of Chapter C, responsibility for Chapter D was undefined as material was still awaited from the Option Secretaries.

Second drafts of Summary Report Chapters were prepared at CEC (A, B and part D) and ANS (C and part D). In the case of Chapter C, the work consisted of: reorganisation of subsections; consequent changes and simplification of text; and taking account of detailed comments made at the 7th PSCM. The revised Chapters were discussed between representatives of CEC, ANS and each Option Secretary in December 1987; although most attention was focused on Chapters A and B. The main actions agreed regarding Chapter C were to adopt a more standardised approach to the selection of Figures and Tables, and consequently reduce and simplify the text as appropriate. ANS are presently preparing a 3rd draft of Chapter C to be available early in February 1988. ANS will also assist in checking the style and consistency of draft Chapters produced by the CEC.

5.2. PACOMA Project

PERFORMANCE EVALUATION OF CONFINEMENT FOR ALPHA-WASTE REPOSITORY IN GRANITE FORMATIONS (PACOMA project)

Contractor : CEA, CEN Fontenay-aux-Roses
Contract No. : FI1W/0040-F
Duration of contract : 1.3.87 - 30.11.88
Period covered : 1.4.87 - 31.12.87
Project leader : J. LEWI

A. OBJECTIVES AND SCOPE

The general objective is the safety assessment of a deep repository in a granitic formation for alpha-bearing radioactive waste. This research has to be carried out with the other PACOMA contractors.
The first phase consists in the definition of a general work methodology and in the adaptation of the models developed for the PAGIS project to the case of alpha waste.

The second phase consists of a further study of the cemented alpha waste and in carrying out the global safety assessment.

B. WORK PROGRAMME

- basic data : a new waste inventory has to be provided
  the sites are the same as in PAGIS (Auriat, Barfleur, notional UK site)
  the repository design has to be defined for alpha- bearing wastes

- the methodology will be analogue to the approaches in the PAGIS project, (deterministic calculations, sensitivity and uncertainty analysis)

- model and calculations tools : as far as possible, the same as for PAGIS; a new version of the source model (CONDIMENT) has to be realized

- calculations : similar to those done for the PAGIS project.

C. PROGRESS OF WORK AND OBTAINED RESULTS

We focused mainly in 1987 on the data collection aspect :

- a detailed waste inventory has been defined and provided to the CEC.

- the repository concept description, realized by CEA-ANDRA, was also provided to the CEC.

- the version of the MELODIE source model, CONDIMENT, developed for the alpha-bearing waste has been realized by the CEA-DRDD.

The effective calculations of the several repositories have, due to time constraints, been postponed to 1988.

Performance Assessment of Confinements for MLW and Alpha Waste (PACOMA Project)

Contractor: NRPB, Chilton, UK
Contract No.: FI1W/0041-UK(H)
Working Period: October 1986 - December 1988
Period covered: January 1987 - December 1987
Project Leader: Ms M D Hill

A. Objectives and Scope

The overall objectives of the UK contribution to the PACOMA Project are to develop and demonstrate procedures for assessing the radiological impact of disposal of intermediate level waste in a deep repository located in a clay formation. The hypothetical repository considered is assumed to be at Harwell in Oxfordshire. The research is co-ordinated by the UK Department of Environment and is being carried out by four organisations:

National Radiological Protection Board (NRPB)
Theoretical Physics Division, UKAEA Harwell Laboratory
Electrowatt Engineering Ltd
CAP Scientific Ltd

The NRPB work is in two phases. The objectives in Phase I are to establish a detailed methodology for the assessment, to collect data for biosphere modelling and to carry out preliminary calculations. In Phase II the aim is to carry out the assessment, using information provided by other UK contractors and in consultation with other participants in PACOMA, particularly CEN/SCK.

B. Work Programme

B.1. Adaptation of PAGIS methodology for use in the assessment of intermediate level waste disposal, identification of radionuclide release scenarios.
B.2. Review of available biosphere data, and preliminary calculations for typical releases.
B.3. Detailed planning of calculations to be carried out in the full assessment, finalising biosphere data and assumptions for each scenario.
B.4. Best estimates of doses and risks to individuals and populations for each scenario.
B.5. Sensitivity and uncertainty calculations.
B.6. Co-ordination of joint report by the four UK contractors.

C. Progress of work and obtained results

State of advancement

Work has continued on items B.1 and B.2 and has started on items B.3 and B.5. Items B.4 and B.6 will be started in 1988. Work on all items is delayed. Preliminary calculations of doses arising from typical releases have been made and a preliminary sensitivity study has been performed. Progress has been made on the design of an interface between the models at UKAEA Harwell and at NRPB. The development of a version of BIOS suitable for uncertainty analysis has started and this will interface with the existing uncertainty analysis executive program.

Progress and Results

1. Assessment methodology and release scenarios (B.1)

A number of areas for further study in the methodology used in PAGIS have been identified previously and a paper discussing one of them, the two alternative ways of calculating risks, has been prepared and circulated to CEC and all PACOMA participants.

2. Review of data and preliminary calculations (B.2)

A review of biosphere data for the Harwell site has been completed and data for the best estimate model BIOS has been selected. It was found that the release from the geosphere to the biosphere could occur directly into the Thames, directly into its tributary (Mill Brook) or into the adjacent deep soil. The relative proportions depended on the exact path the groundwater took within the geosphere.

The available data suggested that the Thames could be divided into 4 river sections, so that each section has approximately constant hydrodynamic parameters. Therefore the model BIOS was set up to represent the Thames in such a way. Best estimate values for the parameters were selected and the model was run for unit releases of the radionuclides ^{129}I, ^{135}Cs and ^{237}Np. These radionuclides were selected on the basis of their inventories, long half-lives and importance in previous assessments. The results are summarised in Table 1. The importance of marine pathways for ^{129}I and ^{237}Np is a consequence of the high volumetric flux of the Thames. A comparison of the results with those from other assessments has been made and showed that they are consistent with them.

Since the release from the geosphere to the biosphere could occur directly to Mill Brook or to the subsoil adjacent to the Thames, the calculations were repeated for these release scenarios. The release to the Mill Brook, which has a volumetric flow rate about 0.3% of the Thames flow rate, gives higher doses via the freshwater pathways for all three radionuclides and via agriculture pathways for ^{129}I and ^{237}Np. The doses via marine pathways and the doses from ^{135}Cs via agricultural pathways are generally unchanged. The release to deep soil gave doses that were very similar to those from release to the river Thames.

The input to BIOS has been modified so that releases to all three parts of the biosphere can be modelled individually or simultaneously.

3. Planning and finalisation of data and assumptions (B.3)

A number of discussions have resulted in agreement over the type of interface to be employed between the geosphere model at UKAEA and the biosphere model at NRPB. This will enable the flux from the geosphere to be input directly into the biosphere. In addition to the flux history, the geosphere model output will contain the location of the release (or the appropriate proportions) and key parameter values (such as K_d values) to ensure continuity across the interface. The model BIOS has been modified to be able to read in flux histories in this form and the full interface will be tested in 1988.

The extra parameter values passed from UKAEA to NRPB will be important in keeping records of the uncertainty analysis results, in which a large number of runs will be performed. It was agreed that the Latin Hypercube Scheme would be used by both organisations and that the sampling would be done independently.

4. Sensitivity and uncertainty calculations (B.5)

A sensitivity study was performed on the deep soil release scenario described in section 2. The area of the deep soil affected by the release was varied from 2.5 km^2 to 100 km^2 and the results are summarised in Table 2. The maximum individual doses from ^{129}I were unchanged but occurred later for a larger area. The individual doses from ^{135}Cs and ^{237}Np from inland pathways were sensitive to the area, smaller areas giving higher doses. Individual doses via marine pathways were unaffected. The collective dose commitments from ^{135}Cs and ^{237}Np were not sensitive whereas that from ^{129}I via agricultural produce was directly correlated with the contaminated soil area.

The best estimate biosphere model BIOS is too complicated to run in a full uncertainty analysis. Therefore a simplified version is being developed for PACOMA. The structure of the model has been defined and it is being designed to allow the form of the biosphere to be changed easily from run to run e.g from a river to a lake. This version of BIOS will interface with the uncertainty analysis executive program developed for PAGIS. This program has recently been modified for use in a limited uncertainty analysis of BIOS in which a subsection of the model was studied. Therefore the substitution of the simplified version of BIOS should be straightforward.

Table 1

Predicted doses for release of 1 TBq of each radionuclide into the Thames

a) Individual doses

Nuclide	Peak individual dose ($Sv\ a^{-1}$)	Time of peak (a)	Pathway
^{129}I	$6\ 10^{-7}$	10^{4}	seaweed
^{135}Cs	$1\ 10^{-6}$	10^{4}	green veg
^{237}Np	$3\ 10^{-6}$	10^{4}	molluscs

b) Collective dose commitments

Nuclide	Collective dose commitment (man Sv)	Pathway
^{129}I	$9\ 10^{4}$	global
^{135}Cs	$3\ 10^{3}$	agricultural
^{237}Np	$9\ 10^{4}$	freshwater

Table 2
Changes in doses caused by variations in area of subsoil to which release occurs

Parameter	Results for soil area of		
	2.5 km^2	25 km^2	100 km^2
a) Peak individual doses ($Sv\ a^{-1}$)			
^{129}I milk (time)	(500 y)	(500 y)	(900 y)
^{135}Cs green veg	10^{-5}	10^{-6}	$4\ 10^{-7}$
ploughing	$4\ 10^{-8}$	$4\ 10^{-9}$	10^{-9}
^{237}Np root veg	$2\ 10^{-6}$	$2\ 10^{-7}$	$6\ 10^{-8}$
ploughing	$2\ 10^{-5}$	$2\ 10^{-6}$	$6\ 10^{-7}$
b) Collective dose commitment (man Sv)			
^{129}I agricultural	14	19	33
global	$9\ 10^{4}$	$9\ 10^{4}$	10^{5}
marine	$4\ 10^{3}$	$4\ 10^{3}$	$5\ 10^{3}$
^{135}Cs all pathways		No change	
^{237}Np all pathways		No change	

Note All other doses were insensitive to changes in soil area. Doses are given for a 1 TBq release of each radionuclide.

ACQUISITION OF SUBJECTIVE DATA FOR USE IN MODELS FOR WASTE SITE ASSESSMENTS (PACOMA PROJECT)

Contractor : CAP Scientific, London UK
Contract No : FI1W/0042-UK(H1)
Working Period : January 1987 - December 1987
Project Leader : M A Bull

A. Objectives and Scope

In the modelling of radionuclide movement from a repository a compromise must be achieved between accuracy and cost. For probabilistic site assessment using Monte Carlo simulation, one dimensional models are used due to their small computational cost whereas for deterministic modelling more detailed two- and three- dimensional models are used. The objectives of this programme of work is to develop and demonstrate consistent data acquisition and preparation techniques for probabilistic site assessment and for detailed deterministic modelling of radionuclide movement from a repository for intermediate level waste under the Harwell site. A comparison of radionuclide risks derived from both assessment procedures will be made and any inconsistencies in the input data and resulting inconsistencies in the risk estimates will be investigated.

B. Work Programme

B.1 Research Programme: development of methodology for comparing probabilistic site assessment codes and detailed deterministic models; planning for the data acquisition exercise.

B.2 Data Acquisition: the use of expert opinion to acquire data for 5 to 10 parameters.

B.3 Model Comparison: comparison of input data and expected risks.

C. Progress of Work and Results Obtained

Summary

The data acquisition exercise were planned and completed. Probability distributions were collected for nineteen parameters at six meetings of experts. As well as collecting probability distributions the meetings also discussed several important modelling issues. The data collected was subsequently used in a flow network model. This was used to derive velocity flow distributions along important flow paths. These velocities will subsequently be used in the model comparison exercise as input to the models. Planning of the model comparison study has continued, the models to be used for this study have been provisionally selected and a methodology for comparison agreed.

Progress and Results

1. Research Programme

B.1: Task B1 is complete and a report on the work has been issued /1/.

B.2: The procedure used for encoding probability distributions from expert opinion is described in detail in reference /2/. In summary the approach contains the following stages:

- introduction and bias: the objectives of the exercises, the participants background the motivation and an illustration of the approach through a simple example.
- definition: agreeing the definition of the parameter and the definition of related parameters.
- assessment: the method of measuring values of the parameter.
- factors and sources of uncertainty: the dependent factors which contribute to the uncertainty about the parameters' value.
- assumptions: identifying the factors that are assumed not be contribute to the uncertainty, ie the distributions are conditional on these assumptions.
- conditioning: discussion of a reference class. Assessing high and low values of a parameter for the specific site and scenarios which lead to such values. The probabilities that values greater or lower than these values can occur.
- encoding: encoding the cummulative distribution function.
- verification: verifying features of the assessed pdf.

Clearly there is considerable amount of structuring and conditioning before encoding begins. In order to assist the encoding stage the cummulative probabilities assessed by the experts are entered into a personal computer and a distribution fitted to the values. The two parameter beta distribution has been chosen for fitting the cdf as it is highly flexible distribution. The fitted cdf is then readily converted to a pdf for viewing by the experts. The computer programme to fit the beta distribution has been developed to provide an iterative least squares fit as a fit on the mean and standard deviation proved to be inadequate with a small number of beta values. In addition the computer programme has been developed to display the mode and tertiles on the pdf to assist the important verification stage.

The data acquisition exercise has been completed; nineteen probability distributions were collected at six meetings of experts. Some of the distributions were used in a flow network model to derive probability distributions of flow velocities. These velocity distributions will be used in the model comparison exercise as input to the one-dimensional groundwater transport models. During the meeting several important issues were raised concerned with the modelling techniques being used:

1) The experts felt that the values of the geological parameters which describe flow and transport in the lower chalk and upper greensand were sufficiently different that they assessed these two geological layers separately. Previous one-dimensional transport modelling has treated these as a single layer.

2) The experts believed there was insufficient information to warrant them assessing the relationship between hydraulic conductivity and porosity with the depth of overburden. This conclusion raises questions about the need to model the depth of overburden.

3) The way that porosity is modelled was felt to be inadequate. The experts recommended that a dual porosity model which could represent both porous and fracture flow should be developed as the phenomena were well understood.

Task B.2 is now complete and a report issued /2/.

B.3 Planning of the final task has proceeded through several meetings between the UK participants. The models to be used for the study have been provisionally selected. The methodology to be used for the comparison has also been discussed and provisional agreement has been reached.

References:

/1/ Laundy, R.S. Data requirements for a comparison of one and two dimensional models using consistent data acquisition procedures. CAP Scientific draft report 3409/TR.1 Feb 1987.

/2/ Dalrymple, C.J. and Phillips, L.D. Using a structured approach to the acquisition of probabilistic data from expert opinion. CAP Scientific draft report. 3409/TR.2 July 1987.

PERFORMANCE ASSESSMENT STUDIES FOR INTERMEDIATE LEVEL WASTE AT AT SINGLE SITE

Contractor : Harwell Laboratory, United Kingdom
Contract No. : FI1W/0043
Duration of contract : November 1986 - November 1988
Period covered : January 1987 - December 1987
Project leader : M.J. Norgett

A. OBJECTIVES AND SCOPE

We shall simulate the transport to the surface of radionuclides released from a hypothetical repository in a clay layer beneath the Harwell site. To this end, Electrowatt Engineering have calculated the rates of release of radionuclides from such a repository containing various waste inventories. CAP Scientific Ltd. are deriving probability distributions for the values of the parameters involved in the groundwater flow and solute transport calculations by structured questioning of groups of experts. Pathways from the repository will be determined primarily by means of two-dimensional flow calculations, with perhaps limited recourse to three-dimensional simulation. We shall examine how the results depend upon numerical approximations in the flow calculations, upon the modelling assumptions and upon the uncertainty in the values of the relevant physical parameters. Radionuclide transport will be calculated by combining both one- and two-dimensional calculations, so as to examine as far as possible within a limited budget the uncertainties in the results for the most radiologically significant nuclides. Radiological risks will be determined by the National Radiological Protection Board. In the final stage CAP Scientific Ltd. will compare radiological risks derived by probabilistic risk analysis and from deterministic modelling of radionuclide migration. This study should contribute to a comparison between the different approaches to radiological safety assessment adopted in the United Kingdom by UK Nirex Ltd. and by the Department of the Environment.

B. WORK PROGRAMME

1 Review, and if necessary revise existing calculations of groundwater flow in the vicinity of the Harwell site, so as to establish numerical accuracy and to examine sensitivity to modelling assumptions.
2 Carry out radionuclide-transport calculations and determine how results depend upon uncertainties in the modelling assumptions and in the values of physical parameters.
3 Assist CAP Scientific Ltd. to compare safety assessments based upon probabilistic amd deterministic simulations.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

We have reviewed previous calculations of groundwater flow in the vicinity of the Harwell site carried out as part of the United Kingdom Department of the Environment's DRY RUN 1 and DRY RUN 2 studies. The DRY RUN 1 calculations are based explicitly upon what is known about the local hydrogeology. The DRY RUN 2 calculations are based upon less specific detail and so need to be carefully calibrated and adjusted to yield realistic results. The numerical accuracy of both sets of calculations is unsatisfactory and we have made significant improvements to the DRY RUN 1 results by a more careful choice of a suitable finite-element grid.

We have demonstrated transfer of results from Electrowatt Engineering's source-term calculations to our solute-transport models. Preliminary transport calculations indicate that nuclides are likely to diffuse through the clay layer containing the repository, but subsequently are transported in solution at the rate of the more rapid flow within the adjacent aquifers.

Progress and Results

1. Review and Revise Groundwater-Flow Calculations

(i) Geology in the Vicinity of the Harwell Site

Figure 1 shows a proposed geological cross-section through the Harwell site running approximately NNW to SSE, that is roughly at right angles to the direction in which the various strata outcrop at the surface. The hypothetical repository about 150m below the surface is at the middle of a band of Gault and Kimmeridge Clay of very low hydraulic conductivity. This Clay is overlaid by permeable Chalk and Upper Greensand, and rests upon a permeable Corallian layer, which in turn rests upon almost impervious Oxford Clay.

(ii) Regional Hydrogeology

Figure 1 also shows the anticipated flow pattern near the Harwell site. A small fraction of the rain falling on the exposed Chalk passes downwards through the Gault and Kimmeridge Clay in the vicinity of the repository, and feeds into the Corallian aquifer. Flow in the Corallian aquifer is up-dip beneath the repository and further to the NNW until diverted upwards through the clay by a down-dip flow fed by rain falling on the exposed Corallian stratum. Thus flow relevant to a repository beneath the Harwell site is confined to three layers: an upper aquifer of Chalk and Upper Greensand; a Gault and Kimmeridge Clay layer containing the repository; and a lower Corallian aquifer. Any perturbation due to flow upwards through the underlying Oxford-Clay layer is negligible.

(iii) DRY RUN 1 Calculations

The DRY RUN 1 flow simulations are described in the DRY RUN 1 report /1/ and in more detail by Brightman and Noy /2/. Flow is calculated for a two-dimensional section divided into three layers (upper aquifer, clay, lower aquifer) with uniform properties. This section extends from a crest SSW of the Harwell site, NNE through the site to a point on the River Thames within the region where the Corallian aquifer overflows. Since flow presumably diverges from the crest and converges to the overflow region, no-flow conditions were imposed over both vertical boundaries of the section. The effect of a prescribed up-dip flow within the Corallian aquifer beneath the crest was also examined. The bottom boundary coincides with the upper limit of the Oxford Clay, and is impermeable. The upper boundary is set to coincide with the observed mean annual water-table, where hydraulic head is equal to the height of the boundary above sea level. In defining this boundary, the surface topography is simplified, in particular to remove an outlying Chalk outcrop that lies across the section, and which has marked local impact upon the flow. In the DRY RUN 1 exercise, flow was calculated by means of the NAMMU finite-element code, with element boundaries aligned with the limits of the separate layers.

The flow pattern is such that pathlines from the repository pass vertically downwards through the Clay layer, then continue up-dip through the Corallian aquifer towards the overflowing region. A two-dimensional section chosen to model such flow should ideally coincide with a streamline through the Corallian aquifer. The two-dimensional section chosen for the DRY RUN 1 flow calculation is approximately perpendicular to the inferred head contours in that aquifer and therefore is close to optimal. Moreover, the section extends between points at local maximum and minimum values of hydraulic head, so that the vertical no-flow boundary conditions are satisfactory. Significantly better flow predictions would require either three-dimensional modelling or, more economically, areal flow simulation within the Corallian aquifer, so as to locate more precise head contours and to take proper account of diverging and converging flow.

We have specifically examined the accuracy of the flow simulations carried out in the DRY RUN 1 exercise, which exhibit spurious oscillations that can be attributed to an insufficient refinement of the finite-element grid, particularly adjacent to discontinuities in the upper boundary. Difficulties of this kind arise because the elements employed in simulations of groundwater flow through such two-dimensional sections are typically elongated, and hence ill-suited to representing variations that are actually localized within a small part of an element. Figure 2 shows streamlines calculated with a grid that is refined extensively adjacent to discontinuities in the upper boundary; limited unphysical oscillations are still evident and indicate a need for yet more careful adjustment of the finite-element grid. However, the set of calculations carried out so far has demonstrated that the remaining limitations of the flow simulations do not significantly effect the route or travel times of computed pathlines that originate in the vicinity of the repository.

(iv) DRY RUN 2 Calculations

In the DRY RUN 2 exercise /3/ groundwater flow was calculated for a two-dimensional section running NNW to SSE through the Harwell site, that is roughly at right angles to the direction in which the various strata outcrop. Flow within part of the section shown in Figure 1, extending between the River Thames and Kennet, was calculated in order to establish the regional flow pattern and in particular to provide specified-flow boundary conditions for a more limited local flow model that extends only to high ground SSE of the Harwell site. Three different assumptions as to the head profile beneath the Kennet at the southern boundary of the regional model led to markedly different predictions of the rate and even the direction of flow at the boundary of the local model. The head profile beneath the Kennet is uncertain because of the unknown impact of major geological features adjacent to but beyond the limits of the regional model. The regional model adopted in the DRY RUN 2 study is therefore too small to provide an unambiguous indication of the regional flow pattern, and hence does nothing to dispel the uncertainty attaching to the boundary conditions of the local model.

A second objective of the DRY RUN 2 study was to substitute a more realistic upper boundary condition for that adopted in the DRY RUN 1 calculations, in which the upper boundary is supposed to conform with the measured water table. The upper boundary in the DRY RUN 2 study approximates the surface; then the position of the water-table is fixed at the Rivers Kennet and Ock and at the spring-line on the chalk scarp face, but elsewhere is determined by calculations that assume a specified surface flux. This infiltration rate is deduced from measured rainfall according to an empirical and dubious correlation. Moreover, the predicted water-table is realistic only if the model is augmented by surface layers of permeable fractured chalk and soil, to enhance drainage to rivers and springs; otherwise the water-table rises above the level of low-lying ground. An advantage of an infiltration model of this kind is that its data can be fixed by surface observation and measurement. However, the evidence of the DRY RUN 2 study is that for realism such a model must be calibrated also against the measured water-table and that therefore it is more straightfoward to use directly a flow model bounded at this level.

In the DRY RUN 2 study, flow was calculated by the finite-difference TARGET code. Since differencing is based upon a rectangular mesh both the surface and the boundaries between the geological layers are necessarily approximated by a sequence of steps. Such discontinuities perturb the calculated flow and introduce considerable errors into the pathlines required to predict radionuclide transport. Moreover, the finite-difference grid is very elongated, and therefore prediction of vertical flow velocity through the clay layer may be significantly in error.

2. Radionuclide-Transport Calculations

Electrowatt Engineering have calculated the rates of release of radionuclides from repositories containing prescribed waste inventories. Radionuclide fluxes calculated for successive intervals have been written to magnetic tape in agreed units and format. We have demonstrated that the content of that tape can serve as data for our radionuclide-transport codes.

Transport calculations with the NAMSOL code, for a hypothetical nuclide but with realistic values of the physical parameters, suggest that diffusion is the dominant transport mechanism within the clay layer containing the repository. Thus if the repository is in the middle of that layer, the nuclide will be released at much the same time into the upper and lower aquifers. Within the aquifers, advection is the dominant transport mechanism. Thus it will be necessary to employ mathematical models and numerical methods appropriate to both diffusion- and advection-dominated transport in calculating radionuclide migration from such a repository.

References

/1/ THOMPSON, B.G.J. and BROYD, T.W., An initial examination of a procedure for the post-closure radiological risk assessment of an underground disposal facility for radioactive waste, Department of the Environment Disposal Assessments Technical Report TR-DOE-4 (1986).

/2/ BRIGHTMAN, M.A. and NOY, D.J., Finite-element modelling of the Harwell regional groundwater flow regime, British Geological Survey Report BGS FLPU 84-1 (1984).

/3/ THOMPSON, B.G.J., KANE, P., NICHOLLS, D.B.N. and GRALEWSKI, Z.A., Development of a methodology for post-closure radiological risk analysis of underground waste repositories: illustrative assessment of the Harwell site, Department of the Environment Report DOE/RW/1986 (1986).

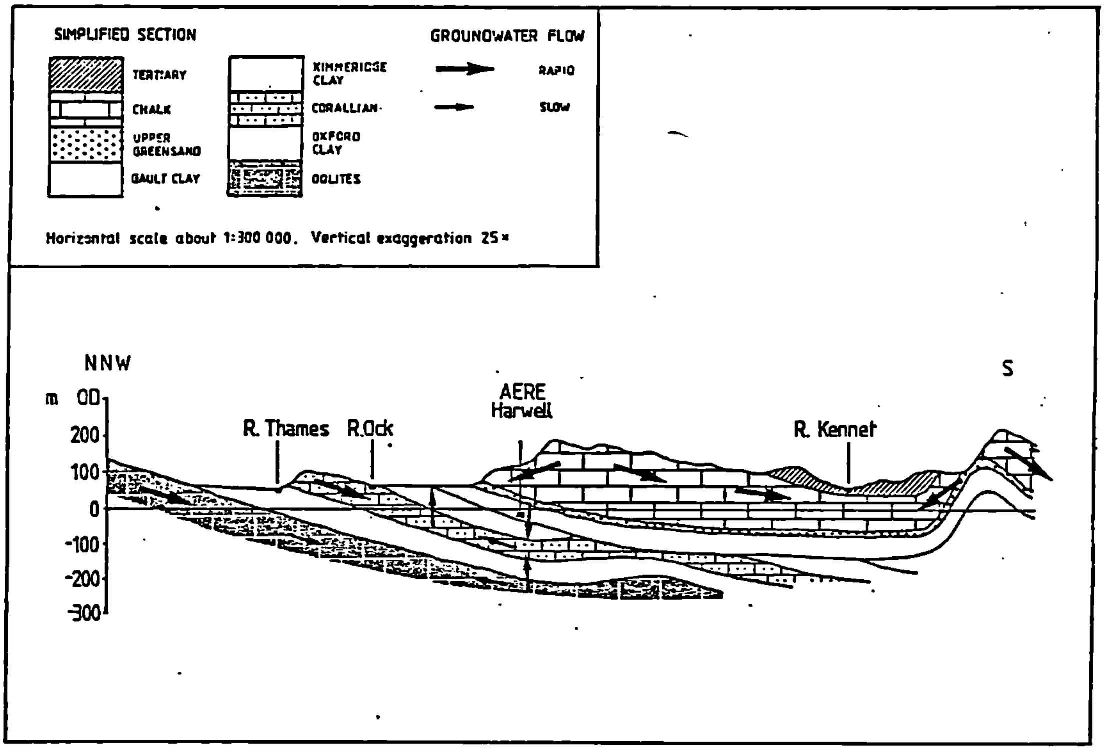


Figure 1. Geological cross-section NNW-SSE through the Harwell site, and conjectured groundwater flow

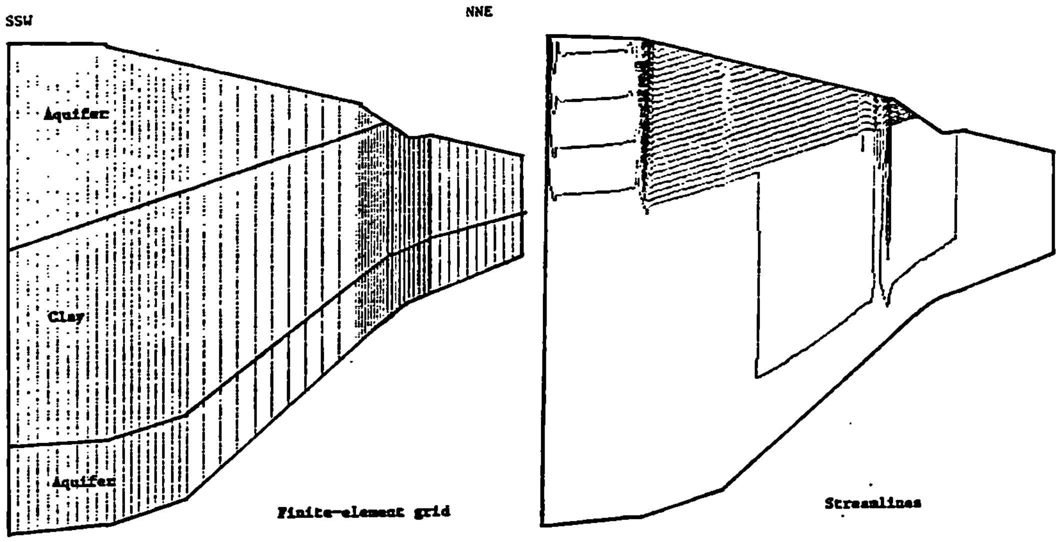


Figure 2. Groundwater-flow calculations for an improved finite-element grid

Safety Evaluation of Geological Disposal Concepts for Low and Medium Level Wastes in Rock Salt - PACOMA Project

Contractor: GSF - IfT Braunschweig, FRG
Contract No.: FI1W/0044-D
Duration of Contract: April 1987 - December 1988
Period covered: April 1987 - December 1987
Project Leader: R. Storck

A. OJECTIVES AND SCOPE

The aim of the PACOMA research work is to carry out, as an extension of the PAGIS action on HLW, a comprehensive assessment of the radiological consequences and risks associated with geological disposal of alpha-bearing wastes and MLW. The study, which covers three types of geological formations (argillaceous rocks, crystalline rocks and salt) will follow the methodology set up in PAGIS.

The essential objective is to show how far appropriate choices of the repository design parameters can improve the performances of the whole system.

The reference repository design will be taken as a basis for the calculation. The evaluations on the variant sites will be made by a change of the parameters or by a modification of the models. The results will be expressed in terms of doses and risks to the individuals and populations.

B. WORK PROGRAMME

B.1. Disposal site
B.2. Repository design
B.3. Scenarios
B.4. Models

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The preliminary repository design is taken from the plans of the national authorities, reducing it to LLW and MLW disposal location for the reference case.

For the variant site geologic data have been collected. A preliminary model for ground-water movement has been established.

Preliminary data for selected waste form and packages were collected. The inventory will be taken from the updated list prepared by the other contractors as far as agreed up to now.

Altered evolution scenarios will be the same as for PAGIS with the exception that the possibility of brine intrusion from a brine pocket into the LLW/MLW wing of the repository should carefully been estimated.

A number of new or revised section models and effect models have been implemented in the EMOS code.

Progress and results

B.1. Disposal site

The reference disposal site is that used for PAGIS. Therefore, all geological data for this site can be taken over without changes. For the variant site geologic data have been collected.

B.2. Repository design

The preliminary repository design is taken from the PSE study /1/ cutting off the HLW wing. For the variant site repository design data are taken from plans of a national variant.

Input data for inventory and waste types have been collected as far as agreed. Final list of inventory has not yet been received.

For the variant site a mixing tank model for the waste disposal has been developed. A data base with geometric and waste specific data and a list of inventories has been set up.

B.3. Scenarios

Scenarios are the same as for PAGIS. Additional investigation about the possibility of brine intrusion from a brine pocket into a LLW/MLW repository seems to be neccessary.

B.4. Models

Additional section models for LLW chambers and MLW boreholes and corresponding drifts have been developed /2/. Boreholes are variants of the HLW boreholes taking into account the transport of cement and the gas production due to corrosion.

A new mobilisation model with element specific degradation rates has been implemented into the EMOS code.

/1/ STORCK, R., et al.: PSE Abschlussbericht, Vol. 16, Projektleitung HMI, Berlin 1985

/2/ HIRSEKORN, R.P.: to be published in Proceedings of the Workshop on Near Field Assessment of Repositories for Low and Medium Level Waste, OECD Nuclear Energy Agency, Paris 1988

SAFETY EVALUATION OF GEOLOGICAL DISPOSAL CONCEPTS FOR LOW AND MEDIUM LEVEL WASTES IN ROCK SALT (PACOMA-PROJECT)

Contractor : ECN, Petten, The Netherlands
Contract No. : FI1W-0045 NL
Duration of contract: April 1987 - December 1988
Period covered : April 1987 - December 1987
Project leader : J. Prij

A. OBJECTIVES AND SCOPE

The research covers the disposal of all types of low and medium level waste in two types of caverns, mined by solution mining in three types of salt formations. The aim of the study is the comparison of the safety of these different concepts. The methodology used is the same as used for PAGIS. The work will be performed in cooperation with GSF in Braunschweig (FRG). A part of the analyses will be executed by the RIVM in Bilthoven (NL).

B. WORK PROGRAMME

1. Basic data

Data will be collected of all types of waste, including the radionuclide inventories and the immobilization models. Also the data defining, the geosphere and biosphere will be collected.

2. Disposal site

Three types of generic formations will be studied; a salt dome, a small pillow and a salt layer.

3. Repository design

Two types of solution mined caverns will be studied. In the first type the waste is dumped in the cavern which is still filled with brine while in the second type the waste is disposed after having removed the brine out of the cavern.

4. Scenario's

The scenario consists of a water intrusion/extrusion type, while the evaluation is based on the best estimate of individual dosis and the probability of occurrence.

5. Models

In principle, the computer codes to be used in PACOMA will be the same as for PAGIS. Where it is appropriate, GSF and ECN will use the same models.

6. Calculations

Best estimate calculations of the dosis to individuals will be performed for the different concepts. The sensitivity of the results will be investigated and a final assessment will be made.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The data for all types of waste have been collected and will be reported below. The dimensions of the generic formations have been fixed and the design study of the different repository concepts has been finished. The main scenario is defined and the analyses for the repository concept of a mine where high level waste is stored in vertical boreholes and the medium and low level waste is stored in excavated rooms are started.

Progress and results

The main result obtained in this year is a detailed description of the different types of waste. In total 36 types of containers have been defined. In accordance with the EMOS-code each type of container is characterized by a code which consists out of a sequence of a letter, two digits and a slash, followed by a sequence number. The letter characterizes the origin of the waste. In this study three different origins are recognized:

W: Waste from the reprocessing unit.
K: Waste from the operation and dismantling of the nuclear power plants.
L: Waste from hospitals, laboratories and industry.

The first digit characterizes the type of the container:

1: a single-walled steel container.
4: a concrete vessel.
5: a thin-walled steel drum.

The second digit characterizes the fixation of the waste:

1: glass matrix.
2: concrete.
3: bitumen.
4: no fixation.

In table I the main characteristics of the 36 containers are summarized. The initial radionuclide inventory to be used in our safety evaluation is given in table II for all 36 types of containers. In the table the inventory is given as Bq per container. In the heading of the table, the number between brackets gives the number of containers. The amount of waste is based on one PWR of 450 MWe and one small BWR of 50 MWe, each having an operational period of 30 years. The amount of categorie "L" is based on a collection period of 70 years.

TABLE I: MAIN CHARACTERISTICS OF THE DIFFERENT WASTE CONTAINERS

CODE	MATRIX MASS [kg]	CONT. MASS [kg]	CONT. VOL. [m³]	EMPTY SPACE [m³]	INTERIM STORAGE [a]	SHORT DESCRIPTION OF THE WASTE
W11-1	412	80	0,175	0,02	50	HAW from reprocessing
W14-1	44	80	0,175	0,09	50	Glass rest.
W12-3	0	358	1,46	0,2	50	Huls & Endcaps.
W13-5	0	20	0,21	0,021	50	Sludge & Casks
W13-8	0	20	0,21	0,021	50	Sludge & Bitumen
W42-7	0	1.060	0,68	0,0926	50	Non-alpha technol. waste
W42-10	0	1.170	1,18	0,15	50	Alpha technol. waste
K42-1	0	15.300	5	0,8	10	Activated steel parts
K42-2	0	15.000	5	0,8	10	Lower grid
K42-3	0	15.000	5	0,6	10	Control rods
K42-4	0	15.000	5	0,6	10	Pumps
K42-5	0	15.000	5	0,6	10	Core box
K42-6	0	15.000	5	0,6	10	Upper grid
K42-7	0	15.000	5	0,6	10	Upper grid ring
K42-8	0	15.000	5	0,67	10	Em. cooling
K42-9	0	15.000	5	0,6	10	Core lid
K42-10	0	15.000	5	0,6	10	Low active metal
K42-11	0	15.000	5	0,72	10	Biological shield
K42-12	0	15.000	5	0,64	10	Medium active steel
K42-13	0	15.000	5	0,61	10	Low active steel
K42-14	0	15.000	5	0,3	10	Low active mixed waste
K42-15	0	15.000	5	0,5	10	Low active secondary waste
K42-16	0	15.000	5	0,4	10	Concentrates
K52-1	0	45	0,216	0,04	10	Ion exchanger
K52-2	0	170	0,215	0,02	10	Ion exchanger
K52-3	0	45	0,216	0,03	10	Ion exchanger + concentrates
K52-4	0	45	0,216	0,04	10	Solid waste, metal, anorganic
K52-5	0	160	0,217	0,01	10	Ash
K52-6	0	45	0,216	0,05	10	Fuel bundle wall (BWR)
K52-7	0	45	0,216	0,05	10	In-core instruments
L52-1-7	0	111	0,217	0,025	10	Waste from laboratories, hospitals, industry

NUCLID	KSA-VERGL. W 11-1 (300)	HULS+ENDCAP W 12-3 (200)	SLUDGE+CASK W 13-5 (40)	SLUDGE+BITU W 13-8 (100)	GLASOVENAEV. W 14-1 (20)	N-ALFA TECHN W 42-7 (2090)	ALFA-TECHN W42-10 (400)
C 14	3.92E+07	5.22E+10	2.69E+07	1.66E+07	.00E+00	4.00E+02	6.88E+03
CO 60	3.63E+12	3.52E+14	1.21E+13	2.24E+10	3.41E+12	6.85E+06	1.18E+08
NI 59	1.81E+09	5.74E+11	2.78E+09	3.96E+06	7.21E+06	5.18E+03	8.92E+04
NI 63	2.37E+11	7.51E+13	3.63E+11	5.25E+06	9.79E+08	6.81E+05	1.17E+07
SE 79	2.03E+10	2.22E+07	9.84E+05	3.62E+05	1.74E+09	2.90E+04	5.00E+05
RB 87	9.27E+05	1.62E+03	5.92E-01	1.18E+02	1.05E+05	9.27E+00	9.27E+01
SR 90	3.34E+15	4.81E+12	3.42E+09	6.14E+10	3.20E+14	4.55E+09	7.88E+10
ZR 93	9.07E+10	1.20E+10	1.15E+08	5.96E+08	8.98E+09	4.29E+04	7.40E+05
MO 93	3.05E+07	2.31E+09	6.14E+02	1.64E+04	6.62E+05	1.44E+01	2.49E+02
NB 94	2.61E+08	9.74E+10	8.29E+03	4.29E+04	1.20E+06	3.08E+00	5.33E+01
TC 99	6.48E+11	1.01E+09	1.31E+07	1.17E+07	6.58E+10	3.08E+05	5.33E+06
PD 107	5.29E+09	2.81E+07	2.56E+05	2.85E+06	5.36E+08	2.50E+03	4.33E+04
SN 126	4.63E+10	5.22E+07	1.79E+06	1.98E+07	2.68E+09	5.29E+04	9.14E+05
J 129	1.53E+06	1.68E+06	3.09E+04	1.65E+05	1.80E+03	2.20E+03	3.77E+04
CS 135	1.84E+10	2.01E+07	3.70E+05	1.97E+06	1.75E+09	2.89E+04	5.00E+05
CS 137	4.66E+15	5.25E+12	9.21E+10	5.14E+11	4.81E+14	7.40E+09	1.27E+11
SM 147	1.84E+05	1.82E+02	4.00E+00	2.04E+01	2.19E+04	2.56E-01	4.44E+00
SM 151	1.75E+13	1.94E+10	3.49E+08	2.16E+09	2.19E+12	2.43E+07	4.22E+08
EU 154	3.55E+14	4.22E+11	6.62E+09	4.47E+10	4.11E+13	4.96E+08	8.55E+09
CM 248	2.09E+03	1.18E+02	1.40E-02	5.88E+01	7.00E+04	6.18E-01	6.18E+01
PU 244	1.46E+02	1.87E+01	9.18E-03	3.62E+00	1.42E+02	2.73E-01	1.14E+01
CM 244	7.14E+13	3.60E+10	3.46E+07	3.38E+08	3.33E+13	1.07E+09	4.48E+10
PU 240	1.49E+11	1.82E+10	8.88E+06	3.51E+09	9.83E+09	2.65E+08	1.10E+10
U 236	2.01E+07	1.39E+07	6.77E+03	2.68E+06	6.24E+06	2.02E+05	8.40E+06
TH 232	3.10E+00	1.51E-03	2.23E-06	6.18E-04	5.69E-01	5.66E-05	2.35E-03
U 232	5.96E+05	3.41E+05	1.75E+02	1.59E+04	1.09E+06	5.11E+03	2.13E+05
CM 245	5.85E+09	2.82E+06	2.93E+03	2.65E+04	1.05E+10	8.73E+04	3.64E+06
PU 241	4.85E+13	6.29E+12	2.92E+09	1.27E+12	1.77E+12	9.07E+10	3.81E+12
AM 241	3.92E+13	1.92E+10	2.95E+07	1.78E+08	8.75E+12	7.36E+08	3.08E+10
NP 237	1.56E+10	7.59E+06	7.84E+03	7.07E+04	1.60E+09	2.34E+05	9.77E+06
U 233	7.66E+04	9.25E+02	5.18E-01	1.78E+02	1.75E+03	1.45E+01	6.03E+02
TH 229	4.48E+03	2.17E+00	2.35E-03	8.92E-01	7.00E+02	6.85E-02	2.86E+00
CM 246	1.12E+09	5.37E+05	5.59E+02	5.07E+03	3.89E+09	1.67E+04	6.96E+05
PU 242	7.40E+08	9.55E+07	4.66E+04	1.85E+07	4.72E+07	1.39E+06	5.81E+07
AM 242M	4.11E+11	2.01E+08	2.06E+05	1.87E+06	9.63E+10	6.14E+06	2.56E+08
U 238	2.36E+07	1.63E+07	7.92E+03	3.12E+06	6.78E+06	2.36E+05	9.84E+06
PU 238	1.02E+12	1.20E+11	5.77E+07	2.32E+10	6.03E+10	1.74E+09	7.25E+10
U 234	9.32E+07	6.25E+07	3.08E+04	1.21E+07	2.08E+07	9.07E+05	3.81E+07
TH 230	3.06E+06	1.49E+03	2.09E+00	6.11E+02	3.28E+05	5.40E+01	2.25E+03
RA 226	5.25E+03	1.92E+00	3.55E-03	7.84E-01	6.56E+02	8.03E-02	3.36E+00
CM 247	4.84E+03	2.72E+01	3.23E-03	1.36E+01	1.62E+04	1.44E-01	1.44E+01
AM 243	8.47E+11	4.11E+08	4.29E+05	3.85E+06	1.93E+11	1.28E+07	5.33E+08
PU 239	1.16E+11	1.50E+10	7.29E+06	2.88E+09	5.11E+09	2.18E+08	9.07E+09
U 235	1.57E+06	1.09E+06	5.29E+02	2.08E+05	3.39E+05	1.58E+04	6.55E+05
PA 231	8.21E+05	4.00E+02	4.37E-01	1.64E+02	1.18E+05	1.27E+01	5.29E+02

TABLE II: RADIONUCLIDE INVENTORY [Bq/CONTAINER]

NUCLID	IONEN WISSEL K 52-1 (14500)	IONEN WISSEL K 52-2 (1100)	IONEN+CONCEN K 52-3 (1500)	VAST.MET.ANOR AS K 52-4 (2000)	K 52-5 (160)
C- 14	1.130E+05	5.590E+06	1.320E+05	2.200E+04	5.660E+05
CO- 60	1.130E+09	5.590E+10	1.320E+09	2.200E+08	5.660E+09
NI- 59	4.510E+06	2.230E+08	5.290E+06	8.810E+05	2.280E+07
NI- 63	4.510E+08	2.230E+10	5.290E+08	8.810E+07	2.280E+09
SE- 79	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
RB- 87	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
SR- 90	8.440E+05	1.340E+08	1.320E+06	3.660E+05	2.410E+07
ZR- 93	1.160E+02	6.140E+03	1.380E+02	2.350E+01	6.660E+02
MO- 93	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
NB- 94	5.070E+02	8.100E+04	7.990E+02	2.210E+02	1.450E+04
TC- 99	1.040E+05	5.290E+06	1.210E+05	2.050E+04	5.590E+05
PD-107	1.680E-01	2.690E+01	2.640E-01	7.330E-02	4.850E+00
SN-126	8.440E+01	1.340E+04	1.320E+02	3.660E+01	2.410E+03
J-129	5.030E+01	8.100E+03	7.920E+01	2.200E+01	1.450E+03
CS-135	5.020E+02	8.100E+04	7.920E+02	2.200E+02	1.450E+04
CS-137	1.690E+08	2.690E+10	2.650E+08	7.330E+07	4.850E+09
SM-147	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
SM-151	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
EU-154	1.350E+08	2.150E+10	2.120E+08	5.850E+07	3.850E+09
CM-248	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-244	4.810E-08	7.700E-06	7.220E-08	2.440E-08	1.610E-06
CM-244	9.620E+02	1.540E+05	1.440E+03	4.880E+02	3.220E+04
PU-240	3.850E+01	6.140E+03	5.770E+01	1.950E+01	1.290E+03
U-236	3.850E-02	6.140E+00	5.770E-02	1.950E-02	1.290E+00
TH-232	9.620E-12	1.540E-09	1.440E-11	4.880E-12	3.220E-10
U-232	5.770E-03	9.210E-01	8.660E-03	2.930E-03	1.930E-01
CM-245	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-241	3.850E+04	6.140E+06	5.770E+04	1.950E+04	1.290E+06
AM-241	1.920E+02	3.070E+04	2.890E+02	9.770E+01	6.440E+03
NP-237	6.730E-02	1.080E+01	1.010E-01	3.420E-02	2.250E+00
U-233	3.850E-06	6.140E-04	5.770E-06	1.950E-06	1.290E-04
TH-229	7.700E-08	1.230E-05	1.150E-07	3.920E-08	2.580E-06
CM-246	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-242	1.920E-01	3.070E+01	2.890E-01	9.770E-02	6.440E+00
AM-242	3.850E+00	6.140E+02	5.770E+00	1.950E+00	1.290E+02
U-238	4.810E-02	7.700E+00	7.220E-02	2.440E-02	1.610E+00
PU-238	2.890E+02	4.630E+04	4.330E+02	1.470E+02	9.660E+03
U-234	7.700E-03	1.230E+00	1.150E-02	3.920E-03	2.580E-01
TH-230	9.620E-06	1.540E-03	1.440E-05	4.880E-06	3.220E-04
RA-226	9.620E-11	1.540E-08	1.440E-10	4.880E-11	3.220E-09
CM-247	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
AM-243	1.920E+01	3.070E+03	2.890E+01	9.770E+00	6.440E+02
PU-239	9.620E+00	1.540E+03	1.440E+01	4.880E+00	3.220E+02
U-235	8.660E-04	1.380E-01	1.300E-03	4.400E-04	2.900E-02
PA-231	3.850E-07	6.140E-05	5.770E-07	1.950E-07	1.290E-05

NUCLID	EL.KAST BWR K 52-6 (855)	INC.INSTRU K 52-7 (193)	ACT.STAALD. K 42-1 (22)	OND.KERNROOS. K 42-2 (4)	REGELSTAVEN K 42-3 (2)
C- 14	2.720E+09	2.280E+08	1.490E+03	5.810E+05	3.110E+05
CO- 60	1.320E+12	1.490E+12	7.570E+10	1.080E+14	5.810E+13
NI- 59	9.840E+07	1.720E+09	2.430E+08	1.960E+11	2.030E+11
NI- 63	1.640E+10	2.070E+11	2.840E+10	2.500E+13	2.700E+13
SE- 79	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
RB- 87	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
SR- 90	3.700E+07	3.700E+06	2.840E+06	3.200E+05	8.940E+05
ZR- 93	2.110E+09	.000E+00	.000E+00	.000E+00	.000E+00
MO- 93	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
NB- 94	.000E+00	.000E+00	2.290E+06	8.780E+08	5.000E+08
TC- 99	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PD-107	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
SN-126	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
J-129	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CS-135	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CS-137	7.400E+07	9.250E+06	2.840E+07	3.200E+06	8.940E+06
SM-147	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
SM-151	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
EU-154	5.550E+07	7.400E+06	.000E+00	.000E+00	.000E+00
CM-248	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-244	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CM-244	1.300E+07	1.480E+06	1.770E+06	2.000E+05	5.590E+05
PU-240	5.550E+05	5.550E+04	2.360E+05	2.660E+04	7.460E+04
U-236	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
TH-232	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
U-232	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CM-245	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-241	5.550E+08	5.550E+07	4.240E+07	4.790E+06	1.340E+07
AM-241	5.550E+06	5.550E+05	4.240E+05	4.790E+04	1.340E+05
NP-237	9.250E+02	9.250E+01	1.770E+02	2.000E+01	5.590E+01
U-233	7.400E-02	9.250E-03	.000E+00	.000E+00	.000E+00
TH-229	1.110E-03	1.480E-04	.000E+00	.000E+00	.000E+00
CM-246	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-242	.000E+00	.000E+00	7.080E+03	7.990E+02	2.240E+03
AM-242	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
U-238	7.400E-02	9.250E+01	.000E+00	.000E+00	.000E+00
PU-238	5.550E+06	6.660E+05	4.240E+05	4.790E+04	1.340E+05
U-234	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
TH-230	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
RA-226	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CM-247	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
AM-243	3.700E+05	3.700E+04	3.310E+03	3.730E+02	1.050E+03
PU-239	1.300E+05	1.300E+04	1.770E+05	2.000E+04	5.590E+04
U-235	.000E+00	6.850E+01	.000E+00	.000E+00	.000E+00
PA-231	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00

TABLE II (continued)

NUCLID	POMPEN K 42-4 (2)	KERNMANTEL K 42-5 (28)	BOV.KERNROOS K 42-6 (32)	BOV.KERNRO.RI K 42-7 (4)	SPR.NOODK.SYS K 42-8 (6)	KERNDEKSEL K 42-9 (4)	ZWAKACT.MET K42-10 (70)	BIOL.SCH+WAP K42-11 (84)	MID.ACT.STAAL K42-12 (72)	LAAGACT.STAAL K42-13 (656)
C- 14	4.320E+04	2.970E+05	3.710E+05	4.590E+05	4.730E+05	4.590E+05	.000E+00	8.140E+06	.000E+00	.000E+00
CO- 60	7.830E+12	5.670E+13	6.640E+13	4.590E+13	8.440E+13	8.100E+13	2.700E+09	1.230E+10	1.760E+10	5.400E+07
NI- 59	2.840E+10	2.030E+11	1.130E+11	1.760E+11	1.490E+11	3.110E+11	9.990E+05	3.690E+05	.000E+00	.000E+00
NI- 63	3.780E+12	2.700E+13	1.520E+13	2.290E+13	2.030E+13	4.050E+13	1.040E+08	4.610E+07	.000E+00	.000E+00
SE- 79	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
RB- 87	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
SR- 90	1.280E+06	4.220E+05	6.440E+04	5.750E+05	1.280E+05	1.030E+06	7.570E+05	4.780E-12	1.760E+07	5.540E+04
ZR- 93	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
MO- 93	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
NB- 94	5.130E+07	2.030E+08	4.380E+08	2.840E+08	5.400E+08	4.590E+08	1.890E+05	1.790E+05	1.760E+05	5.540E+02
TC- 99	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PD-107	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	1.470E-12	.000E+00	.000E+00
SN-126	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
J-129	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CS-135	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CS-137	1.280E+07	4.220E+06	6.440E+05	5.750E+06	1.280E+06	1.030E+07	7.570E+06	2.200E-12	1.760E+08	5.540E+05
SM-147	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
SM-151	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
EU-154	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	5.690E+07	.000E+00	.000E+00
CM-248	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-244	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	6.390E+05	4.730E+05	.000E+00	.000E+00	.000E+00
CM-244	7.980E+05	2.640E+05	4.020E+04	3.590E+05	7.980E+04	.000E+00	.000E+00	.000E+00	1.060E+07	3.380E+04
PU-240	1.060E+05	3.520E+04	5.370E+03	4.790E+04	1.060E+04	8.520E+04	6.350E+03	.000E+00	1.490E+06	4.460E+03
U-236	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
TH-232	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
U-232	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CM-245	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-241	1.910E+07	6.320E+06	9.620E+05	8.610E+06	1.910E+06	1.540E+07	1.110E+07	.000E+00	2.560E+08	7.830E+05
AM-241	1.910E+05	6.320E+04	9.620E+03	8.610E+04	1.910E+04	1.540E+05	1.110E+05	.000E+00	2.560E+06	7.830E+03
NP-237	7.980E+01	2.640E+01	4.020E+00	3.590E+01	7.960E+00	6.390E+01	4.730E+01	.000E+00	1.060E+03	3.380E+00
U-233	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
TH-229	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CM-246	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-242	3.190E+03	1.050E+03	1.610E+02	1.430E+03	3.190E+02	2.550E+03	1.890E+02	.000E+00	4.190E+03	1.340E+01
AM-242	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
U-238	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-238	1.910E+05	6.320E+04	9.620E+03	8.610E+04	1.910E+04	1.540E+05	1.110E+05	.000E+00	2.560E+06	7.830E+03
U-234	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
TH-230	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
RA-226	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CM-247	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
AM-243	1.490E+03	4.910E+02	7.510E+01	6.720E+02	1.490E+02	1.190E+03	6.840E+02	.000E+00	2.030E+04	6.220E+01
PU-239	7.980E+04	2.640E+04	4.020E+03	3.590E+04	7.960E+03	6.390E+04	4.730E+04	.000E+00	1.060E+06	3.380E+03
U-235	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PA-231	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00

TABLE II (continued)

NUCLID	LAAGACT.GEM. K42-14 (88)	LAAGACT.SECAF K42-15 (14)	CONCENTR. K42-16 (204)	DIV.B+G L 52-1 (14000)	ALFA.EX RA L 52-3 (5600)	ALFA.EX RA.INC L 52-4 (3150)	RA AFVAL L 52-5 (1050)	A.B.G STR. L 52-6 (7700)	A.B.G+RA L 52-7 (700)
C- 14	.000E+00	.000E+00	.000E+00	6.480E+08	.000E+00	.000E+00	.000E+00	3.670E+06	.000E+00
CO- 60	1.760E+09	1.760E+09	6.180E+10	3.740E+09	.000E+00	.000E+00	.000E+00	4.480E+08	1.350E+10
NI- 59	.000E+00	.000E+00	.000E+00	6.480E+05	.000E+00	.000E+00	.000E+00	8.100E+04	.000E+00
NI- 63	.000E+00	.C00E+00	.000E+00	8.660E+07	.000E+00	.000E+00	.000E+00	1.080E+07	.000E+00
SE- 79	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
RB- 87	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
SR- 90	1.760E+06	1.760E+06	6.180E+07	5.960E+07	.000E+00	.000E+00	.000E+00	1.240E+10	.000E+00
ZR- 93	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
MO- 93	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
NB- 94	1.760E+04	1.760E+04	6.180E+05	5.180E+01	.000E+00	.000E+00	.000E+00	6.480E+00	.000E+00
TC- 99	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	1.510E+06	.000E+00
PD-107	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
SN-126	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
J-129	.000E+00	.000E+00	.000E+00	6.480E+01	.000E+00	.000E+00	.000E+00	3.570E+03	.000E+00
CS-135	.000E+00	.000E+00	.000E+00	1.730E+04	.000E+00	.000E+00	.000E+00	5.030E+04	5.400E+03
CS-137	1.760E+07	1.760E+07	6.180E+08	4.730E+09	.000E+00	.000E+00	.000E+00	1.240E+10	1.350E+09
SM-147	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
SM-151	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
EU-154	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CM-248	.000E+00	.D00E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-244	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CM-244	1.030E+06	1.030E+06	3.630E+07	.000E+00	5.960E+05	.000E+00	.000E+00	8.660E+06	.000E+00
PU-240	1.350E+05	1.350E+05	4.840E+06	.000E+00	2.110E+07	.000E+00	.000E+00	1.460E+07	.000E+00
U-236	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
TH-232	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
U-232	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CM-245	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-241	2.430E+07	2.430E+07	8.590E+08	.000E+00	1.080E+09	.000E+00	.000E+00	7.550E+08	.000E+00
AM-241	2.430E+05	2.430E+05	8.590E+06	.000E+00	6.480E+06	5.400E+09	.000E+00	4.660E+06	1.620E+09
NP-237	1.030E+02	1.030E+02	3.630E+03	.000E+00	2.700E+03	9.180E+02	.000E+00	1.890E+03	2.700E+02
U-233	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
TH-229	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
CM-246	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
PU-242	4.190E+02	4.190E+02	1.480E+04	.000E+00	5.400E+03	.000E+00	.000E+00	5.960E+03	.000E+00
AM-242	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
U-238	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	1.890E+03	.000E+00
PU-238	2.430E+05	2.430E+05	8.590E+06	.000E+00	4.480E+07	.000E+00	.000E+00	2.540E+08	.000E+00
U-234	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
TH-230	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
RA-226	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	2.160E+09	.000E+00	2.220E+08
CM-247	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00
AM-243	1.890E+03	1.890E+03	6.720E+04	.000E+00	1.840E+04	.000E+00	.000E+00	1.020E+05	.000E+00
PU-239	1.030E+05	1.030E+05	3.630E+06	.000E+00	4.480E+07	.000E+00	.000E+00	3.190E+07	.000E+00
U-235	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	1.240E+02	.000E+00
PA-231	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00	.000E+00

TABLE II (continued)

Assessment of radiological consequences and risk associated with the geological disposal of MLW and alpha-waste in clay formations (PACOMA project)

Contractor : SCK/CEN, Mol, Belgium
Contract No. : FI1W/0046-B
Duration of contract : March 1987 - December 1988
Period covered : March 1987 - December 1987
Project leader : A. Bonne

A. OBJECTIVES AND SCOPE

The aim of the PACOMA project is to carry out, as an extension of the PAGIS action on HLW, a comprehensive assessment of the radiological consequences and risks associated with geological disposal of alpha-bearing and medium level wastes.

The main objectives of the study are :

- best estimates of the dose rates and risks to individuals and populations for the normal and for the relevant altered scenarios ;
- sensitivity studies of the results to variations of data bases, parameters and models ;
- analysis of the uncertainties.

B. MODEL PROGRAMME

B.1. Data collection.
B.2. Adaptations of the computer codes.
B.3. Best estimate calculations.
B.4. Sensitivity study.
B.5. Uncertainty analysis.
B.6. Final assessment.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Radionuclide inventories were collected for the different waste forms which have to be considered for the PACOMA calculations.

Sensitivity studies with respect to modelling assumptions were carried out to evaluate which submodels of the repository system model need to be adapted. Some new computer codes are prepared.

PROGRESS AND RESULTS

The following waste types are proposed to be considered for the PACOMA calculations :

- reactor operation waste (sludges, concentrates, filters, ion exchange resins) ;
- reprocessing waste (hulls, scraps, sludges, ion exchange resins, iodine, technological waste) ;
- MOX fuel fabrication waste (sludges, ashes, technological waste).

The information available on the radionuclide inventories of these waste forms has been collected but an important problem which remains is the unsufficient knowledge on the content in the waste forms of those radionuclides which determine the long-term safety of the disposal practise.

As far as possible the repository system models developed for the PAGIS calculations, will be used for PACOMA. However in the case of MLW, the radionuclide fluxes into the aquifer may be more sensitive to the near-field phenomena, because of the relatively poor quality of the conditioning materials (concrete, cement) used for MLW compared to the glass matrix used for HLW and because of the presence in such wastes types of some poorly retarded radionuclides such as H-3, C-14 and I-129 at a significant level of concentration. Sensitivity studies with respect to modelling assumptions are performed to evaluate which adaptations to the computer codes are necessary. The near field and far field codes are adapted accordingly.

A new regional biosphere model is developed which allows to evaluate the radiological consequences resulting from river pathways and from eventual areas where the contaminated ground water may reach the root zone of vegetables or pasture.

Assimilation of Experimental Data for Validation of Near-field Computer Models of Underground Radioactive Waste Repositories (PACOMA Project)

Contractor : Electrowatt Engineering Services (UK) Ltd, UK
Contract No. : FI1W/0047-UK
Duration of contract: October 1986 - July 1987
Period covered : October 1986 - July 1987
Project leaders : Z.A. Gralewski, J-M Laurens

A. Objectives and Scope

The overall objectives of the UK contribution to the CEC PACOMA project are to develop and demonstrate procedures for the radiological safety assessment of a deep repository for intermediate level radioactive waste in clay. To demonstrate these procedures the safety of a hypothetical repository at Harwell is being assessed.

Electrowatt Engineering Services (UK) Ltd is one of four research organisations undertaking studies in support of the UK contribution outlined above. The specific objectives of their component of the project related to the verification and validation of the near-field computer code VERMIN and the undertaking of 'source term' modelling using the code.

B. Work Programme

Phase I

a) To ensure that VERMIN provides a suitable 'source-term' for the AERE geosphere transport models.

b) To obtain data appropriate to the validation of computer codes modelling the near-field region and thus suggest standard test cases for such codes.

c) To demonstrate the use of such test cases by validation of certain aspects of the VERMIN code and to update VERMIN as required.

d) To identify whether further experimental work is needed in order to validate aspects of VERMIN for which no applicable data exist.

Phase II

e) To carry out the near-field modelling in the UK contribution to the PACOMA project using the VERMIN code.

C. Progress of Work and Obtained Results

State of advancement

Both Phase I and II of the work programme were completed in the period. It was confirmed that VERMIN could provide a suitable 'source-term' for the AERE codes. Near-field modelling studies were undertaken for three different radionuclide inventories and for different groundwater velocities. Output files were transmitted to AERE on magnetic tape to be used as a point source term in the two-dimensional NAMSOL geosphere model.

A substantial number of experiments were identified relevant to the validation of VERMIN and a methodology for verification and validation was developed. Computer simulations identified the limited applicability of some of the experimental studies in respect of validation of near-field models and new experimental studies, designed specifically for this purpose, have been proposed.

Progress and Results

The processes modelled in VERMIN were classified into those not requiring validation (advective flow and radioactive decay); those for which validation would not be relevant (sorption, corrosion and solubility); and those requiring validation (leaching, diffusion and interactions of individual processes). In addition, a review of available data and of the model structure identified some processes which are not currently included in the model, but which may need to be taken into account (radionuclide binding to, and transport by, colloids; variation in Eh and its effects; and gas generation).

A total of 39 experiments relevant to the validation process were identified. Data relating to these experiments was collated and used in validation studies. Results from these studies are summarised below.

a) Leaching: Reasonable agreement with experimental studies was obtained, but it was noted that leaching experiments of short duration may give an inappropriate estimate of leach rate.

b) Diffusion: It was found that considerable confusion can arise from the large diversity of terminology used. Because of the small spatial and temporal scale of the experimental studies an accurate representation of the data was difficult to achieve. Nevertheless, the results obtained were sufficiently good to consider the model to be validated.

c) Advection/sorption transport model: Because the experiments considered were designed for other purposes, it was not possible to configure VERMIN in such a way as to achieve an exact representation of the modelled systems. For this reason, comparisons between the experimental data and the model results required a significant amount of interpretation.

In view of the limitations of the available experimental data, a range of new experiments were suggested. These included out-diffusion, through diffusion, combined out and through diffusion and advection experiments. In addition, an experimental protocol designed to investigate interactions between leaching, diffusion, advection and retardation was proposed. This experimental protocol was described in detail, so as to demonstrate that it could be readily implemented in a conventional radiochemical laboratory.

The near-field modelling studies were undertaken and the results made available to AERE. This was a straight-forward exercise and no particular problems were encountered.

Publications

Laurens, J-M. - Electrowatt Eng. Services Ltd. (UK) "Validation of the vault computer model VERMIN for the post-closure behaviour of repositories in geological formations"
- Final report of contract FI1W/0047-UK - EUR 11375 EN.

Laurens, J-M. and Thorne, M.C.
"The demonstration of a proposed methodology for the verification and validation of near-field models". OECD/NEA Workshop on Near-field Assessment of Repositories for Low and Medium Level Waste, Baden, Switzerland, 23-25 November 1987.

5.3. Support studies

DEFINITION OF STANDARDS OF QUALITY ASSURANCE RELATED TO THE DEVELOPMENT OF DISPOSAL FACILITIES FOR RADIOACTIVE WASTE

Contractor :	Cedar Design Systems Ltd., London, U.K.
Contract No. :	CEC - FI1W/0039 - UK (H1)
	DoE (UK) PECD 7/9/384
	UKAEA - H2C 618390 T
Duration of contract :	January 1987 - March 1989
Period covered :	January 1987 - December 1987
Project leader :	I.E. HILL

A. Objectives and Scope

The research project will produce a definition of an acceptable and appropriate set of procedures for quality assurance, verification, and validation. These procedures would form the basis for establishing uniform standards for risk assessment software, which could be implemented throughout the European radioactive waste disposal programme.

The value and effectiveness of the procedures will be demonstrated by their practical implementation as part of the work of other contractors on the CEC PACOMA projects. Included in this practical implementation will be the introduction of software tools for automating quality assurance procedures, where such tools are available or can be developed.

The work will be subdivided into 4 stages covering respectively, analysis of existing procedures and definition of requirements; a case study of the use of existing procedures in the UK Department of the Environment; definition of procedures; and implementation of procedures.

In order to ensure that the work done is appropriate to the development of risk assessment codes, reference will be made to the other contractors for the CEC PACOMA project.

B. Work Programme

B.1. Review of existing software quality assurance standards and definition of requirements

B.2. Case study of existing UK DoE procedures

B.3. Definition of procedures

B.4. Implementation of procedures

C. Progress of work and obtained results

State of advancement

Work on this project started in January 1987. Tasks 1 and 2 are substantially complete, and significant progress has been made with tasks 3 and 4. Difficulties in arranging mutally convenient dates for interviews led to task 1 falling behind schedule, but all the intended interviews have now been conducted. A definition of requirements has been prepared based on these interviews.

A case study of UK DoE procedures (task 2) has been carried out as part of the review and acceptance procedures for the new probabilistic risk assessement code being developed for the DoE.

A draft version of the procedures to be recommended has been prepared, and will be completed early in 1988. This is about 3 months late as a result of the delay in task 1.

Work on task 4 was started early to compensate for the delay in task 1. The feasibility of the procedures included in the recommendations has been tested by at outline level by the NRPB. Software engineering tools for production of specification and design documentation, and for software configuration management have been evaluated.

Progress and results

1. REVIEW OF EXISTING SOFTWARE QUALITY ASSURANCE STANDARDS

Interviews have been conducted with a total of seven organisations that are involved in producing software for repository safety assessments. Difficulties in arranging mutually convenient dates led to Task 1 falling behind schedule.

These interviews have been used to identify the requirements for software quality assurance, and for verification and validation procedures within groups reponsible for safety assessment codes. It is apparent from these interviews that the formal quality assurance procedures recommended in various Standards documents will not be readily introduced into these organisations. The need for some level of quality assurance is recognised, but there is a general feeling that formal development procedures will be inappropriate. The need therefore is to identify procedures that allow freedom for experimentation, but that also provide a measure of control over the code used for assessments.

The most important general requirements are:

- The overwhelming requirement was that quality assurance procedures should not slow down the software development process significantly;
- Documentation, particularly at the program structure level is a general problem. The time scales for waste disposal are sufficiently long (up to 20 years) for considerable changes in personnel to occur - this greatly increases the need for documented code and for documented quality assurance procedures. Aids for production of documentation were identified as important;

- Some organisations are interested in introducing quality assurance procedures as a way of ensuring code is more accessible to all members the group, and to remove the personal possessiveness associated with individuals code. This was not a general requirement of all groups;
- Related to the above is a need for a way of making general purpose subroutines more widely available within the group;
- There is a need for guidance on the extent to which verification and validation of a program transfer when the program is used on other computers, and by other groups;
- Any pressure that exists for quality assurance procedures comes from outside; the groups responsible for safety assessments are self-regulating;
- Most groups have standards (of varying degrees of formality) at the level of programming practice, but design or specification standards are not used. (There seems to be a need for confirmation that the coding standards used are appropriate);
- The need for configuration management procedures is generally recognised, but most groups only have procedures for control of the executable code for versions of the programs used for assessment purposes.

Detailed records of these interviews have been produced, but for reasons of confidentiality will be kept as internal documents.

2. UK DOE CASE STUDY

The case study of existing UK DoE procedures has taken the form of participation in the review stages of the VANDAL development project, as well reviews of programming level documents produced by various contractors for the full DoE risk assessment programme. A description of this work will not be reported separately, but will be included in the final project report.

3. DEFINITION OF PROCEDURES

Work has started on definition of a full set of procedures for controlling the development, verification and use of software for repository risk assessments. This will be completed early in 1988.

4. IMPLEMENTATION

As a test of the feasibility of the procedures to be included in the recommendations, an outline of the procedures was discussed with the NRPB. They have introduced a version of the procedures for use on a single project, with only the minimum of input from us. This exercise has provided useful feedback to us on the sorts of procedures that can be introduced without making radical changes in existing working practices. Further follow-up is needed to see how durable the procedures have proved.

Part of the work specified for this stage of the project was an evaluation of software tools that would aid in introducing software quality assurance. A report on design and analysis aids has been produced [1], and a second report on aids for configuration management will be ready early in the 1988 .

[1] A preliminary review of Analysis and Design tools as aids to improving software quality. I. E. Hill June 1987

MODELLING THE LONG TERM EVOLUTION OF GEOLOGICAL RADWASTE DISPOSAL FACILITIES

Contractor: Dames & Moore, Twickenham, United Kingdom

Contract No.: FI1W/0169-UK

Duration of contract: November 1987 - February 1989

Period covered : November - December 1987

Project leader : C.J.C. FRIZELLE

A. OBJECTIVES AND SCOPE

The primary objective of the study is to allow more realisitic modelling of the effects of ice sheet advances and retreats on deep underground disposal facilities for radioactive wastes and their environments to be undertaken, by advancing the status of fundamental research in this area. In Northern Europe glacial conditions are expected to return within the next 20,000 to 30,000 years and cycles of ice sheet advance and retreat to continue for the next million years at least. The influences on disposal sites could be significant. It is expected that algorithms will be developed from the work which, if used in a suitable computer code, will allow realistic modelling of ice sheet erosion and deposition and the effects of ice sheet advance/retreat cycles (including the associated ground freezing/thawing) on groundwater flow.

The project is being carried out in collaboration with researchers at the Grant Institute of Geology, University of Edinburgh, United Kingdom.

B. WORK PROGRAMME

2.1 Research status review: a brief review of the status of research into the effects of long-term environmental changes on deep disposal facilities.

2.2 This second task is the major aspect of the work programme and incorporates research into three aspects of glacial processes as well as development of algorithms, as detailed below.

2.2.1 Investigation of approaches to modelling erosion during ice sheet advances and the consequent alteration of topography in the area surrounding a disposal site.

2.2.2 Investigation of approaches to modelling sediment deposition by ice sheets and the dispersion patterns of eroded materials, which could include contaminated geosphere or waste.

2.2.3 Investigation into the combined processes of permafrost development/degradation and ice sheet advance/retreat on groundwater flow systems, together with approaches to modelling such processes.

2.2.4 Specification for further research requirements arising from the project and of outline approaches to addressing these requirements.

2.3 Specification for the incorporation of site evolution modelling into performance assessment of geological disposal of radioactive wastes, with reference to three suitable sites in Europe.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Work carried out to date has focussed on the research status review (item 2.1 above) and investigation into permafrost development (under item 2.2 above).

Progress and results

2.1 Research status review.

A number of organisations investigating the influence of long term environmental change on geological disposal sites have been contacted, with a view to obtaining information on the progress of their studies. This has included workers in Canada, United States, Japan, Finland, Sweden, France, Italy, Belgium, West Germany and the United Kingdom. Useful information has been obtained (although some responses are still awaited) and has supplemented the library of material already available to us. Preparation of a report on the results of this review has begun.

2.2 Permafrost development.

Within a tundra climate state (which is expected to form a major component of the climatic conditions over the next million years), very cold temperatures persist and result in the development of partial or total permanently frozen ground: permafrost. Partial, or discontinuous, permafrost occurs in the earlier or later stages of the tundra climate; total, or continuous, permafrost represents the full development of this climate type. Above the permafrost layer an active layer up to two metres thick exists which thaws in summer and re-freezes in winter. The permafrost layer itself can extend to depths of over 500m.

Theoretical models of permafrost development have largely been developed and used by engineers in cold climate countries in order to estimate the depth of permafrost under various local climatic, geological and vegetation conditions. These can be used to evaluate the effects of construction on the permafrost layer to ensure that no deleterious effects result. An initial review of the literature has indicated that a more fundamental approach is required.

The ground (geosphere) may be considered to be a mixture of rock and water in its normal state. As permafrost develops, part of the ground will consist of a mixture of rock and ice, as shown on Figure 1, a. The ice/rock and water/rock components of the cross-section indicated are separated by a surface, S. It is freezing and melting on this surface, in response to various conditions, that is of interest. A thermo-mechanical description of the permafrost layer, the unfrozen layer and the freezing/melting surface with respect to time has been developed. Continued climatic cooling will result in the development of ice sheets in Europe, which will advance over the permafrost area (Figure 1, b). The combined effect of the ice load and its insulation properties will result in melting of the permafrost layer (Figure 1, c). The ultimate aim of this aspect of the research is to evaulate the influence of this sequence of events on the groundwater flow system. The mathematical framework used is the Continuum Theory of Mixtures.

An initial two-dimensional mathematical description of the problem has been constructed, from which a one-dimensional representation was derived. This latter representation will first be examined in detail, using numerical algorithms to provide a solution. It will then be possible to return more easily to the two-dimensional problem, which will require a more complex numerical approach.

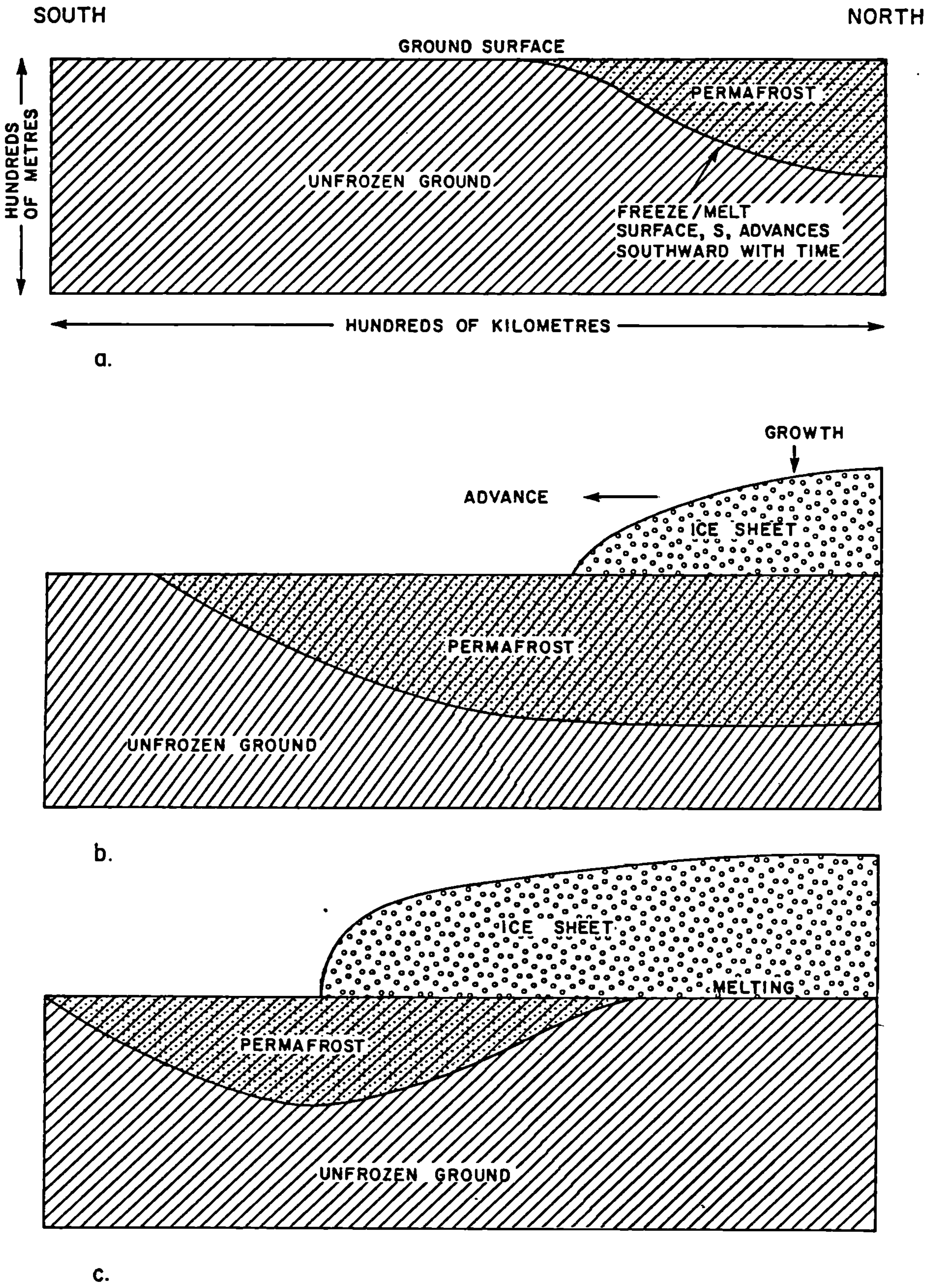


FIGURE I SCHEMATIC ILLUSTRATION OF PERMAFROST DEVELOPMENT.

HUMAN INTRUSION INTO UNDERGROUND REPOSITORIES FOR RADIOACTIVE WASTE

Contractor:	Associated Nuclear Services, UK
Contract No.:	FI1W/0170-UK
Duration of contract:	October 1987 to September 1988
Period covered:	October 1987 to December 1987
Project Leader:	T.J. Sumerling

A. OBJECTIVES AND SCOPE

The objectives of the work are;

- to establish a methodology for the assessment of risks associated with human intrusion events applicable to the types of underground repository studied in the PAGIS and PACOMA projects;

- to delineate the application of the methodology to the alternative disposal concepts, taking into account the characteristics of the host rocks (clay, granite, salt and sub-seabed sediments) and repository designs;

- to produce an authorative source of reference (database and methodology) for use in safety assessment of HLW and ILW disposal facilities.

B. WORK PROGRAMME

1. The various human activities which might result in an intrusion into a repository, or disruption of the host geology leading to enhanced radionuclide migration, will be identified. Relevant information necessary to define and quantify each mode will be collated.

2. The radiological consequences, to potential intruders and to others, from defined intrusion modes will be reviewed and appropriate calculation schemes defined.

3. The probabilities of intrusive events, identified as significant, will be estimated for reference circumstances. Factors affecting these probabilities will be identified and quantified as far as possible.

4. From the analysis made above, a general philosophy for assessment of risk from human intrusions will be developed. The application of the methodology will be outlined for the particular host geologies and repositories considered in PAGIS and PACOMA, with the aid of examples.

5. The capacity for reduction of risks from intrusion by measures to reduce the probability or consequences of intrusion will be examined. This will include an examination of possible anti-intrusion measures.

C. PROGRESS OF WORK AND OBTAINED RESULTS

SUMMARY

A preliminary review has been made of previous assessments of human intrusion events affecting deep underground repositories. Eight major divisions of human intrusion activity have been identified. This initial work forms a basis for the definition of specific information requirements which will be discussed with experts in appropriate fields.

PROGRESS AND RESULTS

1,2 Preliminary review

Information is being collated concerning previous assessments of human intrusion in deep underground repository safety studies. To date this covers the following major projects:
- the CEC PAGIS project, covering disposal of vitrified HLW in clay, granite and salt formations in the EC and disposal in sub-seabed sediments in the North Atlantic;
- Project Gewähr, covering disposal of HLW in granite in Switzerland;
- the Basalt Waste Isolation Project, covering disposal of HLW in basalt formations in the USA;
- the Salt Repository Project, covering disposal of HLW and expended fuel in salt formations in the USA.

An ANS Technical Note has been prepared for submission to the CEC and the UK DoE. This includes a discussion and statement of basis for the work and a preliminary review of previous assessments of human intrusion made in the above projects. Eight major divisions of human intrusive activity have been identified as listed below.

Intrusion mode	Relevant to: Crystalline rocks	Clays	Salt	Sub-seabed
Deep drilling (exploration)	✓	✓	✓	✓
Deep drilling (exploitation)	✓	✓	✓	✓
Water abstraction	✓	✓*		
Underground mining	✓		✓	
Sub-surface construction	✓	✓	✓	
Cavern leaching			✓	
Solution mining			✓	
Geothermal exploitation	✓			
Seabed mining, e.g. Mn nodules				✓

(* from adjacent aquifers)

General information requirements for improved assessment of human intrusion have been defined. The initial review forms a basis for the definition of specific information requirements which will be discussed with experts in appropriate fields e.g. deep ground investigation and mining.

CHAPTER 6

TASK No 6

Joint elaboration of radioactive waste management

CHAPTER 6

TASK No. 6 : JOINT ELABORATION OF RADIOACTIVE WASTE MANAGEMENT POLICIES

A. Objective

Joint elaboration of waste management and disposal criteria

Evaluation of possible approaches, at Community scale, for waste disposal.

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

These research topics were not included in the 1980-1984 programme.

C. 1985-1989 programme

The following activities are foreseen :

- Development and harmonization of acceptance criteria for radioactive waste conditioning with respect to their handling and final disposal

- Development of radiological criteria for disposal, especially for the periods of time involved in geological disposal

- Elaboration of recommendations concerning the satisfactory execution, taking into account the safety and environmental protection standards, of the various operations involved in the management and disposal of radioactive waste

- Study of "de minimis" criteria with regard to alpha/non-alpha and radioactive/non-radioactive waste

- Multi-national dimensions of waste management; influences on its optimization; regional disposal.

D. Implementation of the programme

A working group of national experts has been set up to deal with task 6 activities. Topics of first priority have been identified as items (b) and (d) of paragraph C above; a working plan is being prepared and will be presented to the competent Management and Co-ordination Advisory Committee in 1987.

PART B

CONSTRUCTION AND/OR OPERATION OF UNDERGROUND EXPERIMENTAL FACILITIES OPEN TO COMMUNITY JOINT ACTIVITES

CHAPTER 7

CONSTRUCTION AND/OR OPERATION OF UNDERGROUND EXPERIMENTAL FACILITIES

A. Objective

To confirm the technical options and the numerical values of the parameters to be taken into consideration for building industrial disposal facilities and to develop radioactive waste emplacement techniques.

B. Research performed under the 1980-1984 programme

The large-scale verification of the properties and behaviour of geological formations started thanks to the construction and the putting into service of experimental cavities or underground laboratories.
In this way, an experimental chamber was constructed at a depth of 225m in the plastic Boom clay formation beneath the Mol site in Belgium.

Some existing galleries in the Asse salt mine were adapted to receive full-scale tests, i.e. in-situ heating tests, stress and strain measurements and surveys of the quantities of fluids and gases released by the salt. In addition, a 300 m deep borehole between the -750m and -1050m levels was dry-drilled from one chamber of the mine and its stability was monitored over almost two years.

C. 1985-1989 programme

The specific projects involved in this part of the programme are open to Community co-operation by the responsible bodies in the Member States on whose territory the facilities will be built. They deal with experimental and pilot facilities without industrial utilization.

These facilities will reproduce at full scale and in real geological conditions the essential parts of a large and industrial underground disposal plan of the future.

These facilities will also make it possible to confirm on site the numerical values of the parameters to be taken into consideration for building industrial facilities and to develop radioactive waste emplacement techniques.

Radioactive waste or materials, which will be used in some projects for studying the operating conditions of an industrial facility, will be retrievable.

The co-operation includes, inter alia, participation of scientists of other Member States to the above-mentioned projects, especially by means of temporary secondment of personnel, and the possibility of completing the programmes with own specific activities, according to modalities to be specified on a case-by-case basis.

The control and the responsibility of the projects will be ensured by the hosting bodies.

In addition to the following three projects, other projects could be added in the course of the programme.

PROJECT No. 1 : PILOT UNDERGROUND FACILITY IN THE ASSE SALT MINE (FEDERAL REPUBLIC OF GERMANY)

PROJECT No. 2 : PILOT UNDERGROUND FACILITY IN THE ARGILLACEOUS LAYER UNDER THE MOL NUCLEAR SITE (BELGIUM)

PROJECT No. 3 : EXPERIMENTAL UNDERGROUND FACILITY IN FRANCE IN A GEOLOGICAL MEDIUM OF COMPLEMENTARY NATURE

D. Programme implementation

Contracts have been signed for projects no. 1 and 2.
The launch of project no. 3 has been delayed by the French authorities to a later date.

Available information dealing with projects no. 1 (so called HAW project) and no. 2 (so called HADES project) is given thereafter.

THE HAW PROJECT: DEMONSTRATION FACILITY FOR HIGH-LEVEL RADIOACTIVE WASTE DISPOSAL IN THE ASSE SALT MINE

Contractor: GSF-IfT, Braunschweig, Federal Republic of Germany
Contract No.: FI1W/0003/D
Duration of Contract: from January 1985 to December 1989
Period covered: January 1987 - December 1987
Project Leader: T. Rothfuchs

A. OBJECTIVES AND SCOPE

Since 1968 the GSF has been carrying out research and development programs for the final disposal of high-level radioactive waste (HAW) in salt formations. The heat producing waste has been simulated so far by means of electrical heaters and also cobalt-60-sources. In order to improve the final concept for HAW disposal in salt formations the complete technical system of an underground repository is to be tested in a one-to-one scale test facility.

To satisfy the test objectives thirty high radioactive canisters containing the radionuclides Cs-137 and Sr-90 will be emplaced in six boreholes located in two test galleries (Figure 1) at the 800 m-level in the Asse Salt Mine. The duration of testing will be approximately five years.

For the handling of the radioactive canisters and their emplacement into the boreholes a system consisting of transportation casks, transportation vehicle, disposal machine, and borehole slider will be developed and tested. The actual scientific investigation program is based on the estimation and observation of the interaction between the radioactive canisters and the rock salt. This program includes measurement of thermally and radiolytically induced water and gas release from the rock salt and the radiolytical decomposition of salt minerals. Also the thermally induced stress and deformation fields in the surrounding rock mass will be investigated carefully.

The project is funded by the BMFT and the CEC and carried out in close cooperation with the Netherlands Energy Research Foundation (ECN)

B. WORK PROGRAM

B.1. Elaboration of the test plan and the supporting documents for the licensing procedure.

B.2. Development and procurement of the technical components for handling and emplacement of the radioactive canisters.

B.3. Procurement and installation of the data collection system.

B.4. Mining of the test field, drilling of the boreholes, installation of the measuring equipment and preparation for the emplacement of the HAW canisters.

B.5. Test disposal including operation of electrical tests for comparison and assessment of the technical components.

B.6. In situ measurements of released water and gas from the salt, of thermally induced stress and deformation in the rock mass, and performance of seismic and ultrasonic measurements.

B.7. Accompanying and complementary laboratory investigations to ensure the transferability of the results to other sites.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The test disposal of HAW canisters in the Asse salt mine will be performed with a view to the planning, design and licensing procedure for a national repository in the FRG. In 1987 most emphasis has been given to the construction of the technical components and the installation of the geotechnical instrumentation in the underground test field. The present schedule of the project foresees the emplacement of the radioactive canisters in late 1988. Therefore, in situ results from the interaction between the HAW canisters and the rock salt are not available at this time.

Progress and results

1. Elaboration of the test plan

The test plan was prepared in 1984/1985 and the final version was issued in December 1985/1/. It contains a detailed description of the scope, issues, and objectives and also of the test program.

All the technical papers for the canister handling system, including the design calculations, were submitted to the responsible licensing authority (Bergamt Goslar) or its consultant (TÜV Hannover).

2. Development and procurement of the technical components

The design of the system (Figure 2) for handling and emplacement of the radioactive canisters was completed in 1985. The construction of the components proceeded very well in 1987.

The Asse internal transportation cask Asse TB1, which needs a type B(U) certification by the Physikalisch-Technische Bundesanstalt (PTB), has undergone the required fire test successfully in July 1987. Two casks are being fabricated and will be delivered in early 1988. The transportation vehicle was delivered in December 1987. Fabrication of the disposal machine and of the transfer station at the surface is in the final stage.

The test programs of both the canister guiding system (CGS) as well as the gap monitoring system (GMS) have been successfully completed. The systems have been approved by the licensing authorities and are now under construction. One of the two heaters which simulates the canisters during the prewarning heat-up and the operational phase of the HAW test field has been constructed and assembled. The other heater is under construction, together with the special equipment for the A1-hole.

3. Procurement and installation of the data collection system

The Data Collection System (DCS) hardware components have been assembled at ECN. A thorough test programme of the DCS is being executed. At short term the components will be transported to the Asse mine after which they will be installed in the HAW test field. The development of the application software for the heater control and the handling of the data in the HAW field has nearly been completed. A test programme is being performed.

4. Mining and preparation of the test field

The underground test field, consisting of two parallel galleries, each 60 m long, 10 m wide, and 8 m high, was completely mined in 1985. By the end of 1987 all measuring boreholes were drilled and nearly the complete measuring instrumentation was installed. The floor of the test field was paved, including cable channels running from the boreholes to the underground computer room. The cellars at top of the emplacement boreholes were prepared to receive the shielding borehole sliders. The complete power supply system, including two 175 kVA Diesel generators for emergency power supply, was installed.

5. Test Disposal

Due to delayed fabrication of the radioactive canisters and the time consuming final definition and specification of retrievability requirements and technical components the time schedule of the project is delayed. The emplacement of the radioactive canisters is now foreseen for November 1988.

6. In situ measurements

In the surroundings of the emplacement boreholes the temperature distribution, stresses, deformations, and the gas release from the heated and irradiated salt will be measured. The deformation measurements and some stress measurement were already started during excavation of the test galleries in 1985. Especially the stress redistribution and resulting deformation of the pillar between the galleries was observed. At the end of 1987, 2.5 years after excavation of the galleries, the vertical stress component in the pillar is about 20 MPa. The average horizontal strain rate in the pillar is quite constant with 6.3×10^{-6}/day (2.3×10^{-3}/year). This corresponds to an increase of the thickness of the pillar in the order of 23 mm/year.

In order to determine the gases liberated and generated during emplacement of the high-level waste containers, 48 boreholes with a diameter of 76 mm and a depth of 15 m were drilled in the test field. 34 of these boreholes were sealed gastight with a special packer and rinsed afterwards with pure nitrogen to obtain a definite gas concentration at the beginning. The following maximal concentrations have been found:

CO	up to	46 vpm
CO_2	up to	600 vpm
CH_4	up to	102 vpm
C_2H_6	up to	23 vpm
H_2S	up to	40 vpm
H_2O	up to	38 mg/l

It is planned to continue the gas sampling and analysis during the emplacement of the radioactive canisters.

7. Accompanying laboratory investigations

Salt samples from the test field have been analyzed within this program to determine the water and gas content as well as the mineralogical composition. The investigation of the predrilling of the emplacement boreholes showed that the average water content in the area between 0 and 8 m below the floor is about 0.15 wt %, whereas it is about 0.04 wt % in the area between 8 and 15 m. This correlates directly with the mineralogical composition. In the upper level and in the gallery the rock salt contains polyhalite in the range of 2 wt %, whereas in the lower level polyhalite is negligible while anhydrite is present in the range of 3 wt %. In the whole test field only traces of kieserite and sylvine have been found.

In order to determine the total gas content and the thermal liberation behaviour of the different gas components salt samples from the predrilling are investigated in the laboratory. This investigation indicates that significant amounts of gases are already liberated at room temperature. This investigation will be extended to elevated temperatures up to 200 °C.

The special instrumentation developed to obtain the salt pressure from borehole tube deformation is under construction. The acoustic measuring techniques to be used for crack detection are further tested. The acoustic measuring tubes with transmitters and receivers have been installed in the pillar, in the wall and in the floor. Preliminary measurements have been carried out.

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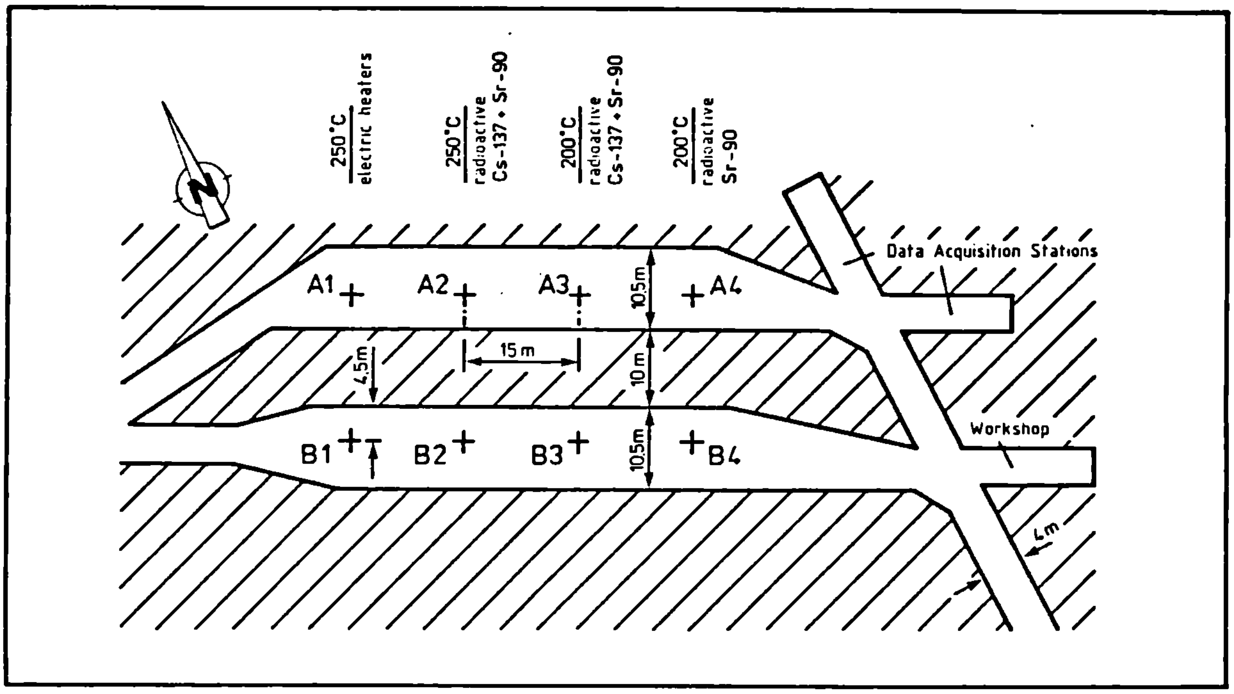

Figure 1: HAW Test Field at the Asse Salt Mine

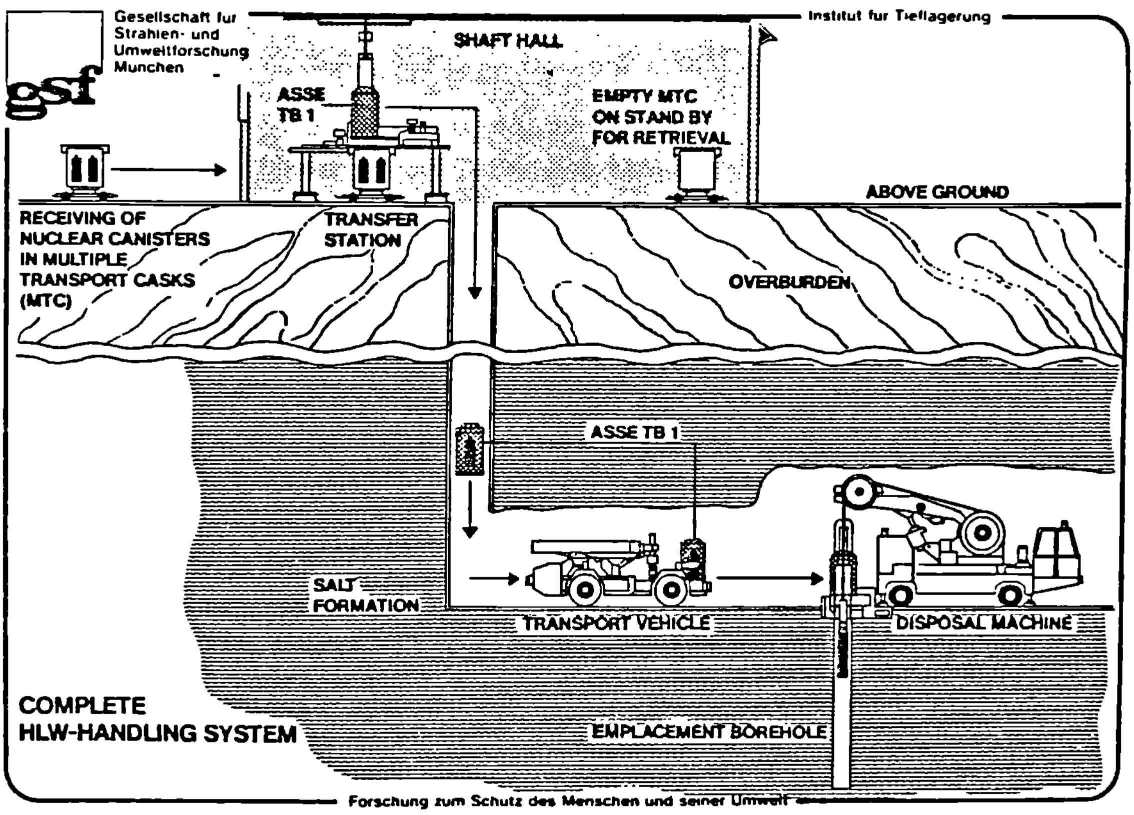

Fig. 2: HAW Handling System

The HADES Project : a pilot facility in the argillaceous layer beneath the nuclear site at Mol

Contractor : SCK/CEN, Mol, Belgium
Contract No. : FI1W/004/B
Duration of contract : from January 1985 to December 1989
Period covered : January 1987 - December 1987
Project leader : A.A. Bonne

A. OBJECTIVE AND SCOPE

In 1974 SCK/CEN launched a R&D-programme concerning the possibilities for disposal of high level solidified and alpha-bearing radioactive wastes in a continental stratiform clay formation (Boom clay) situated below its own site. Site investigations, safety studies, repository design, conceptualisations and in situ research confirm progressively the favourable characteristics of the host rock and the site for disposal of radioactive wastes.

Many particular areas require further studies and technological tests on a larger scale and in situ demonstrations under realistic conditions. These technological tests, studies and demonstrations will contribute to increase the confidence in the technical practicability, the economical feasibility and the safety of the disposal option in deep clay.

The direct demonstrations deal with the constructibility of real scale galleries without particular conditioning of the rock, the choice and dimensioning of a realistic lining and support system, the interaction between the underground structures and the immediate geological environment (e.g. the influence of heat and radiation), the handling of hot and radioactive canisters, the backfilling and its behaviour in time, the performance of various system components during the operational phase and of monitoring systems.

Within the HADES project a technological test related to a gallery lining technique according to the convergence-confinement principle is performed by ANDRA (France) (see contract FI1W/0112)

B. WORK PROGRAMME

The demonstration/pilot phase of the HADES project is scheduled in two phases, which are complementary to each other and may be developed in parallel.

B.1. Phase I : the construction and operation of a test drift with tests related to :

B.1.1. Mining technology (digging, lining, extrados backfilling, rheology).

B.1.2. Radioactive waste disposal (experimental emplacement, backfilling, degradation of waste matrices and migration of radionuclides, in situ irradiation of clay, thermo-mechanical behaviour of clay and gallery structures, monitoring and auscultation systems).

B.2. Phase II :

B.2.1. The construction of a pilot facility with a new shaft and extended gallery, connecting chamber and utility structures ;

B.2.2. Tests and observations on handling, emplacement, backfilling and retrieval of dummies and finally of actual radioactive wastes.

(The performance of B.2. is scheduled beyond the present contract period).

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The construction of the Test Drift (TD), that was to be built in phase I of the HADES-demonstration and pilot programme, started in March 1987 and ended in December 1987. The total length of the TD (access gallery, concrete lined portion, sliding steel ribs portion and transition zone) is about 63 m. The excavation with a diameter of 5 m, lining and extrados filling could be made without major difficulties. The TD itself and the surrounding clay is fully instrumented enabling a long term follow-up of the test (Mine-by-test).

The technological test programme related to the radioactive waste disposal, to be performed in the TD has been defined in more detail taking into account their mutual influencing and the interferences with the ongoing and planned research in other sectors of the URF. The short term test programme covers the following tests sponsored by the CEC : Cerberus-test (combined radiation/heating test) and GHT (Gallery Heating Test). Activities related to these tests are foreseen in the present contractual period. Other tests are planned beyond this period.

The design of the Cerberus-test is completed, construction of parts and operational tools and purchase of instrumentation and equipment for this test has been undertaken progressively.

Operation license for the UFR extended with the TD has been obtained and principal approval by a special committee for the Cerberus-test to be run with a 15 kCi Co-60 source has also been got. The latter still has to be consolidated by the release of a Royal Decrete in the State Journal.

By sake of harmonisation with NIRAS/ONDRAF's waste management plan the preparating activities for the phase II (design and detailed programme definition) have not been launched yet.

PROGRESS AND RESULTS

The construction of the TD (issue B.1.1 of the programme)

With regard to the plans for the TD the major differences of the as-built situation concern the length of the main concrete lined portion of it (40 m instead of 20 m), the addition of a 12 m long portion with sliding steel ribs lining and the completion of the TD with a converging terminal front instead of a thick monolithic stiff concrete plug.

The TD now completed is built up of :

- an opening in the crossing chamber at the bottom of the access shaft of the URF, acting as the entrance to the TD ;
- a 4.66 m long access gallery lined with concrete blocks and with an inner diameter of 2.64 m ;
- a conical transition of reinforced concrete, enlarging the TD to the main circular section of 3.5 m ;
- the main portion of the TD, lined with concrete blocks, 42 m long (the last 2 m acting as a buffer/transition zone with regard to the next portion of the TD lined with converging steel ribs). The TD is built up of subsequent rings of 64 concrete blocks with a thickness of 60 cm and a length of 33 cm. The useful diameter of the TD is 3.5 m. The extrados is filled with calibrated sand and injected afterwards with cimenticeous milk or gunite ;
- a 12 m long portion of TD lined with sliding ribs, braces and plates. The purpose of this test, undertaken by ANDRA is to investigate the application of the convergence-confinement principle for this particular environment. The extrados here is backfilled with the same material as the concrete lined portion of the TD ;

- a 2 m long transition zone between the terminal front and the previous section in order to limit short term perturbations on the convergence/confinement test by the "flow" of the terminal front ; this transition zone is built in the same manner as the main portion of the TD (concrete blocks, 3.5 m diameter) ;
- a free standing concave front lined with a 10-15 cm thick shotcrete cask, which is not unified with the TD lining and thus allowing convergence of the front wall. The non-lined interspace between the last concrete lining ring and the cask is 30 cm ; the thickness of the cast was minimised in order to obtain the best as possible information about the rheology of the tunnel front.

  93 port holes are built in the lining in order to have easy access to the clay mass for future tests.

Mine-by-test around the stiff section of the TD (issue B.1.1. of the programme)

The geotechnical observations and survey undertaken in the TD and around it in the clay mass are briefly described hereafter.

- Convergence measurements and pressure build-up on the lining

  The deformation of the concrete lining, the pressures acting upon it and the loading of the concrete blocks is surveyed in seven instrumented sections of the drift. The observed deformations are evident in the first days after the placement of the liners. On the average the diameter is decreased by about 0.5 percent of the initial diameter in the first 10 days. Afterwards the deformation slows down and a total convergence of only 1 percent is observed after 90 days. The total pressure acting upon the lining after six months is 21 bars and 80 % of this pressure is already acting upon the lining after one month.
- Underground topographic surveying

  The above mentioned seven measuring sections are also equipped with fixed nods (studs) allowing a detailed topographic survey. Reference supports for the measuring stations were therefore implanted in the TD, the whole materialising a planimetric networks. For each of the seven sections the x,y,z-position of several convergence studs is followed in function of time. Up to now no important deviations and deformations are to be reported.
- Deformations in the clay mass

  The displacements inside the clay body itself are recorded at three positions in the roof of the test drift. At the end of 1987 the vertical displacements measured reach respectively 10 cm at 5.1 m, 4.4 cm at 6.9 m and 3.6 cm at 7.8 m distance from the axis of the TD. These values are in good agreement with the deformations predicted by the EPLAST-code. The radius of the plastified volume around the TD may be estimated to be about 3.6 m which is in corroboration with the measurements recorded along a vertical extensometer which was installed in the ring 35 of the TD immediately following the linings emplacement of this ring.
- Pore pressure measurements

  The dissipation of pore water pressure is an essential aspect of the clay response to excavation. The changes observed are given in Fig. 2, the distances of the sensors with regard to the extrados on the TD being mentioned in the figure caption. After a pseudo-equilibrium state and in direct relation with the excavation progress, each sensor, even at relatively larger distance from the excavated front is affected by the construction works ; they are now showing an increase in the interstitial water pressure tending towards a new equilibrium state.

- Clay front auscultation

  At the drift end the clay mass beyond the front was instrumented by a 10 m long Glötzl 4-points fibre extensometer equipped with transducers for continuous monitoring of the relative deformations. Reflectors were also mounted on the front itself in order to measure the displacements as a function of time using an infrared interferometer. These instrumentation being emplaced at the very end of 1987, no significant interpretable results are available yet.

Geotechnical auscultation of the clay (issue B.1.1. of the programme)

The planned geotechnical auscultation aiming at determining the coefficient of earth pressure at rest and to be done in addition to the geotechnical auscultation related to the mine-by-test, had to be postponed because of the prolongation of the TD. This test is to be performed by a self boring pressuremeter and is scheduled now in the first semester of 1988.

CERBERUS-test (issue B.1.2. of the programme)

The design of this combined radiation/heater test (CERBERUS = Control Experiment with Radiation of the BElgian Repository for Underground Storgae) reached its final version. The purposes of this test is the observation under simulated conditions of the heat and radiation yielded in the clay environment by a high level solidified waste source. This is calculated to be feasible with a linear Co-60 source of 13 kCi and two linear heaters (one above and one below the radiation source) in an experimental set-up as it given in Figure 3.

For this experiment a special handling container has been designed, complying with the safety requirements for the operations on the SCK/CEN-site and in the HADES-URF. The electromagnetic handling system for loading and unloading and required to be operational in combination with this container was fully designed and tested at various temperatures between 25 and 150 °C and in a shielded cell with a Co-60 source (total dose 140 KGy). The performance of the electromagnetic handling system in this test was successful. The CERBERUS-test is planned to be installed mid-1988 and to be loaded with the Co-sources end 1988.

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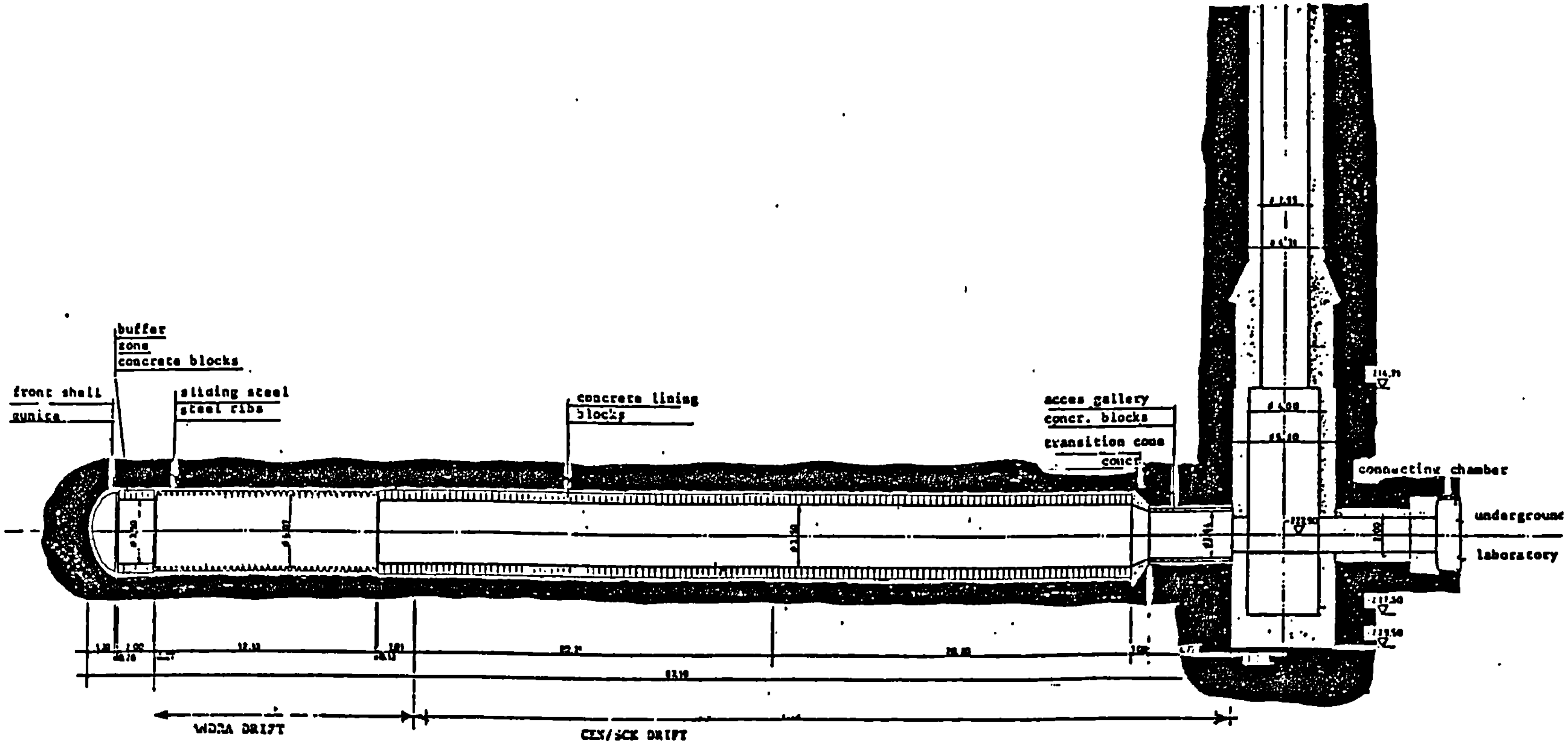

Fig. 1. Scheme of the test drift (as built)

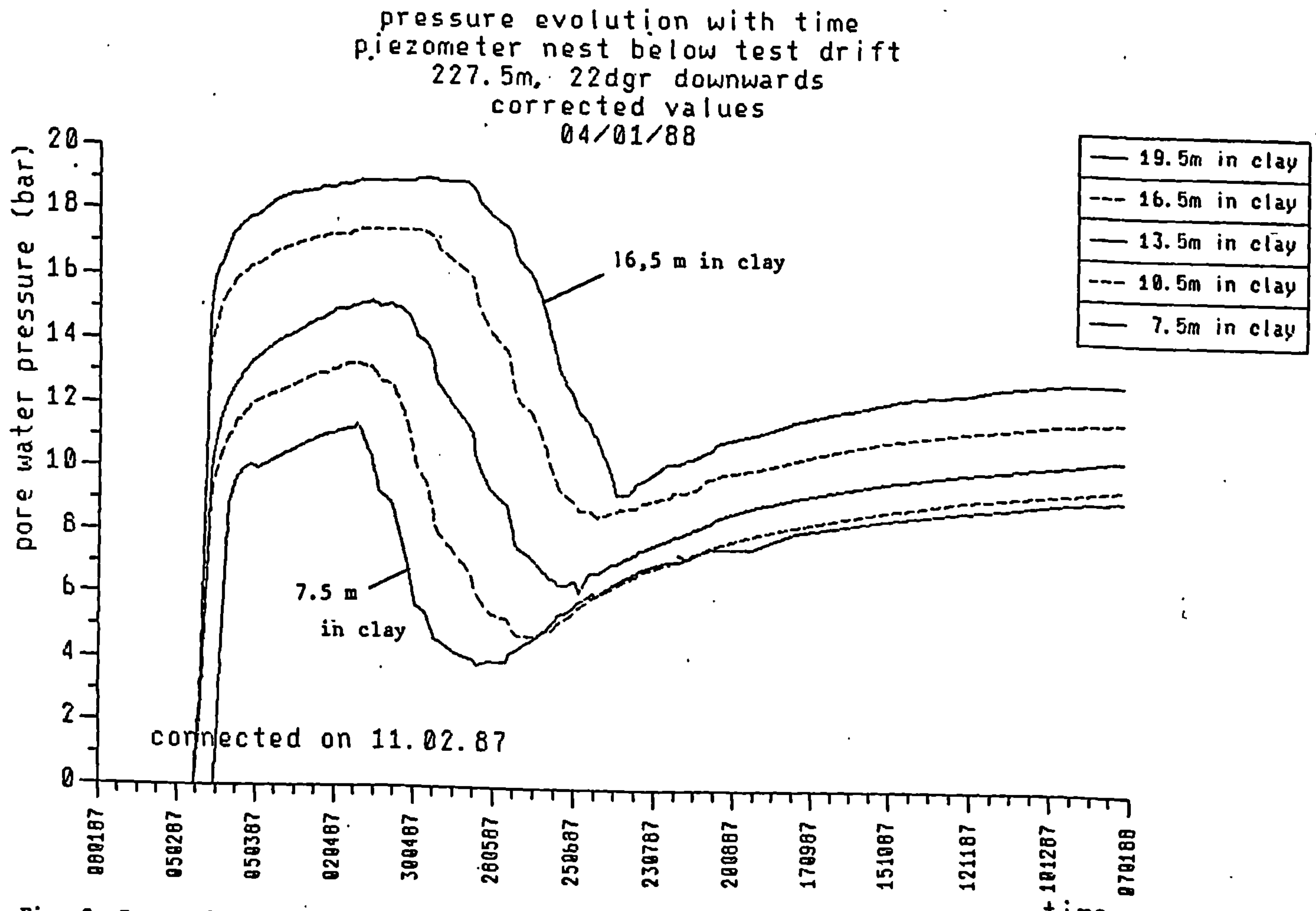

Fig. 2. Interstitial pore water pressure changes during and after excavation of TD

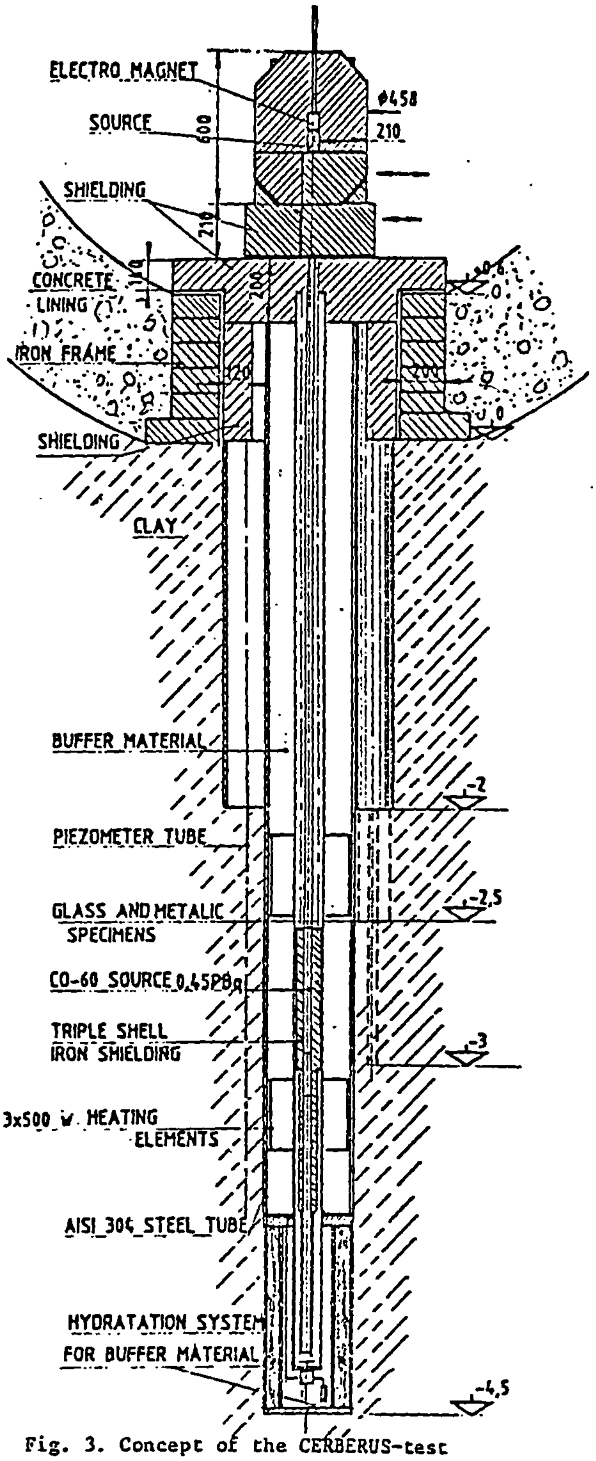

Fig. 3. Concept of the CERBERUS-test

DIMENSIONING OF LINING OF GALLERIES EXCAVATED IN DEEP CLAY FORMATIONS

Contractor : ANDRA, PARIS, FRANCE
Contract n° : F I1W/0112
Duration of contract : January 87 - March 90
Period covered : January 87 - December 87
Project leader : R. ANDRE JEHAN

A - OBJECTIVES AND SCOPE

The dimensioning of lining of galleries in deep clay formations depends directly on the long term stress undergone by the support.

The mechanical characteristics of the clay formation could be used to optimize the lining. It seems possible to minimize the pressure in the support, by allowing the excavation wall to converge enough with time. Different factors can be considered to reach this objective, as the time lag for the rock to come to contact with the support or the flexibility of the lining.

The objective of this work is to implement a lining wich answers this criterium. It is made of steel ribs showing a significant st iffness with sliding devices adapted at the joint elements, allowing the convergence. This configuration will test the closure - confinement concept : the convergence of the wall prevents the confinement to rise above a certain threshold. Moreover this thin lining presents practical advantages i.e. the handiness and ease of transport, the rapidity for building and the small volume of material to dig and dispose.

The conception of the project and the study of the massif-lining behaviour are conducted by LMS (Laboratoire de Mécanique des Solides de l'Ecole Polytechnique). Engineering department of SIMECSOL is responsible for the instrumentation and measurements.

B - WORK PROGRAM

1. Build up of a 12.5 m long test gallery in the continuation of a concrete drift made by the CEN/SCK. A transition zone of 2 m with concrete archstones prevent any perturbation of the CEN gallery.
2. Measurements of :
   - closure of implemented rings,
   - sliding of the ribs,
   - rib strain,
   - pressure on the outer face lining,
   - displacement inside the clay formation,

   during and after excavation, for 24 months at least.
3. Interpretation of results

C – PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The excavation, lining and instrumentation of the gallery were performed from 20/10/87 to 3 /12/87. A buffer zone was set up at the end of the drift. It consists of a portion of a circular gallery 2 m long lined with concrete archstones. Its end is completed by a hemispheric front stabilized with gunite (figure 1). The measurement started during the digging and is still underway. The results are not yet interpreted.

Progress and results

1. Realization of gallery

The test gallery was excavated with an average progression rate of 0.60 m/day, without break exceeding 48 h. The lining was implemented at a maximum distance from the working face of 1.40 m.

The frame work of the support is made of rings of 4 steel ribs. The elements are joined with attachs and can slide when the normal stress in the rib exceeds a threshold defined by the clamping of the joints. The recovering zone is 50 cm long initially and 78 cm after maximum sliding.

Between two consecutive ribs a system of braces and plates makes the support continuous. A grouting of sand, bentonite and cement is injected to fill the space between the lining and the clay.

A safety lining is provided for an eventual collapse of the support.

The internal diameter of the gallery is 4.0 m in average at the beginning and 3,6 m after maximum convergence.

2. Measurements

The instrumentation is set up following the progression of the excavation. Four rings has been completely instrumented (measurement ring). The parameters measured are :

- the convergence of the rings, using an extensometer with Invar wire tightened between plots fixed on the ribs. Normal rings bear 4 plots, measurement rings 8 plots,
- the sliding of the rib joints with a ruler fixed on the elements of the measurement rings, or with a visual marker of the initial position of the sliding device for the normal rings,
- the rib strain with Kovari extensometer (nine measures for a measurement ring) in order to estimate the normal load and the bending moment in the ribs,
- the stress applied by the massif on the back of the lining wich is measured by Gloetzl cells disposed on the interface clay formation-back filling (3 cells for a measurement ring),
- the displacement inside the clay formation, with extensometer implemented by 3 measurement points, set up in 2 radial boreholes.

The measurements will keep on for 24 months at least. The frequency is daily during the excavation phase, weekly during the first month after the completion of the work, bi-monthly during the 6 next months, then monthly and eventually quarterly during the last year. Some measures are already automatically taken.

3. Interpretation

Interpretation of results will start in 1988

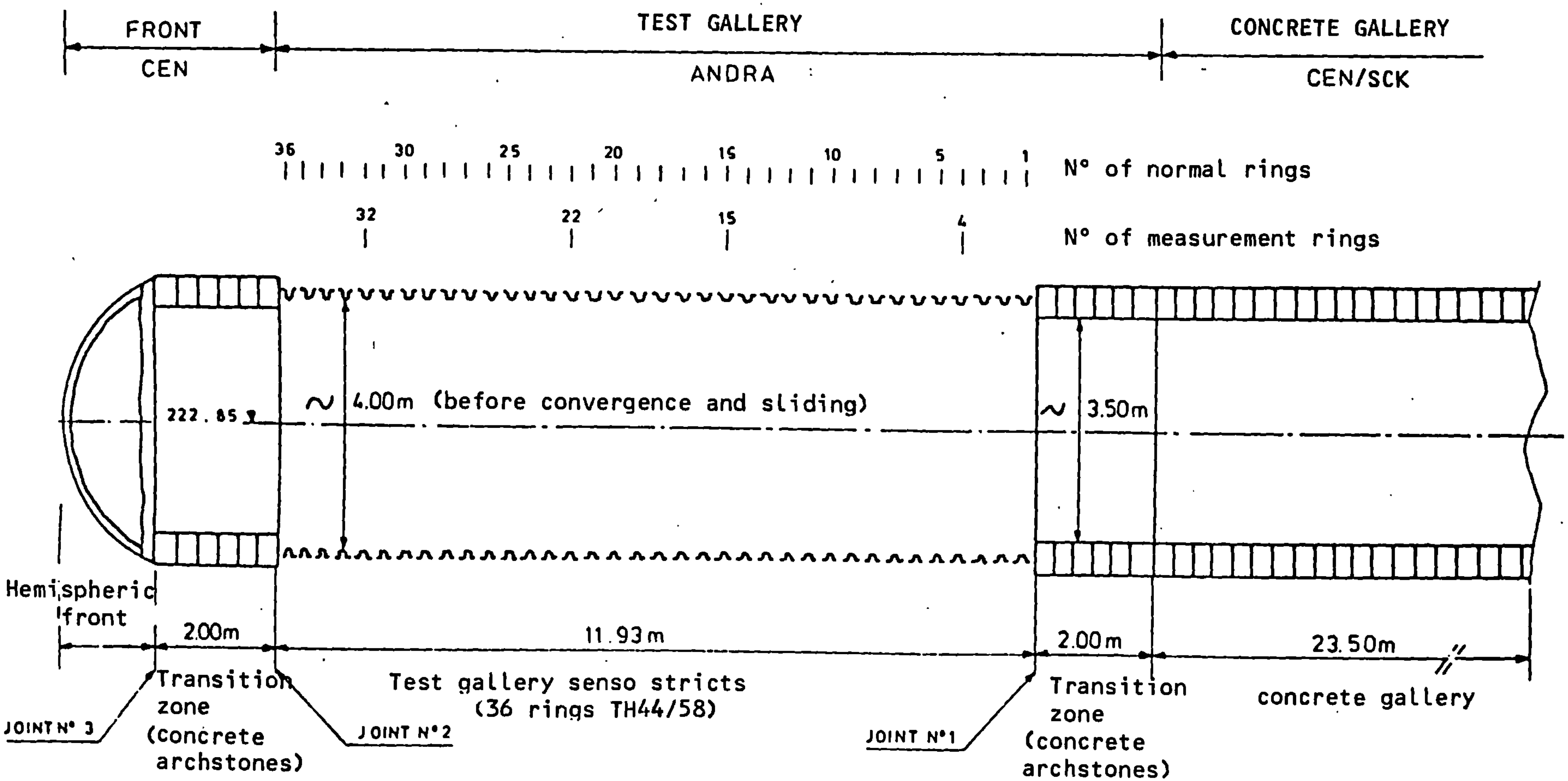

Fig. 1 : ANDRA TEST GALLERY

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(1) This Committee was established by the Council Decision of 29 June 1984 dealing with structures and procedures for the management and coordination of Community research, development and demonstration activities (OJ N° L 177, 4. 7. 1984, p. 25).

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European Communities — Commission

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Annual progress report 1987

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