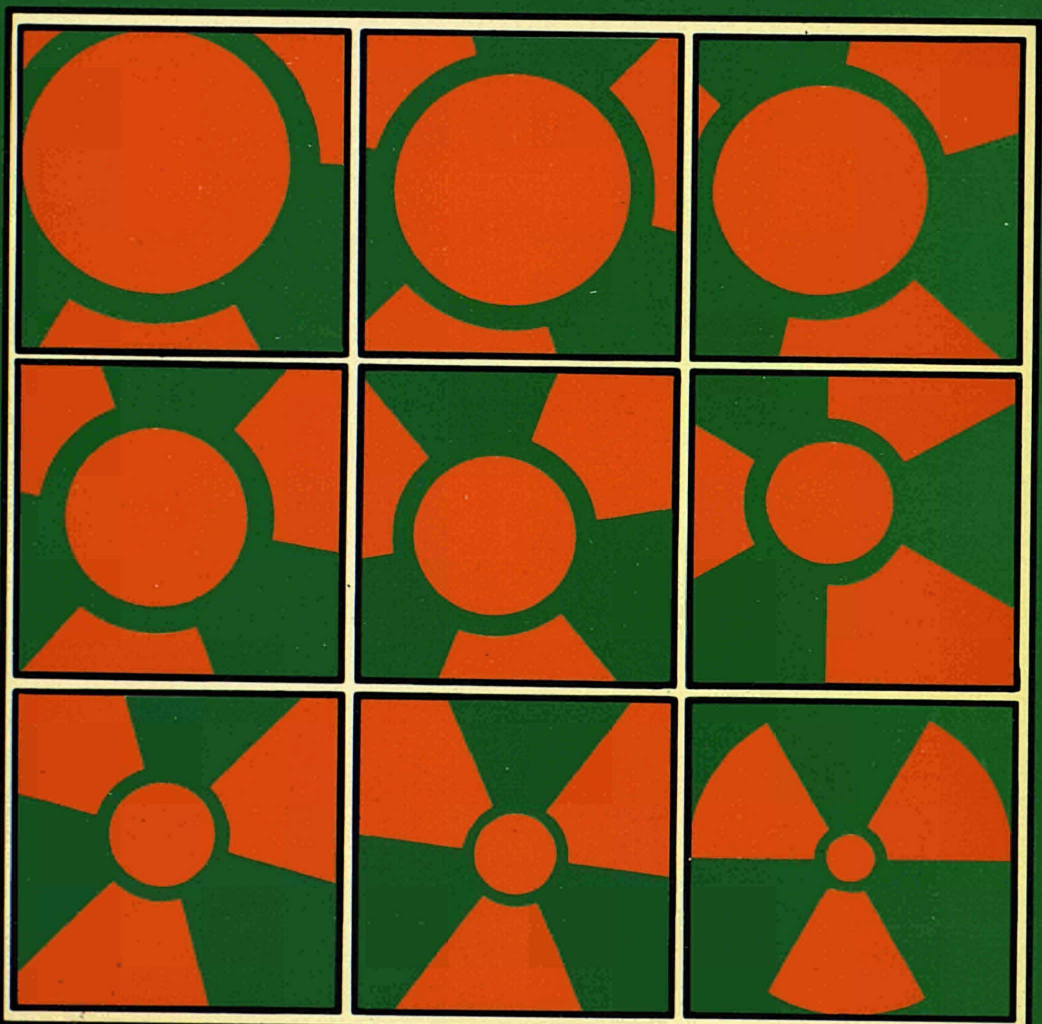
Research and Development on Radioactive Waste Management and Storage

Annual Progress Report 1982 of the European Community Programme 1980-1984



RADIOACTIVE WASTE MANAGEMENT
A Series of Monographs and Tracts
Volume 12

harwood academic publishers
for the Commission of the European Communities

RESEARCH AND DEVELOPMENT ON RADIOACTIVE WASTE MANAGEMENT AND STORAGE

Annual Progress Report 1982 of the European Community Programme 1980-1984

RADIOACTIVE WASTE MANAGEMENT

A Series of Monographs and Tracts

Editors : D. R. Anderson, Sandia Laboratories, A. M. Platt, Battelle Pacific Northwest Laboratories, F. Girardi, Joint Research Center, S. Orlowski, Commission of the European Communities

---

VOLUME 1

Radioactive Waste : Advanced Management Methods for Medium Active Liquid Waste edited by K. W. Carley-Macauly *et al.*

VOLUME 2

Radioactive Waste Disposal into a Plastic Clay Formation (A Site Specific Exercise of Probabilistic Assessment of Geological Containment) by Marco d'Alessandro and Arnold Bonne

VOLUME 3

Management of Plutonium Contaminated Waste edited by J. R. Grover

VOLUME 4

Research and Development on Radioactive Waste Management and Storage (First Annual Progress Report of the European Community Programme 1980-1984) Commission of the European Communities

VOLUME 5

Migration Phenomena of Radionuclides into the Geosphere edited by B. Skytte Jensen

VOLUME 6

Actinide Recovery from Waste and Low-Grade Sources edited by J. D. Navratil and W. W. Schulz

VOLUME 7

Management Modes for Iodine-129 edited by W. Hebel and G. Cottone

VOLUME 8

Research and Development on Radioactive Waste Management and Storage (Second Annual Progress Report of the European Community Programme 1980-1984) Commission of the European Communities.

VOLUME 9

Conditioning and Storage of Spent Fuel Element Hulls edited by W. Hebel and G. Cottone

VOLUME 10

Methods of Krypton-85 Management edited by W. Hebel and G. Cottone

VOLUME 11

The Acid Digestion Process for Radioactive Waste edited by L. Cécille and R. Simon

VOLUME 12

Research and Development on Radioactive Waste Management and Storage (Annual Progress Report 1982 of the European Community Programme 1980-1984) Commission of the European Communities

Additional volumes in preparation

The publisher will accept continuation orders at reduced price for this series, which may be cancelled at any time and which provide for automatic billing and shipping of each title in the series upon publication. Please write for details.

ISSN : 0275-7273

RESEARCH AND DEVELOPMENT ON RADIOACTIVE WASTE MANAGEMENT AND STORAGE

Annual Progress Report 1982 of the European Community Programme 1980-1984

harwood academic publishers
for the Commission of the European Communities

PARL. EUROP. Biblioth.
N. C.
Com. 38.756/1

Publication arranged by :

Commission of the European Communities
Directorate-General Information Market and Innovation
Luxembourg

Published under license by :

Harwood Academic Publishers GmbH

Harwood Academic Publishers :

Poststrasse 22
7000 Chur
Switzerland

42 William IV Street
London, WC2N 4DE
England

58, rue Lhomond
75005 Paris
France

P.O. Box 15053
3501 BB Utrecht
The Netherlands

P.O. Box 786
Cooper Station
New York, NY 10276
United States of America

© ECSC, EEC, EAEC, Brussels and Luxembourg, 1983

EUR 8843

Legal Notice

Neither the Commission of the European Communities nor any person acting on behalf of the Commission is responsible for the use which might be made of the following information.

Library of Congress Cataloging in Publication Data
Main entry under title :

Research and development on radioactive waste management and storage.

(Radioactive waste management, ISSN 0275-7273 ; v. 12)
1. Radioactive waste disposal. 2. Nuclear facilities—Waste disposal. I. Commission of the European Communities. II. Series.
TD898.R47 1983 621.48'38 83-22643
ISBN 3-7186-0191-5 (The Commission)

ISBN 3-7186-0191-5 ISSN 0275-7273. All rights reserved. No part of this work may be reproduced or utilized in any form or by any means, electrical or mechanical, including photocopying or by any information storage and retrieval system, without permission in writing from the copyright holders. Printed in France by Imprimerie Paillart.

PREFACE TO THE SERIES

Radioactive waste management is not a new question — it arose at the very beginning of nuclear energy. Supporting research and management concepts were exposed and discussed within the worldwide scientific community as early as 1955, during the first Conference on the Peaceful Uses of Atomic Energy in Geneva. Since then several management techniques have been developed and put into practice. Specific topics may be found in the proceedings of the numerous national and international conferences held during the last decade.

However, today radioactive waste management has become a matter of great public concern. An acute awareness of the pollution and other potential hazards generally associated with industrial development has to a great extent crystallized during the last years around nuclear energy and waste management. Its final step, the disposal of the waste, introduces a new dimension, i.e., safety over long periods of time. Radioactive waste management is therefore to be viewed as multidisciplinary, involving scientists, engineers, industrialists, lawyers and even specialists in the social sciences and ethics.

It is our hope that this series will provide a permanent record of the development of the various aspects of radioactive waste management which will provide an international overview of the following areas :

— Material research
— Waste treatment conditioning and disposal technologies and practices
— Safety and risk assessment
— Economics
— Administrative, legal and financial controls
— Societal aspects

CONTENTS

FOREWORD

This is the third progress report of the second European Community's five-year R&D programme (1980-1984) on radioactive waste management and storage (shared expense action). It covers the year 1982 and shows the status of the programme on 31 December of that year.

The Council of the European Communities adopted the second programme in March 1980*, as a follow-up of the first programme (1975-1979), considering :

> "The (first) programme has yielded positive results and opened up encouraging prospects of attaining the desired objectives**. The particular nature of the waste is such as to require monitoring of its potential effects and reinforcement of the project and research activities undertaken to ensure the protection of the environment".

The aim of the programme is the joint development and improvement of a management system of radioactive waste produced by the nuclear industry which, at its various stages, ensures the safety and protection of both man and his environment.

The programme covers :

a) Work to solve certain technological problems in the processing, storage and disposal of radioactive waste.

   Processing :

   - immobilization of low and intermediate level waste; development of processes and operation of pilot installations;

---

* OJ N° L 78, 25.3.1980, p. 22.

** One may consult here the annual progress reports for 1977, 78, 79, 80 and 81 (references on p. 394) and also the proceedings of the First European Community Conference, Luxembourg, May 20-23, 1980 (EUR 6871).

- conditioning of high level waste : fuel claddings and residues from dissolvers;
- processing of medium level liquid waste;
- processing of waste contaminated by alpha emitters;
- examination and evaluation of high level solidified waste;
- immobilization and storage of gaseous waste.

Storage and disposal :

- burial of low level solid waste at shallow depth;
- storage and disposal in geological formations;
- performance and safety evaluation of waste disposal in geological formations.

b) Work to define the general framework for the projects relating to the storage and disposal of radioactive waste.

The programme is carried out by contracts on an expense sharing basis (shared expense action) with qualified public or private bodies in the Community; the Commission's financial participation amounts to 43 millions European Currency Units (ECU)*.

The Commission is responsible for managing the programme and is assisted in this task by an Advisory Committee on Programme Management, which consists of experts appointed by the Member State's governments and of Commission officials**.

The programme is closely coordinated with the activities related to radioactive waste management conducted by the Joint Research Centre of the Commission within its pluriannual research programme.

---

* see footnote on p. 388.

** see pp. 398-399.

Results of the work during 1982 and performed under about 135 R&D contracts are reported contract by contract with an appropriate introduction for each paragraph or in the form of a joint annual report (chapters 1.1. and 1.5.). However most of these contracts are pluriannual and therefore most of these results represent progress made in 1982; the complete contractual results are often for 1983 or later.

Some in-situ experiments for geologic disposal expected to take place in France and the United Kingdom have been cancelled or postponed due to reevaluations or changes in national programmes and policies.

Coordinated activities involving several national laboratories and the JRC have been carried out or initated, inter alia :

- Characterization of low and medium activity waste forms (§ 1.1.).
- Testing and evaluation of high level waste glasses, including the development of a static, high temperature leach test (§ 1.5.).
- Assessment of the corrosion behaviour of candidate materials for HLW container design (§ 2.2.3.).

The performances of geological confinement systems have received an increased attention during the period under consideration. The implementation of the coordinated project PAGIS (performance assesment of geological isolation systems) has begun for the clay, granite, salt and the sub-seabed options (§ 2.3.).

A second project, aimed at improving knowledge on the migration of significant radionuclides through the geosphere (the MIRAGE project), will start in 1983 by means of a coordinated series of contracts involving laboratories of various disciplines. It will be based upon a common set of nuclides, matrix materials, groundwaters and hostrocks (§ 2.2.5.).

It is hoped that such an approach will further increase the usefulness and efficiency of the R&D cooperation at Community level.

International collaboration has been achieved by the implementation of a cooperation agreement with the Atomic Energy of Canada Ltd (AECL) in the field of high level waste disposal in crystalline formations. Another agreement was signed with the Department of Energy (USA) on cooperation in the field of waste characterization and waste disposal.

The professional staff in charge of the management of the programme during 1982 were :

N. CADELLI
L. CECILLE
B. COME
A. CRICCHIO
W. HEBEL
F. REICHARDT
R. SIMON
P. VENET

with the assistance of G. COTTONE, C. EID, J.M. GANDOLFO, B. HAIJTINK, W. KRISCHER and W. FALKE.

S. ORLOWSKI,
Head, Division,
"Nuclear fuel cycle"

1. WASTE TREATMENT AND CONDITIONING

1.1. CHARACTERIZATION OF CONDITIONNED LOW AND MEDIUM LEVEL WASTE FORMS* (joint annual report)

Since 1980 ten European Laboratories have participated in a co-ordinated programme of the CEC to test and evaluate waste forms containing low and medium active waste including medium level alpha bearing wastes.

The aim of this action is to identify and investigate mechanisms, which under conceivable or existing management and disposal situations could lead to a release of the immobilized activity. The resulting data will be applied in design, risk analysis and in quality assurance.

Industrial immobilization processes are available for most of the medium active waste streams and a number of development projects for further waste types or particular requirements are approaching the stage of active pilot application.

Under the current EC Programme ten combinations of common low and medium active waste with appropriate matrix materials have been selected and specified as reference waste forms, see Table 1.

Identical sample material is used in the participating laboratories to ensure maximum reproductibility and consistency of experimental data. In addition to the typical waste/matrix combinations, certain new waste products or specific variants of the chosen reference materials are tested in parallel.

* The presentation of chapters 1.1. and 1.5. is slightly different from the other chapters, where reporting is done contract by contract.

The joint annual report of the R&D work performed during 1982, is presented under the following subparagraphs :

<table>
<tr><th rowspan="2"></th><th rowspan="2">Page</th><th colspan="4">Reported contracts
for matrix materials</th></tr>
<tr><th>bitumen</th><th>cement</th><th>polymers</th><th>slags</th></tr>
<tr><td rowspan="2">1.1.1. Waste/matrix compatibility</td><td rowspan="2">13</td><td colspan="2">← 244 →</td><td rowspan="2"></td><td rowspan="2"></td></tr>
<tr><td>245</td><td>242</td></tr>
<tr><td>1.1.2. Radiation Effects . . . .</td><td>19</td><td colspan="4">← 243 →</td></tr>
<tr><td>1.1.3. Leaching of condition waste (under disposal conditions) . . . .</td><td>23</td><td>240</td><td></td><td></td><td>245</td></tr>
<tr><td>1.1.4. Full scale leach tests . .</td><td>29</td><td colspan="3">← 244 →</td><td></td></tr>
<tr><td rowspan="3">1.1.5. Basic mechanisms of leaching . . . .</td><td rowspan="3">32</td><td colspan="3">244</td><td rowspan="3">245</td></tr>
<tr><td colspan="2">← 235 →</td><td rowspan="2"></td></tr>
<tr><td></td><td>242</td></tr>
<tr><td>1.1.6. Microbiological attack and its consequences . . . . .</td><td>38</td><td>244,235</td><td></td><td></td><td></td></tr>
<tr><td>1.1.7. Swelling, mechanical properties . . . .</td><td>41</td><td>235</td><td>241</td><td></td><td></td></tr>
<tr><td>1.1.8. Thermal effects . . . . .</td><td>43</td><td colspan="2">← 240 →</td><td></td><td>245</td></tr>
</table>

The afore mentionned contracts refer to the following laboratories, titels, etc. :

240-81-13 WASD, KfK, Karlsruhe, "Activity release from cement and bitumen matrices" (see pp. 23, 44)

241-81-15 WASI, Nucleco, Casaccia, "Testing of waste/matrix compatibility and scaling-up effects" (see p. 42)

242-81-13 WASUK, Univ. of Aberdeen, "Leaching mechanisms of cement matrix" (see pp. 16, 34)

243-81-13 WASUK, AERE, Harwell, "Comparative evaluation of alpha and beta/gamma irradiated MLW forms" (see p. 19)

244-81-15 WASF, CEA, Cadarache - Saclay - Grenoble - Fontenay, "Evaluation and characterization of immobilized and solidified waste packages of low and medium activity" (see pp. 13, 29, 32, 37, 38)

245-81-15 WASB, SCK/CEN Mol, "Characterization of solidified medium active and alpha-bearing waste forms" (see pp. 18, 27, 43)

235-81-13 WASDK, RNL, Risø, "Test methods for bituminized and other low medium level solidified waste materiels" (see pp. 35, 41)

First results of the work under this programme were presented at the Fifth International Symposium of the Materials Research Society, Berlin 7-10 June 1982 (see Seminars nr 2) and at the IAEA/CEC/OECD Symposium, Utrecht 21-25 June 1982 (see Seminars nr 3).

Nr.	Waste Type/Origin	Matrix	Lead. Organization	Principal Nuclides
1	BWR evaporator concentrate/ Garigliano	cement	ENA Italy	^{137}Cs ^{134}Cs ^{90}Sr ^{60}Co
2	PWR evaporator concentrate/ EdF	cement	CEA France	
3	PWR evaporator concentrate/ Chooz	polyester	CEA France	
4	PWR ion exchange resins/ EdF	polystyrene	CEA France	^{137}Cs, ^{60}Co ^{54}Mn
5	PWR ion exchange resins/ EdF	polyester/ epoxy	CEA France	^{137}Cs, ^{60}Co
6	Magnox fuel pond sludges/ CEGB	cement	AERE UK	^{137}Cs, ^{90}Sr ^{106}Ru, ^{241}Pu
7	Reprocessing concentrate/ KfK	bitumen	KfK Germany	^{239}Pu, ^{241}Am
8	Reprocessing concentrate/ WAK	cement	KfK Germany	^{239}Pu, ^{241}Am ^{137}Cs, ^{90}Sr
9	Reprocessing sludges/ Marcoule (La Hague)	bitumen	CEA France	^{239}Pu, ^{137}Cs ^{90}Sr
10	Mixed solid waste Mol	incinerator slag	SCK-CEN Belgium	^{137}Cs, ^{90}Sr ^{239}Pu, ^{241}Am

Table 1 : Reference waste forms

1.1.1. WASTE/MATRIX COMPATIBILITY

- Characterization of a bituminized cement waste form

Contractor : CEA, Saclay (244-81-15 WASF)

The characteristics have been obtained on a composition which is actually used in the CEN-CADARACHE for embedding a solid waste :

OPC CEMENT	:	150 kg/m^3
BITUMINOUS EMULSION	:	75 kg/m^3
SAND 0/2	:	300 kg/m^3
WATER	:	100 l/m^3

Measurements concerning its mortar stability, its mechanical properties and permeability are given in tables 2, 3 and 4. Optimization tests were carried out on cement-bituminous emulsion matrices in order to determine the best structure for the immobilization of the solid waste (and retention of the main radionucleides). New experiments have been carried out. The results are reported in table 5.

Density of the fresh mortar	Sweating in %	Setting (Marsh Method)
1.90	< 0.2	15 cm

Table 2 : Mortar stability before setting of the cement-bituminous matrix.

Curing Time in months	Tensile Strength (MPA)	Compressive Strength (MPA)
1	2,15 2,12 2,15	10 10,5 11,5
2	4,31 3,80 4,10	14,2 14,2 16,0
3	4,20 4,10 4,15	15,3 14,5 16,2

Table 3 : Mechanical properties of the cement-bituminous matrix.

under air	$1,70.10^{-16}$ m2
under water	$0,80.10^{\cdot 14}$ m2

Table 4 : Permeability of the cement-bituminous matrix.

Kind of cement and % of E.B	Water/cement ratio	sweating in %	shrinkage (μ mm)	Tensile Strength (en MPa)	Compressive Strength (en MPa)
Hig Alumina	0,53	0,55	346	6,3	62,5
5%	0,52	0,70	380	5,7	52,8
10%	0,50	0,63	386	5,6	42
20%	0,47	0,50	453	4,6	34
Pozzolanic cement	0,59	1,5	340	2,9	18,6
5%	0,57	0,13	353	2,8	13
10%	0,52	0	360	2,9	11,8
20%	0,51	0	406	2,8	11,6
O P C	0,60	1,23	340	3,2	16,8
5%	0,57	1,12	340	3	17,1
10%	0,54	0,85	313	3	17
20%	0,52	1,1	366	2,9	12
SLAG	0,55	0,95	593	2,8	15,8
5%	0,48	0,55	500	3	15
10%	0,49	0,53	600	2,5	12
20%	0,50	0	653	2,2	9
C.P.J.	0,57	1,22	366	2,9	15,8
5%	0,55	0,71	406	2,6	11,8
10%	0,54	0,47	440	2,8	11
20%	0,54	0	523	2,5	9

Table 5 : Optimization tests on cement-bituminous emulsion (E.B.) matrices (values obtained after 7 days curing time in air at 20° C and 65 % relative humidity.

- Zeolite-cement interactions and microstructure

Contractor : Univ. of Aberdeen (242-81-13 WASUK)

The reaction of two zeolites, clinoptilolite and ferrierite, with cement have been studied. Data are most complete for clinoptilolite. The reaction occurs by two principal mechanisms : ion exchange between zeolite (containing Cs, Sr) and the pore fluid of cement, which contains initially Na, K, Ca, and also, by pozzolanic reaction of cement and zeolite. In this latter mechanism, zeolite is chemically consumed by its reaction with $Ca(OH)_2$ and with lime-rich C - S - H. The two reaction mechanisms can be distinguished experimentally. Ion exchange occurs rapidly, usually within hours of mixing. The rate of the pozzolanic reaction is, in general, slower but its rate is also sharply temperature-dependent. The pozzolanic contribution to the overall reactivity can be separately assessed either by quantitative X-ray diffraction or by a chemical dissolution method which recovers selectively from solid composites that fraction of zeolite remaining unreacted.

Leaching of cement-zeolite composites in Soxhlet tests accelerates the pozzolanic component of the reaction.

Scanning electron micrographs confirm that zeolite tends to disappear, but its consumption is accompanied by increased microcracking; Fig. 1 compares the microstructure of cubes aged at 18° C with those subject to Soxhlet extraction at 100° C.

Mercury intrusion porosimetry confirms that Soxhlet extraction results in a marked increase in porosity, particularly in the 0.1-1.0 µm range, which we associate with the pressure of microcracking.

The reactions between cement and several of the CEC reference waste forms have been studied. Borate rich wastes strongly retard setting cement. Pretreatment with $Ca(OH)_2$ neutralizes the acidity of boric acid and partially precipitates the boric oxide component as calcium borate hydrates. Nitrate- and sulphate-rich evaporator concentrate simulants do not inhibit normal setting reactions. However, progressive withdrawal of water, necessary to satisfy the hydration demands of the cement, results in precipitations. This process may be followed by X-ray diffraction of the composites as well as by scanning electron microscopy.

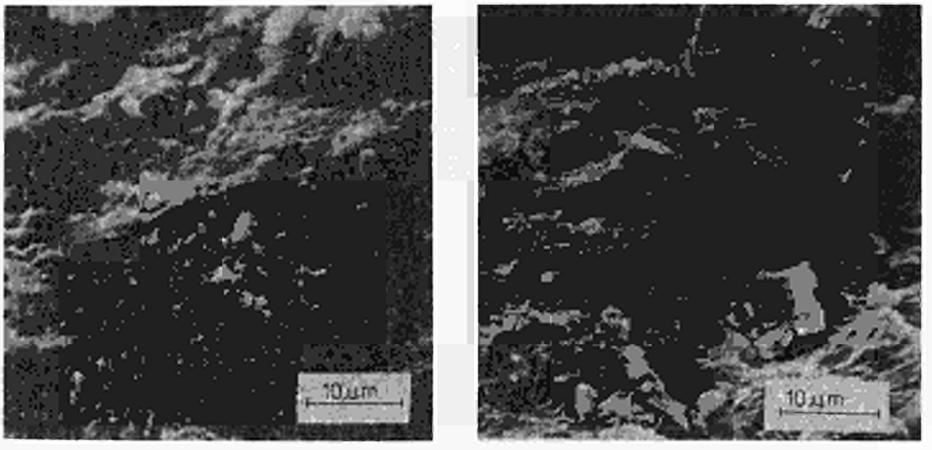


Fig. 1 : Clinoptilolite-cement (50:50) Mixtures. Left : showing unreacted zeolite after 28d. Right : showing less zeolite but more microcracking following 14d Soxhlet extration at 100° C.

The nucleation of $NaNO_3$ crystals may be initiated in pores, but their subsequent growth is apparently not restricted by the size and shape of pores. The crystals instead tend to express their normal growth morphology, presumably by pushing aside the cement-gel phase to achieve the necessary space. The development of relatively large crystallites is viewed as introducing local internal expansive strains and, from the mechanical standpoint, acts to weaken the matrix.

PARLEMENT EUROPEEN
BIBLIOTHÈQUE

Fig. 2 shows precipitation of $NaNO_3$ occurring in a set cement.

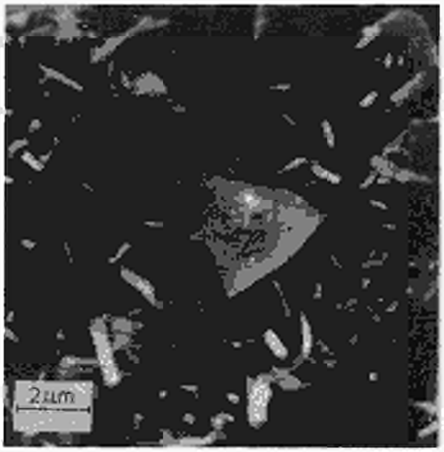


Fig. 2 : Microstructural Development in cement-nitrate reference waste mixture. Precipitation of $NaNO_3$ occurred.

- Stability of bituminized reprocessing concentrate

<u>Contractor</u> : SCK/CEN Mol (245-81-15 WASB)

Corrosion experiments have been started, in which real Eurobitumen samples are exposed to either distilled water or a clay-water mixture at 40° C.

1.1.2. RADIATION EFFECTS

Contractor : AERE, Harwell (243-81-13 WASUK)

The aim of this research is to identify and quantify the effects due to self-irradiation in MLW forms. The data will allow comparison of the performance of ten reference waste forms (RWF) plus additional waste forms of national interest. Also, the data will be used for model testing; in this respect a more fundamental approach is required since understanding of the mechanism in play will be required if reliable long term extrapolations are to be made.

- Sample acquisition and preparation

  To date simulants of the RWFs have been prepared in-house, following carefully the instructions supplied by the lead laboratory for each waste form. An exception is RWF10 - a glassy material, of which samples have been supplied by CEN Mol.

- Irradiation procedure

  Self gamma-irradiation is simulated by placing samples in either a ^{60}Co flux or a fuel element storage pond flux.

  No alpha irradiations have yet been carried out. The intention is to incorporate sufficient ^{241}Am in the waste form to simulate up to 100 years damage in 12 months. This work will commence early in 1983.

- Characterization of radiation effects

  Apart from RWF10, which is an alpha bearing waste form, the principal effect will be gamma-radiolysis. Because of the differences in the physical and chemical nature of the organics and cement, different effects have to be characterised, eg swelling in organics, chemical reactivity in cement. However, in all cases the effect on dimensional stability, mechanical properties and leach rate will be assessed as a function of dose rate and cumulative dose.

- Results on cement-based waste forms

  . Effect on hydration kinetics of cement

  It has been shown that if a freshly mixed paste of cement and water is γ-irradiated there is a slight acceleration in the setting rate of the cement, but conversely the compressive strenght of the cured paste is reduced significantly.

  . Radiolysis effects

  Hydrogen and oxygen are evolved during the γ-irradiation of RWFs 1, 2 and 6. Figure 3 shows the H_2 evolution rate for RWF1 at a dose rate of 0.1 Mrad h^{-1}. It has been observed that oxygen is consumed. No significant difference is observed in the dimensions or the compressive strenght of irradiated or unirradiated samples of RWFs 1, 2 and 6 up to a total dose of $\sim$ 900 Mrad. There are no apparent differences if a pozzolana cement is used in place of ordinary Portland cement. Work has only just commenced on measuring leach rates and no comments can be made at this stage.

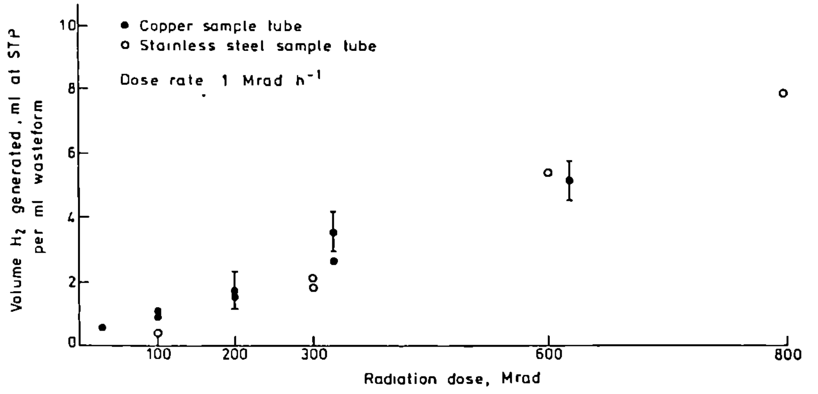


Fig. 3 : Radiolytic hydrogen evolution form magnesium hydroxide/ carbonate sludge in OPC - RWF6.

- Results on bituminised waste forms

Swelling is observed in bitumen and bitumenisates when γ-irradiated. In general it is less in the case of the bitumenisate. For example, for a given size of sample and given dose rate an unfilled R85/40 bitumen swelled 40 % while RWF7, a bitumenisate based on R85/40, only swelled 10 % (see fig. 4). Figure 2 also demonstrates that the swelling in RWF7, as a function of size and dose rate, gives good agreement with the Harwell I D^2 model such that I D^2 = 8 Mrad cm^2 h^{-1} where I is the dose rate and D is the diameter and height of a right cylinder of the sample.

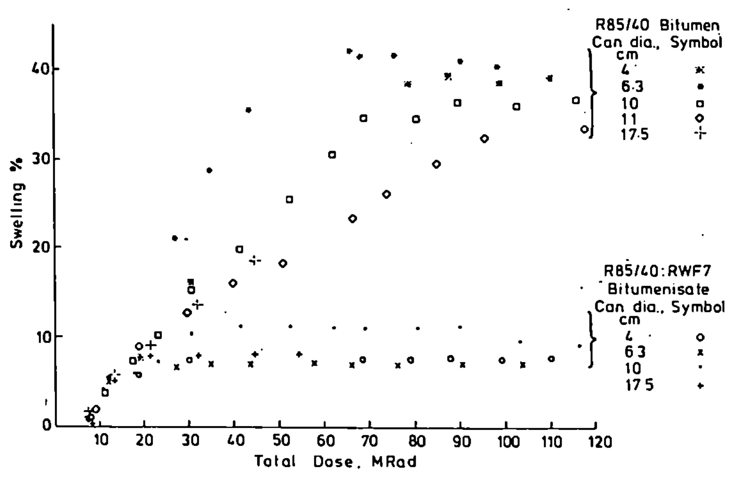


Fig. 4 : Radiation induced swelling of unfilled bitumen R85/40 and bitumenisate simulated waste form RWF7.

- Results on polymer-based waste form

. Water-filled polymers

When a water-filled, water tolerant resin is allowed to stand it loses water by natural evaporation and this effect has to be allowed for when measuring weight losses due to gamma-irradiation. From figure 5 it can be seen that the slopes of water loss versus time for irradiated and unirradiated polyester samples are different. This suggests that the mechanism for water loss is different in these two cases. By contrast the slopes of similar graphs for an epoxide were parallel so water loss may occur by the same mechanism in this case.

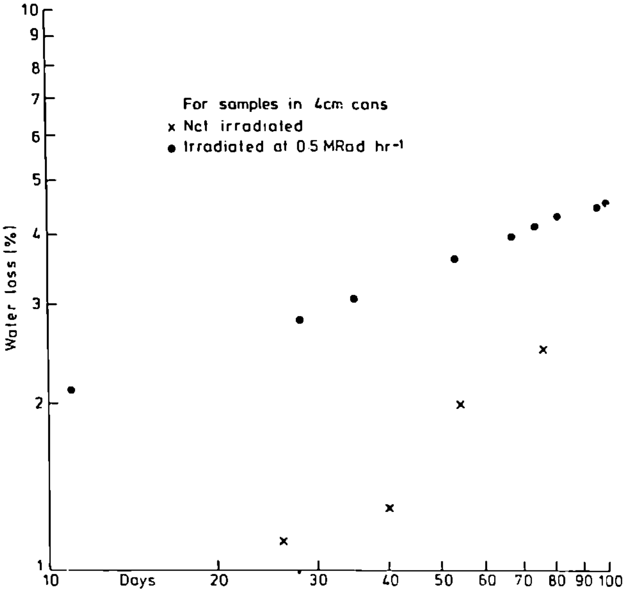


Fig. 5 : Water loss from samples of water extendable polyester resin "A" containing emulsified water droplets.

. Wet ion exchange media in non-water-extended polymer

An example of this system is RWF5 based on polyester resins. Shrinkage rather than swelling is observed in this system. Two fac-factors are thought to contribute to this (i) radiation induced cross-linking causing densification of the matrix and (ii) loss of water from the wet ion-exchange resin either by simple diffusion or radiolysis of water.

1.1.3. LEACHING OF CONDITIONED WASTE (under disposal conditions)

- Leaching and corrosion of cemented waste in brine

  Contractor : KfK, Karlsruhe (240-81-13 WASD)

After the conclusion of a preliminary six-monthly programme, a two year test programme was defined to determine the effects of the parameters : cement type, waste-matrix ratio, additives, prestoring time, stress and temperature on the corrosion resistance and activity release of cement waste forms in quinary salt brine. Some tests are also performed on bituminized waste.

- Investigation of the corrosion resistance of reprocessing evaporator concentrates immobilized in a cement matrix

  First conclusions form the test results especially from the finished test series performed at 90° C show, that the corrosion resistance of cement products based on high furnace slag cement is remarkably better than that of products based on ordinary Portland cement. The corrosion ressistance could be further improved by lowering, as far as possible, the water/cement ratio. The practicable water/cement-ratio is determined by the technical process for the manufacturing of the cement products and by the requested waste loading.

  Using an in drum - mixing system for the cementation of a defined waste concentrate, the water/cement/ratio is determined by the viscosity of the mixture.

- Investigations for the formulation of the leachability source term for the long-term prediction of activity release from MLW-cement waste forms

  A series of corrosion tests with specified product compositions was carried out with the aim to provide well defined experimental data which allow to extrapolate to long-term activity releases. The specimens tested either contain none or 5 wt. % of bentonite. The tests are conducted in quinary solution at temperatures of 40°, 55°

and 90° C and pressure of 1 and 130 bars over a period of up to one year.

The test programme is finished and the obtained results are now summarized. Based on a preliminary evaluation of the results, the following conclusions can be drawn :

- samples made from high furnace slag cement are more resistant against the corrosive attack of quinary salt brine than samples made from ordinary Portland cement
- by the addition of only 5 wt. % of bentonite, the corrosion resistance of the cement sample is not negatively affected
- the corrosion of the cement samples is not accelerated under hydrostatic pressure of 130 bars
- obtained concentration profiles of specific elements, see fig. 6 and 7, show clearly the release of Ca^{2+} from the cement matrix and the enrichment of Mg^{2+} in the upper layer of the samples. Similar behaviour is observed for Na^{+} and Cl^{-}.

After a detailed analysis of all the results obtained, it should be possible to extrapolate the long-term corrosion behaviour of cemented waste forms in quinary salt brine.

- Full scale leaching and corrosion tests of cement waste forms

Tests with unprotected, inactive simulated full scale cement products started in spring 1982.

The products are tracered with inactive $CsNO_3$. The experiments are performed at 40° C using quinary salt brine as leachant. Up to now, results for a leach period of 154 days are available. The average leach rate after this period is $2,7.10^{-3} g.cm^{-2}.d^{-1}$. This value agrees very well with results from laboratory experiments.

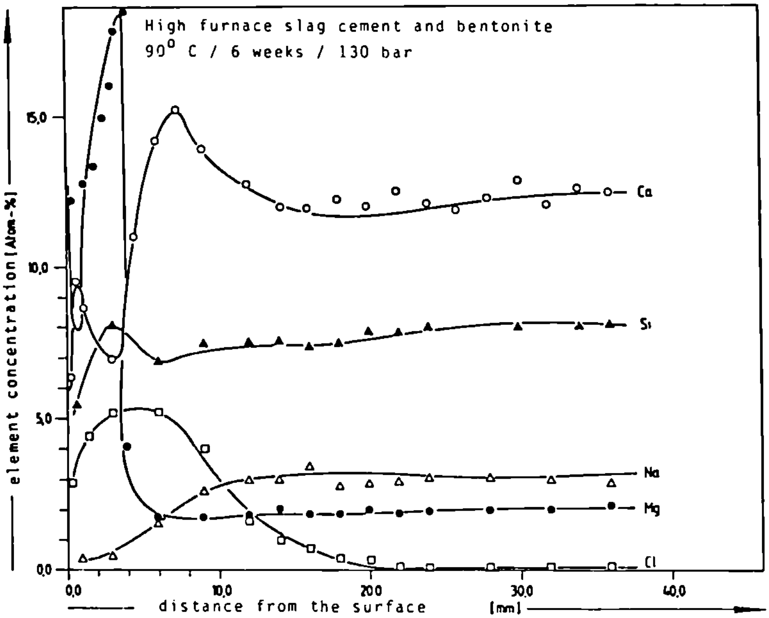


Fig. 6 : Depth-Concentration profiles of selected elements in cement samples from one dimensional corrosion experiments in quinary brine at 90° C and 130 bars after 6 weeks duration (high furnace slag cement, w/c-ratio = 0.4, 10 weight % $NaNO_3$, 5 weight % bentonite).

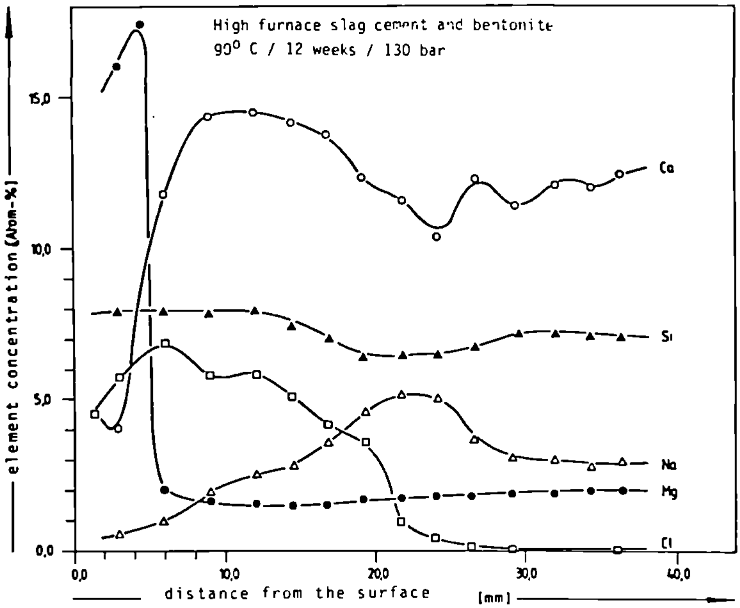


Fig. 7 : Depth-Concentration profiles of selected elements in cement samples from one dimensional corrosion experiments in quinary salt brine at 90° C and 130 bars after 12 weeks duration (high furnace slag cement, w/c-ratio = 0.4, 10 weight % $NaNO_3$, 5 weight % bentonite).

- Leaching and corrosion of incinerator slags

Contractor : SCK/CEN, Mol (245-31-15 WASB)

- Corrosion stability in standard dynamic conditions (see table 6)

The Soxhlet corrosion rate for the (inactive) FLK compacts compares very well with the corrosion rate for glass 124, whose composition was derived from the FLK granulate.

a. Before crystallization	
WG 119	44.6
WG 122	85.5
WG 122A*	142.3
WG 123	3.7
WG 124	19.5
UWG 119	49.8
UWG 122	64.1
UWG 123	3.6
UWG 124	13.9
PWG 119	32.6
FLK 77	20.8
AFLK 78	12.6
FLK 79	7.0

b. After crystallization		
WG 119	(10 d 800°C)	9.8
WG 122	(10 d 800°C)	14.1
WG 123	(10 d 900°C)	3.8
WG 124	(10 d 1000°C)	4.0
UWG 119	(10 d 800°C)	11.1
UWG 122	(10 d 800°C)	14.6
UWG 123	(10 d 900°C)	4.5
UWG 124	(10 d 1000°C)	3.2

*Has the same nominal composition as WG122, but has been prepared under argon atmosphere.

Table 6 : Soxhlet corrosion rates (in 10^{-5} g $cm^{-2}d^{-1}$) after removal of the surface layer for the FLK reference glasses (the UWG and PWG samples were derived from the WG samples by adding 2 wt % UO_2 and (UO_2+PuO_2), respectively) and FLK compacts (77, 78 and 79).

As for the reference glasses, the presence of 2 wt % homogeneously incorporated UO_2 or (UO_2+PuO_2) does not influence the overall corrosivity. Pu leaches out more than 100 times slower than the bulk. Increasing the Fe^{2+} content, at the expense of Fe^{3+}, results in an increased corrosion rate. Replacing FeO_x by (Al_2O_3+FeO_x), however, yields an improvement in corrosion resistance with a factor ≈ 20.

A surface layer about 25 μm thick can be removed upon drying the corroded glasses 119 and 122, and is found to contain essentially Fe, Mg and U (if present).

- Parametric study of the corrosion stability

  . Corrosion in distilled water at 90° C

  As reference condition a static leachant is taken with a surface area to solution volume ($SA.V^{-1}$) ratio of 1 cm^{-1}. Only the inactive reference glasses were considered. From weight loss measurements, the corrosion rates are found to decrease sharply with time (between 2 minutes and 8 months). The concentration of Si in solution is expected to saturate; for glass 123, a maximum concentration of about 25 ppm is observed. The corrosion behaviour of the glasses is much less glass composition dependent than during earlier experiments. Infrared reflection spectroscopic analyses reveal some surface roughening, indicating matrix dissolution. In case of the FLK compacts, weight increases were often observed as a result of corrosion. Further interpretation of these experiments is in progress.

  Analogous experiments with the reference glasses containing 2 wt % UO_2+PuO_2 have been started.

  The influence of $SA.V^{-1}$ was investigated in additional experiments at 0.1 and 2 cm^{-1}. After 3 days of corrosion at 0.1 cm^{-1}, the SWL's were already larger (yielding slopes ≈ 0.50 in a log SWL vs log t plot) than at 2 cm^{-1}. The differences increased with increasing corrosion time.

  . Influence of pH

  Corrosion experiments in water buffered at pH values 9.5 and 5.7 are underway (90° C, 0.1 cm^{-1}).

  . Influence of the corrosion medium (clay-water mixture, wet clay)

  Corrosion experiments are conducted under oxidizing conditions at 90° C and 1 cm^{-1}, both on the reference glasses and the FLK compacts. After 3 months, SWL's are 5 to 10 (clay-water mixture) or 30 to 40 (wet clay) times larger than in distilled water. The major reason for this increased corrosivity seems to be the smaller influence of saturation effects in the leachate, due to the sorption capacity of the clay particles. Surface analysis after one year of corrosion, as well as corrosion experiments in reducing clay media, are in progress.

- Influence of temperature (40, 70, 90, 120, 150, 200° C)

  Analysis of the corrosion experiments at 40 and 70° C is difficult due to the fact that the measured weight losses do not exceed very much the sensitivity (10^{-4}g) of the balance. The temperature dependence between 40 and 200° C is very complex, since the slopes of Arrhenius plots between 40 and 200° C are not constant, and, moreover, they change with leaching time. The interpretation of the autoclave experiments at 200° C in the different corrosion media, in terms of surface and leachate analysis, is in progress.

1.1.4. FULL SCALE LEACH TESTS

<u>Contractor</u> : CEA, Saclay (244-81-15 WASF)

- Objectives

The full scale leach test procedure applied to the different specimens was developed to satisfy the following requirements :

(i) observance of IAEA recommendations concerning leach tests;

(ii) observance of specs of ANDRA, responsible in France for the management of final storage sites;

(iii) the aim to simulate the leaching and physico-chemical degradation processes undergone by the matrices.

- Experimental method

For these tests, the waste form is removed from its container, to expose the primary containment barrier. The leach tests were performed under the following conditions :

. Leachant : tap water.

. Temperature : 23 ± 3° C.

. Flow : Leachant circulated to simulate a ground water flow rate of 2.5 cm h^{-1}.

. Sampling : periodically after 15, 2 x 30, 3 x 90 and n x 180 days for the following purposes :

◊ Count of leachate activities, to determine the fraction of radionuclide release ($\Sigma a_n/A_o$), where Σa_n is the cumulative amount released after time, t_n and A_o is the original activity in the sample.

◊ Chemical analysis of non-radioactive components present in the leachates, to assess changes in the matrices.

- Definition of the waste products

During 1982, leaching tests on the five waste blacks, started in 1981, continued : two cement matrices, two bitumen matrices and one bituminized cement matrix, viz RWF 2, RWF 7, RWF 8, RWF 9 and WF 14. All the samples tested were obtained from the waste form producers, viz. EDF, COGEMA, CEA.

The leaching equipment consists of a concrete cell containing ten loops. Each loop has a unit volume of 3000 L, the active samples are held in stainless steel baskets. Full scale blocks with a maximum volume of 1000 L and a maximum surface dose rate of 10 rad h^{-1} can be leached in the facility.

- Results

Leach testing :

Table 7 presents the release fractions measured by the end on 1982.

Waste	Matrix	Duration in days	$\Sigma \frac{an}{Ao}$: (Total fractions released for nucleides)			
			137 Cs	90 Sr	239 Pu	241 Am
WF 2	concrete	1000	6.10^{-2}	$1,3.10^{-3}$	non present	non present
WF8	concrete	1000	$5,5.10^{-2}$	$8,5.10^{-3}$	$< 10^{-5}$	$< 2.10^{-6}$.
WF7	bitumen	1000	non present	$< 10^{-4}$	$1,5.10^{-4}$	2.10^{-5}
WF9	bitumen	800	$1,2.10^{-3}$	$1,9.10^{-3}$	$< 2,5.10^{-5}$	$< 2,1\ 10^{-5}$
M1	cement bitumen	365	$1.1.10^{-3}$	non detected	$< 10^{-6}$	$< 2.10^{-6}$

Table 7 : Cumulative release fractions from five full-scale products.

Physico-Chemical Analyses

The different matrices showed a number of changes occurring with time. Physico-chemical analysis allows observation of these changes by measuring the anion-cation exchanges between the matrix and the leachant; for this purpose, pH total salinity, and the amount of K^+, Na^+, Ca^{2+}, Mg^{2+}, SiO_2, HCO_3-, Cl^-, NO_3-, SO_4^{2-}, PO_3^{3-} in the leachates were measured.

A proper analysis of all the results obtained is difficult. For example, equilibrium between solid and liquid phases is never reached. Nevertheless it is possible to make some pertinent observations :

pH : For each sample the pH is always between 10.5 to 7; the higher pH's were obtained with concrete samples. In general these values will not affect the durability of the waste forms.

Total salinity : Changes in total salinity are indicative of changes occurring in the matrix. For example, a change in total weight versus time. The more spectacular results have been obtained with RWF 8 and RWF 9 (cement/nitrate and bitumen/sludge respectively).

For RWF 8, the cumulative loss of weight after 885 days represents 1.31 % (5.8 kg); this value indicates a beginning of ageing of the concrete, resulting from :

. elution of the sample,

. mechanical erosion due to water flow,

. dissolution of soluble components.

The loss in weight is partially compensated for by carbonation of the surface. The decrease in weight of about 1.3 % represents an increase in the open porosity of the block; the change in porosity can lead to an increase in leachability, especially with soluble forms of radionuclides.

1.1.5. BASIC MECHANISMS OF LEACHING

- Diffusion of radionuclides in polymers

Contractor : CEA, Grenoble (244-81-15 WASF)

Relative concentration profiles (arbitrary units) of Cobalt, Cesium and Strontium have been obtained in epoxy resins membranes by laser mass spectrometry (see fig. 8).

The analysis have shown in the polymer the presence of a disturbed layer of 10 μm thickness.

That disturbance should result from the presence in the plasma of carbonaceous fragments of which the mass is different of ^{12}C mass : the high mass carbonaceous fragments hide partly the analysis of cesium and strontium.

The analysis of Cobalt seems to be less affected by the presence of carbonaceous fragments.

The work in progress could permit :

- to specify the limits of sensibility of cobalt, cesium, and strontium
- to obtain profiles of mass concentration.

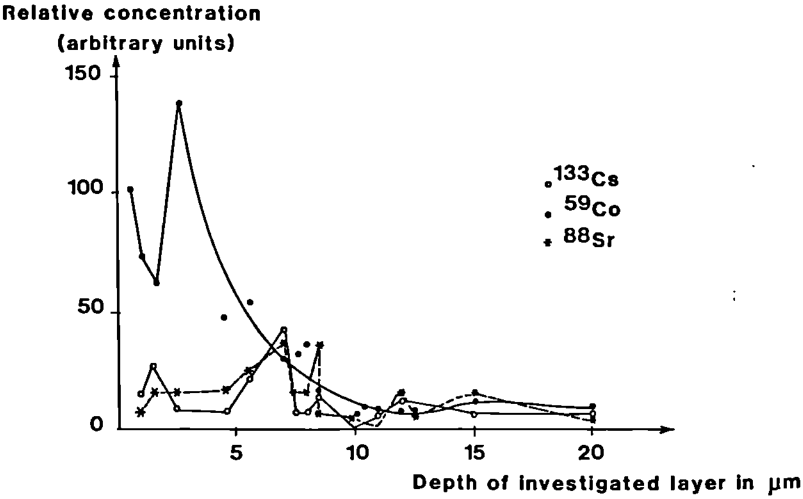


Fig. 8 : Diffusion of Cs, Sr, Co in epoxy matrix
(laser investigation)

- The absorption capacity of cement for specific radionuclides

Contractor : Univ. of Aberdeen (242-81-13 WASUK)

Silica and siliceous materials such as slag, natural pozzolan and PFA are often added to cement-based formulations to lower their short-term heat evolution and reduce permeability. However, we have shown that these materials exhibit sorption potential, especially for Cs. Moreover, the normal alkalinity of cement pore fluids enhances the sorptive effect, relative to neutral solutions. Sorption occurs relatively rapidly. However, some silica is consumed by a slower pozzolanic reaction between portlandite, $Ca(OH)_2$, SiO_2. The reaction product is an amorphous calcium silicate hydrate, C - S - H, having little sorption potential. Fig. 9 illustrates the dependence of these reactions with time, with and without $Ca(OH)_2$.

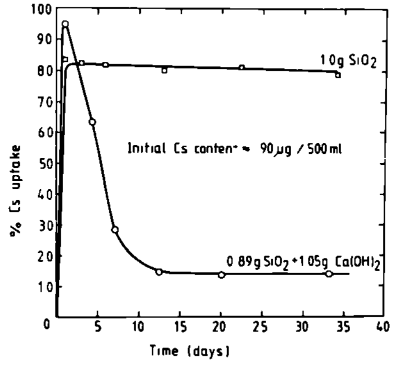


Fig. 9 : The effect of $Ca(OH)_2$ on the SiO_2/Cs interaction

The data were obtained from spiked solutions, initially $\sim 10^{-6}$M in Cs. The rapid uptake of SiO_2 in essentially neutral solutions (square data marks) remains stable with time while in alkaline solution, (circled data points) the initial uptake is enhanced, but at longer ages the pozzolanic reaction leads to a decrease in the free SiO_2 content and hence a decrease in overall sorption. In this example, the SiO_2 was chosen to give a very rapid pozzolanic reaction; it is an amorphous

SiO_2 made by flame hydrolysis with an equivalent spherical radius of $\sim$ 20 nm. PFA materials exhibit broadly similar features although on a slower time scale. Moreover, a Freundlich treatment of data suggests that at least two different sorptive mechanisms occur. Care must be taken in assessing the sorptive efficiency of different pozzolans on a merit basis : sorption per unit weight as well as per unit surface area must be considered.

The influence of SiO_2 additions on the physical texture has been explored using mercury intrusion porosimetry to map the pore size distribution. This distribution is believed to be closely related to leach rates for potentially soluble radwaste species, e.g., Cs, Sr. Studies have been completed for one sorbate : Degussa silica fume. In general, additions of ca 10 % fume give total pore volumes similar to those encountered for unmodified cement, but the mean pore size is decreased by SiO_2 additions. However, 30 and 50 % SiO_2 additions result in a pore structure which is less favourable for radwaste retention.

- Leaching mechanisms in bitumen and cement

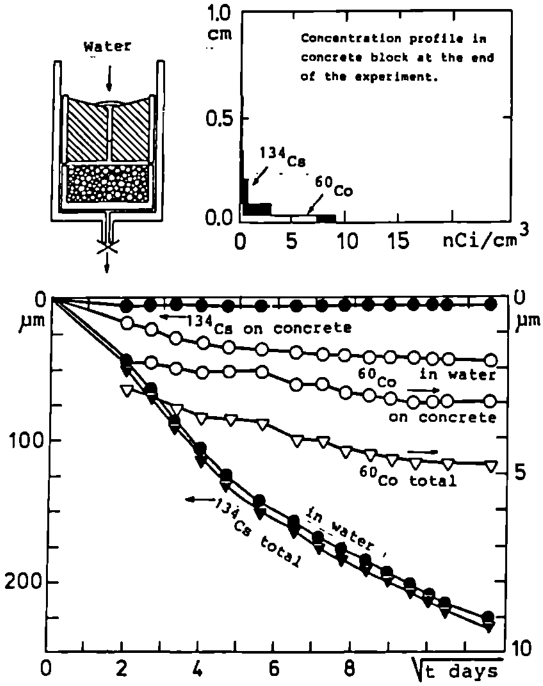
Contractor : RNL, Risø (235-31-13 WASDK)

Water transport in pure bitumen

The rate of transport of water in pure Mexphalte 40/50 was determined using the weighing method and methods based on tritiated water. Preliminary results indicate a solubility of 10^{-4} g water per g bitumen and a diffusion coefficient about 10^{-9} cm^2/sec.

Leaching in contact with concrete

Bituminized waste will in a real repository probably be exposed to water with a chemistry primarily determined by contact with concrete. Some experiments simulating this situation have been run using four different sample configurations. An example is shown in fig. 10 together with the obtained results. The overall leach rate for Cs was 0.4-0.7 10^{-4} cm/day while the overall leach rates for Co were about two decades lower probably due to the alkaline leach water. About half of the leached Co tend to accumulated on the concrete while most Cs is carried away, if there is a water flow through the system.



Equivalent leached thichness corresponding to ^{134}Cs and ^{60}Co removed with leach water or absorbed in concrete block placed on top of sample of bituminized cation exchange resin.

Fig. 10 : ^{134}Cs and ^{60}Co removed with leach water or transferred to a concrete block placed on top of a sample of bituminized cation exchange resin.

60 % Mexphalte 40/50 + 40 % granular IR 120 on sodium form.

Water changed in connection with sampling.

Leaching of cemented sodium nitrate

Leaching of ^{134}Cs, Na^{+} and Ca^{++} from samples of cemented sodium nitrate was investigated using various sample configurations, rates of water replacements and systems with and without access of CO_2 from the atmosphere. Systematic trends in leach rates and in the development of the water chemistry were observed, but they are probably of minor importance for safety evaluations. However, the possibility of creation of circulation systems driven by density differences in solutions in gaps between waste material and container was demonstrated and could be of considerable importance.

The use of silica fume as an additive to cemented waste was found to reduce the leach rate by a factor 4 as compared with samples of unmodified cemented sodium nitrate which typically had a leach rate about 10^{-3} cm/day.

- Nuclide chemistry in matrix and leachate

Contractor : CEA, Fontenay (244-31-15 WASF)

The Saclay Leaching Facility provided leachates form waste forms 7,8 and 9 on which measurements by liquid scintillation and alpha spectrometry were carried out. Taking into account the very low concentrations of transuranic elements, the leachate solution has been concentrated by coprecipitation of Nd F_3. The precipitate is then dissolved. Plutonium, isolated on anionic ion exchanger in nitric medium, is eluted and recovered in a medium suitable for electrodeposition. The spectrometry is carried out either by diode or grid chamber.

At the present state of experiments, the liquid scintillation allows a very fast differentiation of the leachates by reason of the different nature of the contained radionuclides and a qualitative evaluation of β^{-} emitters importance (^{90}Sr, ^{137}Cs). The presence of alpha emitter(s) has been revealed in the energy spectrum of a leachate (waste form 8).

With regard to α spectrometry, special efforts were devoted to plutonium. The content of Pu in the analysed leachates is 10^{-8} to 10^{-9} ci/m^3, as far as the sampling of leachates is representative. At such low contents, either during storage or during analysis, secondary phenomena (mainly adsorption) may become preponderant although a maximum of precautions are taken to avoid them.

Qualitatively (and not quantitatively by reason of measurement uncertainty which can reach 50 %) it is doubtless that the form of part of the Pu is a particulate as shown by ultrafiltration tests.

Our next goal is to improve the foregoing results by upgrading the measurement conditions of α spectrometry (use of ^{242}Pu tracer, laboratory thermoregulation) and to determine the quantity of Americium contained in some leachates.

1.1.6. MICROBIOLOGICAL ATTACK AND ITS CONSEQUENCES

- The effect of soil micro-organisms on bituminized waste forms

Contractor : CEA, Cadarache (244-31-15 WASF)

The bituminized waste used in Cadarache and described earlier (pp. 13-15), which is disposed of in the ground at shallow depth, is liable to be damaged by many of the microorganisms existing in the soil.

In order to assess the risks of biological degradation, similated samples of bituminized waste have been buried in biologicaly active soil samples of la Hague, in approaching conditions of the actual disposal. The follow-up of the biological activity of the soil in contact with the waste form samples has been carried on during the experiment after the spectrum of microbial population has been drawn up taking into account the main functional families.

The results of the analysis carried out after six months of burying in aerobic and anaerobic conditions are presented in table 8.

Organisms	Number of germs per gramme of soil		
	$1^{st.}$ Analysis of soil	After 6 months aerobic incubation sample 29	After 6 months anaerobic incubation sample 29
Total germs	$5,7.10^6$	7.10^6	$1,5.10^6$
Azotobacter	$3,2.10^2$	10^6	$9\ .10^4$
Clostridies	$3,2.10^3$	3.10^2	$3,5.10^3$
Ammonificators	$5,7.10^5$	10^8	$4\ .10^8$
Nitrifiant. B	$3,2.10^3$	3.10^2	$9\ .10^3$
Denitrifiant. B	$3,2.10^4$	2.10^4	$9\ .10^4$
Cellulolytics aérobic.B	—	8.10^2	75
Cellulolytics anaérobic.B	$2,6.10^5$	2.10^2	—
Fungae	$1,3.10^4$	9.10^5	$3\ .10^5$
Actynomycetes	$6,3.10^6$	9.10^5	$3\ .10^5$
Ferroxydising. B	—	—	—

Table 8 : Microbiological analysis of soil samples

From the analysis it emerges that several functional families have been increased, but two kinds are prevalent :

. Azotobacters (nitrogen fixing bacteria)

. Ammonifers.

Among the later ones, a lot of bacteria can induce a degradation of hydrocarbons.

In order to carry out a quantitative determination of the participation of ammonifers bacteria in the degradation of the bituminized waste form and a measurement of that biodegradation the following investigation requirements were settled :

Samples of the soil in contact with the waste form are taken at regular period and seeded on solid and liquid media containing, as growth substrates, hydrocarbons such as :

. Malthene extracted from bitumen

. Naphtalene and hexadecane representing hydrocarbons in bitumen.

Those substrates permit to show up and to isolate those bacteria capable of damaging hydrocarbons. The development and the utilization of a recipe using ^{14}C marked hydrocarbons will permit the measurement of bitumen degradation versus bacteria families.

- Degradation of bituminized waste by micro-organisms

Contractor : RNL, Risø (235-81-13 WASDK)

The studies of degradation of bitumen by micro-organisms were continued. Only aerobic systems have so far been investigated. By measurement of the slow pressure decrease due to oxygen consumption in closed systems was it possible to demonstrate rates of attack from 10^{-7} to 2.10^{-6} cm bitumen/day. The higher value was obtained with a sample of bituminized sodium nitrate, i.e. in a system with a large supply of nitrogen nutrient.

Methods for the study of anaerobic systems are under development.

1.1.7. SWELLING, MECHANICAL PROPERTIES

- Swelling due to water uptake in bituminized waste

Contractor : RNL, Risø (235-81-13 WASDK)

The work on development of a method for simultaneous measurement of swelling due to water uptake and leaching from bituminized materials has been continued.

It was demonstrated that the manipulations necessary for the measurement of the water uptake and swelling by a weighing method can be done without significant influence on the measured leach rates.

The use of the method on a simulated bituminized waste product containing 40 % dry granular cation exchange resin on sodium form gave the results shown in table 9.

The results indicate - as could be expected - that the rate of water penetration is higher than the leach rates and that especially the leach rate for the divalent Sr ion is dependent on the concentration of ions in the leach solution. The swelling of the samples in the weak solution was considerable while a slight contraction was noticed in saturated sodium chloride. The rate of indiffusion of cations in the material was also investigated.

	Rate of water penetration	Leach rates Cs^{+}	Sr^{++}
Leach solution	10^{-4} cm/day		
0.01 M NaCl	10	0.4	0.004
Saturated NaCl	1	0.4	0.1

Table 9 : Leach rates and water uptake, measured on a simulated bituminized waste product

- Mechanical properties of cement-based waste forms

<u>Contractor</u> : Nucleco (ENEA/Agip), Milan (241-81-15 WASI)

Two kinds of hydraulic cement were used as matrix for the incorporation : 425 Portland and 325 pozzolanic (see table 10).

<u>Sulphate solutions</u>	0.37	0.41	0.44	0.48
Portland cement				
density, g/cc	2.16	2.11	2.10	2.04
free standing water	absent	absent	absent	present
compressive strength, kg/cm^2	556	528	488	442
fall test from 9 m	resistant	resistant	resistant	resistant
freez-thaw cycles cracks after	40	35	35	35 cycl
<u>Borate solutions</u>	0.46	0.52	0.58	0.63
pozzolanic cement				
density, g/cc	1.91	1.88	1.85	1.83
free standing water	absent	absent	absent	absent
compressive strength, kg/cm^2	292	258	238	230
fall test from 9 m	cracked	cracked	cracked	cracked
freez-thaw cycles:	cracks just after preliminary cycles			

Table 10 : Compositions and properties of evaporator concentrates/ cement products

Compressive strength, fall test from 9 m, water resistance, high temperature (800° C) resistance, freezing-thawing cycles and chemicals resistance have been evaluated.

Electron microscopy, X-rays powder diffraction and TGA analysis have been performed for further characterization.

The main results of the tests are shown in table 10.

Sulphate solutions are satisfactorily incorporated in cement. On the contrary further work is required to improve the quality of products embedding borate solutions.

Addition of siliceous sand does not seem to produce any improvement in both cases.

1.1.8. THERMAL EFFECTS

- Thermal stability of FLK reference glasses

Contractor : SCK/CEN, Mol (245-81-15 WASB)

Both inactive (composition, see table 11) and U-active glasses were heat treated during 10 days at temperatures from 700 to 1000° C. From XRD and EMPA analyses, the following crystalline phases were identified : pyroxene $(NaFe^{3+})_x(Ca,Mg)_{2-2x}Si_2O_6$ (glasses 119, 122 and 123), spinel $(Fe,Mg,Cu,Ni)(Cr,Fe)_2O_4$ (glass 124) and uraninite UO_2 (U-doped glasses). The Soxhlet corrosion resistance of the partially crystallized glasses is a factor of up to five better compared to the parent glasses.

	WG 119	WG 122	WG 123	WG 124
SiO_2	66	66	66	70
Al_2O_3	-	-	5	2
Fe_2O_3	10	-	-	-
Fe_2O_2	-	10	5	6
Na_2O	6	6	6	4
K_2O	6	6	6	1
MgO	6	6	6	5
CaO	6	6	6	5
BaO	-	-	-	2
MoO_3, Cu_2O_3, CuO, NiO, TiO_2	-	-	-	5

Table 11 : Nominal composition of the inactive FLK reference glasses (in mole %)

- Activity release from ignited bituminized waste forms

Contractor : KfK, Karlsruhe (240-81-13 WASD)

The experiments with bituminized evaporator concentrates with inactive and active samples on the laboratory scale and with inactive full-scale samples containing Eu_2O_3 as PuO_2-simulate were finished. By performing laboratory experiments with inactive samples of the same composition as the full-scale sample it could be shown, that the Eu-release in the laboratory experiments is comparable with the Pu-release from active samples under the same experimental conditions.

First experiments with inactive simulated full-scale samples cemented evaporator concentrates were performed. Under the experimental conditions (30 min. oil fire) a weight loss of about 3 wt. % was measured, independent if a closed or open drum was used.

Laboratory experiments with tracered samples (Cs-137, Pu) are under way.

1.2. CONDITIONING OF HIGH ACTIVITY SOLID WASTE : FUEL CLADDINGS AND DISSOLUTION RESIDUES

All of the eight experimental activities comprised under this chapter continued with work during the reporting period.

Three main topics on research can be distinguished. They concern first the development of methods for embedding the waste scrap into a solid and resistant matrix material in order to confine the radioactivity and to prevent it from dispersion. The matrix materials being investigated, are lead alloys, ceramics and compacted graphite or aluminium powder. Next to the usual cement matrix, they constitute potential embedding matrices with interesting properties. However, none of them has yet been tested under representative radioactive conditions, the methods being in their exploratory stages of development.

The lead alloy matrix shows still an unsatisfactory bonding of the matrix material with the embedded cuttings of fuel hulls. Small crevices at the interface give rise to activity release.

The use of lead alloys with lower melting temperature is being studied to overcome this problem.

The compounds of hulls in compacted graphite or aluminium powder show positive results so far, although in one of the matrix variants, in the graphite/nickel-sulfide composition, crevices are being observed.

A good leach resistance is reported from the ceramic matrix materials. Different aspects of the fabrication process need further development work.

A second topic concerns the treatment of fuel hulls by melting or chemical conversion. The melting process has been experimented with real, radioactive hulls. Activity redistribution has been observed during the high temperature treatment and the corresponding phenomena are going to be further investigated.

The work on the chemical conversion of Zircaloy hull pieces into Zirconium-oxide (Zirconia) was brought to an end and will no longer be continued. Nevertheless, useful conclusions could be drawn from it.

Under a third heading, those projects are grouped which deal with the determination of the properties and characteristics of the waste materials themselves or the conditioned waste products. The two experimental works being undertaken at present, concern the characterization of cemented hulls and the pyrophoricity of Zircaloy fines.

Interesting results have been obtained concerning in particular the release of tritium (hydrogen) and krypton activity from the cement compounds.

As to the pyrophoricity of Zircaloy fines, the experimental results are presented which have been observed, under well defined conditions, with non-radioactive material in a first stage. Comparison tests will follow with radioactive material.

In January 1982, the Commission has organized a specialists meeting on the methods for conditioning and storage of spent fuel element hulls*. The intention was to make a review of the state of the art based on a joint study drawn up by KfK and CEA in the scope of the first Community programme.

The following contracts are reported :

1.2.1. EMBEDDING INTO MATRIX MATERIAL

Press compaction and encapsulation of hulls into lead alloy matrix

Contract 167-81-2, SCK/CEN, Mol.

Scope and Objective

The present studies primarily aim at an evaluation of the densification and product quality obtained in active conditions. Small-scale tests are therefore made with hulls from irradiated fuel rods. By compaction and subsequent embedment, samples are produced for leach tests which will bring information on the immobilization of the contaminating nuclides.

In addition to the active experiments, the corrosion and wetting behaviour of different alloys are examined in a continued search for the most efficient matrix material.

Basic equipment for a hot-cell test facility is under development in view of a future demonstration of the process at a kilogramme scale with active hull waste.

Progress and Results

Active tests

Compaction and embedment tests have been made which claddings from irradiated MOX-fuel. Zircaloy hulls were obtained from Pu-recycle fuel rods (3.1 w/o Pu) irradiated to about 30.000 MWd/tHM in BR3, stainless steel hulls from DFR-fuel rods (30 w/o Pu) irradiated to 5.3 % FIMA.

- Characterization of the hull waste

  The activities of the fission products and TRU-elements present on the hull surfaces were determined by alpha and gamma spectrometry. In addition, Zircaloy samples have been examined by microprobe analysis to obtain information on the nature of the nuclide deposits.

Contamination levels given below are expressed as percentage of the nuclide content in the fuel, that is associated with the cladding. The reference data also are based on radiochemical analysises.

. Stainless steel hulls

Two batches totalizing about 326 g, were received from FBR fuel dissolution experiments. The material had been severely attacked by the nitric acid dissolvent in one case, to a lesser extent in the other. This had a drastic effect on the contamination levels found for Pu (0.04 % as compared to 0.70 %) and Cs (0.03 % and 0.50 %). In contrast the Ru-deposits (7.0 % and 10.0 %) and Ce-contamination (0.55 % and 0.50 %) did not differ much.

. Zircaloy hulls

Single hull sections from the BR3-rods, separated from the fuel by mechanical action and subsequently leached during 4 h in an excess of boiling 8 M-HNO_3, have been analyzed at several occasions. The average contamination levels thus found were : Pu : 0.34 % of its content in the fuel; ^{134}Cs : 0.94 %; ^{137}Cs : 0.78 %; ^{106}Pu : 0.27 %.

Microprobe analysis of hull samples prepared in the same way indicated that remainings of the fuel-cladding interaction products formed during the irradiation, were present on the inner surfaces and thus seem to resist to the acid leach. The oxide layer on the base metal contained cesium zirconate at some places. A distinct second layer was made-up of Zr(Sn)-Cs-U-Pu-O. Nodules of $(UPu)O_2$ were also seen in this layer.

Analytical data for the 203 g batch of zircaloy hulls, prepared in a 8 h fuel-dissolving run with 8 %-HNO_3, are not yet available. Results will be reported later.

- Embedment tests with uncompacted hulls

Zircaloy hull sections from the BR3-rods have been embedded, without preliminar compaction, in Pb 1.5 Sb at 893 K and in Pb 1.5 Sb and Pb 2 Sn 0.5 Ca at 648°K. The products were afterwards leach-tested in simulated claywater at ambient temperature.

From the two samples prepared at 893 K, up to 0.2 % of the Pu content and 21 % of the Cs were released in the first six days of exposure, up to 0.4 % of the Pu and 50 % of the Cs after 72 days.

The 648 K-samples on the contrary lost only 0.01 % of Pu and 0.04 - 0.05 % of the Cs in 7 days.

These results, added to previous data for bare hulls and samples prepared at 723 K, suggest that the contaminating nuclides are brought to a more releasable form during the embedment if this is carried out at temperatures above 673 K, whether by thermal decomposition or by interaction with the lead alloy. Further work should be directed therefore to a reduction of the embedment temperature by using alloys with a lower casting temperature.

- Compaction of irradiated hulls

A compaction unit, providing a maximum force of 0.6 MN, was installed in the hot cell and fitted with a die of 50 mm diameter. Compaction of 100 g - batches of hulls were produced (see table 12).

Test No	Material	Hull dimensions ID/OD (mm)	Weight of hulls (g)	Compaction pressure (MPa)	% TD obtained
31	DFR/stainless steel	5.1 /5.84	86	300	65.2
32	"	"	83	250	63.2
33	"	"	85	200	57.6
35	BR3/Zircaloy 4	7.58/8.7	68	200	53.8
36	"	"	67	200	53.8
37	"	"	67	250	54.6

Table 12 : Densification rates obtained with press-compaction

- Embedment of compacted active hulls

The compacts formed with the DFR and BR3 hulls have been embedded separately to obtain six samples for leach tests. One specimen of each was prepared at 723 K with Pb 1.5 Sb, the others at 623 K with Pb 4 Sn 12 Sb.

Visual inspection indicated that all samples are sound. In order to allow leach testing of the bottom and top surfaces separately, polyethylene cylinders, serving as leachout containers, have been fixed to both sides with Araldite.

This also prevents the exposed surface area of being contaminated during the manipulations in the cells. The leach tests will be started at the beginning of 1983.

Testing of embedment alloys

- Corrosion resistance

Low-alloyed lead compositions are exposed, at 298° K and 323° K, to simulated claywaters and salt brines in the laboratory, and at 286°K to direct contact with the clay formation at the near-surface testing site of Terhagen. Samples have been withdrawn for examination after 4 and 9 months of exposure. As extrapolated from the weight changes measured after 9 months, the highest corrosion rates range from 0.83 to 1.84 $\mu m.y^{-1}$ in clay waters.

Contact with clay resulted in metal losses of the order of 0.13 to 0.69 $\mu m.y^{-1}$.

In the salt brine, the rate was 0.40 to 1.49 $\mu m.y^{-1}$ in the 9 months test at 298°K. At 323°K this increased to values of 2.48 to 12.2 $\mu m.y^{-1}$.

- Wetting characteristics

Tests with the sessile drop method, carred-out at the Max Planck Institut für Metallforschung at Stuttgart, indicated that oxidized zircaloy was not wet by Pb, Pb 10 Sn and Pb 1.5 Sb, at 723°K in a pure argon atmosphere. In experiments made at the SCK/CEN, zircaloy plates were contacted, under a vacuum of less than 0.1 Pa or in an argon - 5 % H_2 stream, by Pb 0.8 Sb and Pb 0.1 Zr 2.2 Mg for 3 h and 5 h at 723°K or 823°K. There was no wetting either.

Higher-alloyed lead compositions (Pb 4 Sn 12 Sb and Pb 10 Sn 15 Sb) behaved no better in 3 h and 5 h-tests made at 623°K.

Hot-cell test facility

A 3 MN-compaction press for use in hot-cells was designed. It is a two column unit with an upward stroke. Hull waste will be loaded to the press in steel cans of diameter 100 mm and height 140 mm. The punch, die and anvil can be remately exchanged. Provisions are build-in that allow a future adaptation for hot-pressing at temperatures up to 723 K.

Delivery of the press is foreseen for february 1983.

Embedding of hulls into graphite and aluminium

Contract : 169-81-2 WASD, NUKEM, Hanau.

Scope and Objective

The aim of this research and development program was to find a material suitable for the embedding of spent fuel hulls and for the final disposal in deep salt formations.

Three matrix materials - graphite/nickelsulfide, aluminium, graphite/sulfur - and the corresponding embedding processes were investigated and developed.

Progress and Results

- Graphite/Nickelsulfide Matrix

  The physical properties as well as the corrosion rates of molded graphite/nickelsulfide samples, consisting of 43.7 w/o graphite, 41.3 w/o nickel, and 15.0 w/o sulfur, have been determined. The corresponding values are listed in tables 13a and 13b.

  The leaching rates of waste-containing graphite/nickelsufide samples, i.e. cladding sections and feed clarification sludge, have not been established, because in saturated brine at 90° C most of the samples cracked within a period of 6 months.

- Aluminium Matrix

High-density aluminium samples (> 98 % of th. density) with a core loading of about 50 w/o of hulls were produced by the warm-pressing-process. A temperature of 450° C and a pressure of 50 MN/m^2 was maintained for one hour. The body was than ejected and slowly cooled to room temperature (within 6 hours).

The physical properties and the corrosion and leaching rates of aluminium samples are listed in tables 13a and 13b.

- Graphite/Sulfur Matrix

A bench-scale embedding process for cladding sections in graphite/sulfur matrix (consisting of 80 w/o graphite and 20 w/o sulfur) has been developed (Ø = 66 mm; L = 70 - 80 mm); subsequently it was scaled up to a technical scale (Ø = 190 mm; L = 200 mm). At first the floating die was filled with molding powder (80 w/o graphite, 20 w/o sulfur) and 25 mm-cladding sections in such a way, that the waste containing core was surrounded by a waste-free shell. Then the slightly premolded body (~ 3 MN/m^2) was evacuated, heated to 130° C, molded with a pressure of 20 MN/m^2 at 130° C, and heated to 150° C. After holding the temperature (150° C) for 10 minutes the body was cooled and ejected at 80° C. The steel cladding section loading of the resulting body was 14 w/o, the density lay between 97 % and 98 % of the theoretical value.

The physical properties as well as the corrosion and leaching rates (in saturated brine at 90° C) of graphite/sulfur samples have been determined (see tables 13a and 13b).

Compared with the other embedding materials and processes the encapsulation in graphite/sulfur matrix is distinguished by the following advantages :

- extremely low leaching rates in saturated brine (up to 90° C);
- sufficient mechanical and thermal stability;
- very simple process because of :
  - . reduced temperature ($\leq$ 150° C instead of 450° C required for aluminium and graphite/nickelsulfide);
  - . low pressure (≤ 20 MN/m^2 instead of 50 - 100 MN/m^2).

MATERIAL / PROPERTIES	Graphite/ Nickel Sulfide Matrix	Aluminium Matrix	Graphite/ Sulfur Matrix
Density (g/cm^3)	3,28	2,67	2,17
Th. Density (%)	94,8	98,9	97,7
CTE $(\mu m/m \cdot K)$	$\perp$ 4,92 $\parallel$ 11,82	23,1	-
Heat Conductivity $(W/cm \cdot K)$	$\perp$ 0,92 $\parallel$ 0,29	1,26	$\perp$ 0,72 $\parallel$ 0,21
Compressive Strength (MN/m^2)	$\perp$ 74,5 $\parallel$ 98,9	-	$\perp$ 54,2 $\parallel$ 59,1
Tensile Strength (MN/m^2)	$\perp$ 20,8 $\parallel$ 11,5	-	-
Bending Strength (MN/m^2)	$\perp$ 69,5 $\parallel$ 23,3	> 170	$\perp$ 42,5 $\parallel$ 23,3
Young's Modulus $(MN/m^2) \times 10^3$	$\perp$ 76,8 $\parallel$ 17,7	-	$\perp$ 58,7 $\parallel$ 22,2

$\perp$ radial

$\parallel$ axial

Table 13a : Physical properties of three matrix materials

MATERIAL / PROPERTIES	Graphite/ Nickel Sulfide Matrix	Aluminium Matrix	Graphite/ Sulfur Matrix
Leaching Rate for Cs at 90 °C ($g/cm^2 \cdot d$)	-	$< 3 \cdot 10^{-5}$	$< 1 \cdot 10^{-6}$ – $< 8 \cdot 10^{-6}$
Corrosion Rate			
at 90 °C ($g/cm^2 \cdot d$)	-	$3,9 \cdot 10^{-4}$	$< 9,5 \cdot 10^{-5}$
at 100 °C ($g/cm^2 \cdot d$)	$2,5 \cdot 10^{-6}$	-	-
at 150 °C ($g/cm^2 \cdot d$)	$2,0 \cdot 10^{-5}$	-	-

Table 13b : Leach and corrosion resistance in saturated brine of three matrix materials

Embedding of hulls and dissolution residues into alumino-ceramics

Contract : 172-81-2 WASF, CEA, Saclay.

Scope and Objective

- The work covered by the above-mentioned contract aims to develop and make "embedded waste" blocks consisting of a first central barrier (Al_2O_3 core) in which the wastes or dissolution residues are embedded and a second impermeable barrier or enveloppe, made also of alumina (figure 14).

- The waterproof enveloppe is made up of a high-purity alumina, impervious to fluids and very little leachable by slightly acid or slightly basic waters.

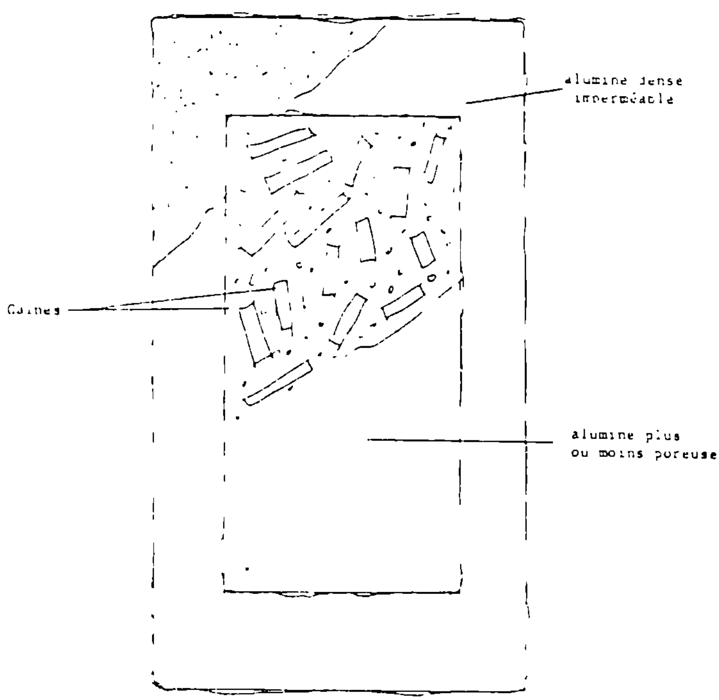


Fig. 14 : Schematic presentation of the embedded waste block

Progress and Results

- Blocks with good physical and mechanical and excellent impermeability properties have now been obtained ; their dimensions are : external diameter, Ø = 150 mm, total height, h = 300 mm, thickness, e = 20 mm.

  The next stage should be the production of larger blocks : Ø = 400, h = 600 - 800 mm, e $\cong$ 40 - 50 mm.

- The cladding or residue content of the central part of the blocks can range from 50 to 75 % cladding by weight according to the degree of lamination of the cans.

- Characterisation of the "embedded waste" blocks

  . Apparent density

  The density of the waterproof envelope lies between 3.75 and 3.80 (theoretical density of alumina : 3.98). That of the core - more porous in the manufacture - reaches 2.80 to 2.85.

  . Porosity/permeability

  The pore size and distribution were determined by mercury porosimetry. This method gives the porosity accessible to fluids and covers pore radii within the 100/200 µm to about 15 Å range.

  Results : Porosity expressed in % total volume :

Waterproof envelope	Al_2O_3	0.38
Porous core	Al_2O_3	40.0

  Gas permeability under P = 50 bars is practically zero.

  . Lixiviation

  Leaching tests are in progress.

  . Mechanical properties

  The breaking load under compression and the hardness were measured at room temperature.

	Al_2O_3 (E)	Al_2O_3 (C)
R_c, in Pa	16.10^8	7-8 10^8
hardness, in Vickers	1.500	200

Solidification of alpha-bearing wastes into a ceramic matrix

Contract : 173-81-2 WASD, KfK, Karlsruhe.

Objective and Scope

This program aims to continue the investigations on :

- the solidification of original alpha-bearing waste from different orig: in a sintered alumo-silicatic matrix and the characterization of the final products,
- the development of a process to produce alpha-waste ceramics on a technical scale.

Progress and Results

- Product investigations

Within the working period of 1982 experiments were carried out to investigate the suitability of an alumo-silicatic matrix, consisting of 78-87 wt. % Al_2O_3 and 22-13 wt. % SiO_2, for :

a) original dissolver residues from the fuel element dissolution,

b) Plutonium ash from the dry incineration of burnable apha-waste.

For the production of the green pellets of the original-dissolver-residue ceramics (matrix material : 78 wt. % Al_2O_3/22 wt. % SiO_2) a remote controlled extruder for total amounts smaller than 100 g of greenware had to be constructed, because only 13,5 g of original dissolver residues were available. During the heat treatment of the pellets (1300° C/1 h) no Ruthenium in the off-gas system could be observed. Only minor amounts of RuO_2 have been detected at the end of the hot part of the furnace. The average density of the products formed is 2,32 g/cm^3. The alpha-emitters are distributed homogeneously within the specimen. The following product investigations are still going on : detailed phase composition, specific activity, open porosity, mechanical strength, leach resistance against salt brines and distilled water at room temperature and 55° C.

Ceramic products containing 20 wt. % Plutonium ash from the dry incineration of combustible alpha waste had been synthetized using different kinds of matrix materials as well as different preparation methods. The matrix compositions, the forming procedure, the heat treatment are reported together with measured product properties in table 14 (density, mechanical strength, leach rate, phase composition). A higher Al_2O_3 content within the matrix material yields increasing densities and mechanical stabilities of the final products, while the leach rates show no significant change in function of the matrix composition after 14 days leaching time in distilled water at room temperature.

Matrixcomposition $\frac{Al_2O_3}{Al_2O_3 + SiO_2}$ - ratio		Forming procedure	Sintering- temperature [°C]	time [h]	Density [g/cm^3]	Mechanical strength [kp/cm^2]	Phases present	Leach rate for Pu after 14 day in H_2O-dist(RT) [$g/cm^2 \cdot d$]
0,38	(Kaoline + Bentonite)	* e	1300	1,5	1,90(3)	640(100)	Mullite, PuO_2 glassy phase[2]	$9,1 \cdot 10^{-7}$
0,78	(reactive Corundum + Kaoline)	* e	1300	2,0	2,75(4)	1710(95)	Corundum, PuO_2	$1,1 \cdot 10^{-7}$
		**p	1600	1,0	2,63(3)	1633(105)		$2,9 \cdot 10^{-7}$
0,87	(reactive Corundum + Kaoline)	* e	1300	2,0	2,68(2	1518(178)		$6,2 \cdot 10^{-8}$
		**p	1600	1,0	2,86(3)	2121(560)		$3,6 \cdot 10^{-7}$

* extruded

** cold-pressed

Table 14 : Properties of alumosilicatic products containing 20 wt.% of Plutonium ash

In order to achieve a suitable package for final disposal, characterized by easy handling and storage of the ceramic pellets, experiments were carried out by embedding them into a monolithic block of an inactive glass as an overpack. Monolithic blocks of a volume of 1.2 l could be prepared by filling a ceramic container together with ceramic pellets and borosilicate glasspowder, heating up the assemblage to 1300° C and cooling it down 0.6° C/min. The ceramic pellets, the glass overpack, the container material form one mechanically stable unit. Only few cracks and bubbles are detectable within the glass overpack. The filling degree was 41 %.

- Evaluation of a technical process

  Evaluation of the technical process has been continued by experiments concerning optimalization of the heat treatment of ceramic greenware, the homogeneity of the ceramic Al_2O_3-SiO_2 mixture and the development of a flow sheet diagram.

1.2.2. MELTING AND CONVERSION OF ZIRCALOY

Conditioning of cladding waste by eutectoïdic melting and by embedding in glass

Contract : 170-81-2 WASF, CEA, Marcoule.

Scope and Objectives

The goal of the study is the compaction, mainly by eutectoïdic melting (using copper) of radioactive Zircaloy 4 cladding hulls generated by the reprocessing of LWR fuel.

Investigations are concerned with the measurement of volatilisation or off gas release (tritium) and the characterization of the final material, alloy or composite metal/glass, particularly the stability as regards to leaching. The α β γ activity of the hulls is mesured to draw an activity balance.

Progress and Results

The balance of volatile elements which was evaluated at the end of 1981 during the first melting, has gone further into details.

The zircaloy-Cu ingot, which was made, was leached over 160 days with tap water at room temperature.

- Specific activity of the hulls measured from dissolution

  The dissolutions are achieved using a HNO_3 3N/HF 3M mixed up and about 10 g of zircaloy corresponding to 2 to 4 pieces of hulls. Depending on the source of the waste, with different burn up and reprocessing treatment, the gross β γ activity is in the range of 1.5 and 3 Ci/kg mainly due to Sb^{125} and to $^{137+134}Cs$.

  The gross α activity of the Würgassen hulls seems yet smaller than the Borssele one : 1 $mCi.kg^{-1}$ for the first to be compared to 20 to 35 $mCi.kg^{-1}$ for the latter. The type of the α contamination is not accurate for the moment (table 15).

-

		$^{144}Ce+^{144}Pr$	^{125}Sb	$^{106}Ru+^{106}Rh$	^{134}Cs	$^{137}Cs+^{137m}Ba$	^{60}Co	$^{90}Sr+^{90}Y$	$\Sigma\ \beta\ \gamma$	$\Sigma\ \alpha$
coques Borssele	$\mu Ci.g^{-1}$	95	750	253	123	937	33	646	2837	23
	%	3,3	26,4	8,9	4,3	33,0	1,2	24,8	100	/
Coques Würgassen	$\mu Ci.g^{-1}$	35	643	92	57	473	47	289	1635	1,2
	%	2,1	39,3	5,6	3,5	28,9	2,9	17,7	100	/

Table 15 : Mean specific activity of the Borssele and Würgassen hulls in june 1982

- Volatility occuring in the course of the first eutectoïdic meting

The activity of volatile elements from 379 g of Borssele hull which is trapped, is about 35 mCl (βγ) mainly due to ^{137}Cs (8 % of the involved ^{137}Cs activity) as shown in table 16. The activity is mainly gathered at the top of the muffle which is the first cold part met by the stream (fig. 15).

	$(Ce + Pr)^{144}$	Sb^{125}	$(Ru + Rh)^{106}$	^{137}Cs
Activité βγ des coques $(mCi.kg^{-1})$ au 24.04.1982	80	693	221	457
Activité piégée $(mCi.kg^{-1})$	0,167	0,089	0,231	34,48
% d'activité piégée	0,2	0,01	0,1	7,5

Table 16 : Trapped activity versus total activity

- Leaching at room temperature of the first ingot made from Borssele hulls

The duration was over 160 days. It was carried out in Vulcain cell under daily water removal.

The very high value (table 17) of the various leaching rates for Cs, Sr, Ru, Ce, Sb, Co (10^{-5} to 10^{-7} $g.cm^{2}.d^{-1}$) could be explained by considering that the activity is in fact contained in a surface layer, the cross section of which is much lower than the one of the ingot which was taken into account to calculate the leach rate.

	β	Cs	Sr	Ru	Ce	Sb	Co
$^{1}20\text{-}40$	$1,2\ 10^{-4}$	$1,6\ 10^{-4}$	$2,6\ 10^{-4}$	$4,3\ 10^{-6}$	$1,7\ 10^{-5}$	$2,1\ 10^{-7}$	$6,9\ 10^{-5}$
$^{1}120\text{-}160$	$1,5\ 10^{-5}$	$2,8\ 10^{-5}$	$3,3\ 10^{-5}$	$4,7\ 10^{-6}$	$1,1\ 10^{-5}$	$1,9\ 10^{-7}$	$1,1\ 10^{-4}$

Table 17 : Assessment of the leach rate of various elements included in the first zircaloy-Cu Borssele ingot

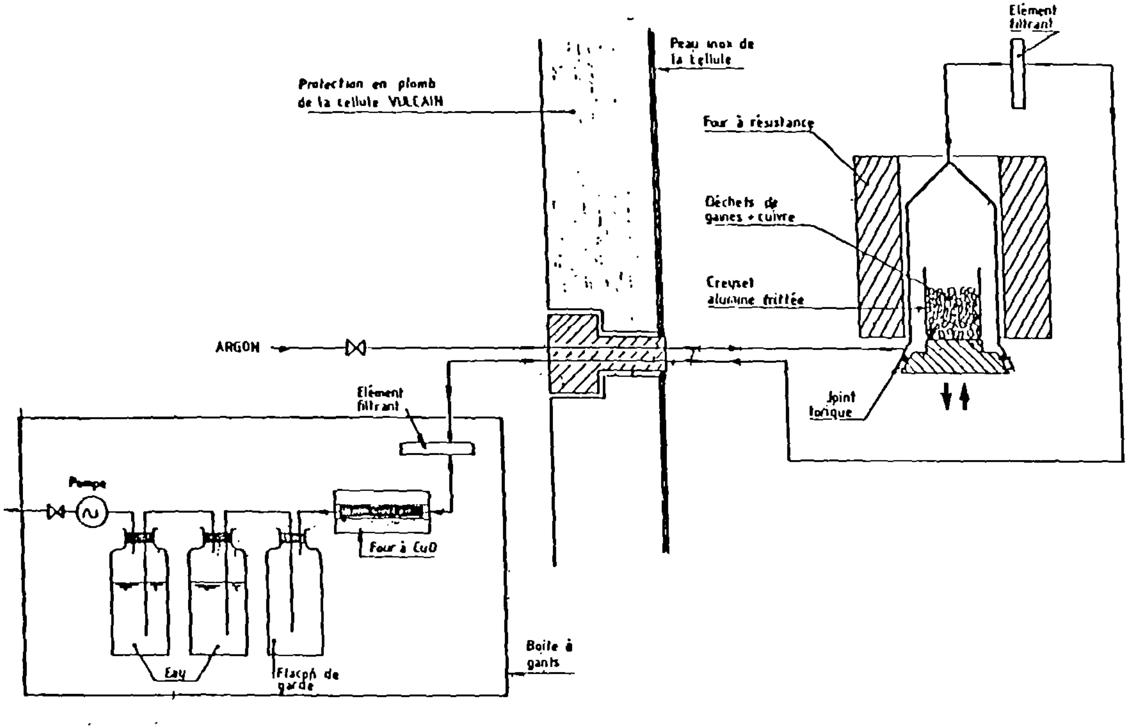


Figure 15 : Principle of the melting and off gas treatment devices

This rate is expressed according to the usual formula :

$$L\ (g.cm^2.d^{-1}) = \frac{a}{A} \times \frac{P}{S}$$

a : activity of the leachant

A : calculated gross activity of the ingot

P : mass of the ingot (g)

S : surface area of the ingot (cm^2)

Conversion of zircaloy cladding into zirconia

Contract : 171-80-2 WASUK, UKAEA, Harwell.

Scope and Objective

This aim of this research programme, which has now been completed, has been to develop a process for the conversion of Zircaloy fuel element cladding to a stable immobilised oxide product, thus avoiding the problems associated with the handling and disposal of Zircaloy in the metallic form. In the conversion process (see figure 16) Zircaloy is dissolved in 3% ammonium fluoride and then precipitated as hydrous zirconium oxide using ammonia solution (the latter step yielding ammonium fluoride which is recycled). The hydrous oxide, after washing and filtration, can then be immobilised in massive form an the present studies have investigated both incorporation with cement and hot pressing.

Progress and Results

- Conversion process development

  The investigation of the removal of residual fluoride from the hydrous zirconia precipitate by multistage countercurrent batch washing has been completed with a series of experiments carried out in a newly constructed five stage process. The data obtained showed that attainment of the 80 % residual fluoride removal necessary to give an oxide suitable for hot pressing requires a wash volume of

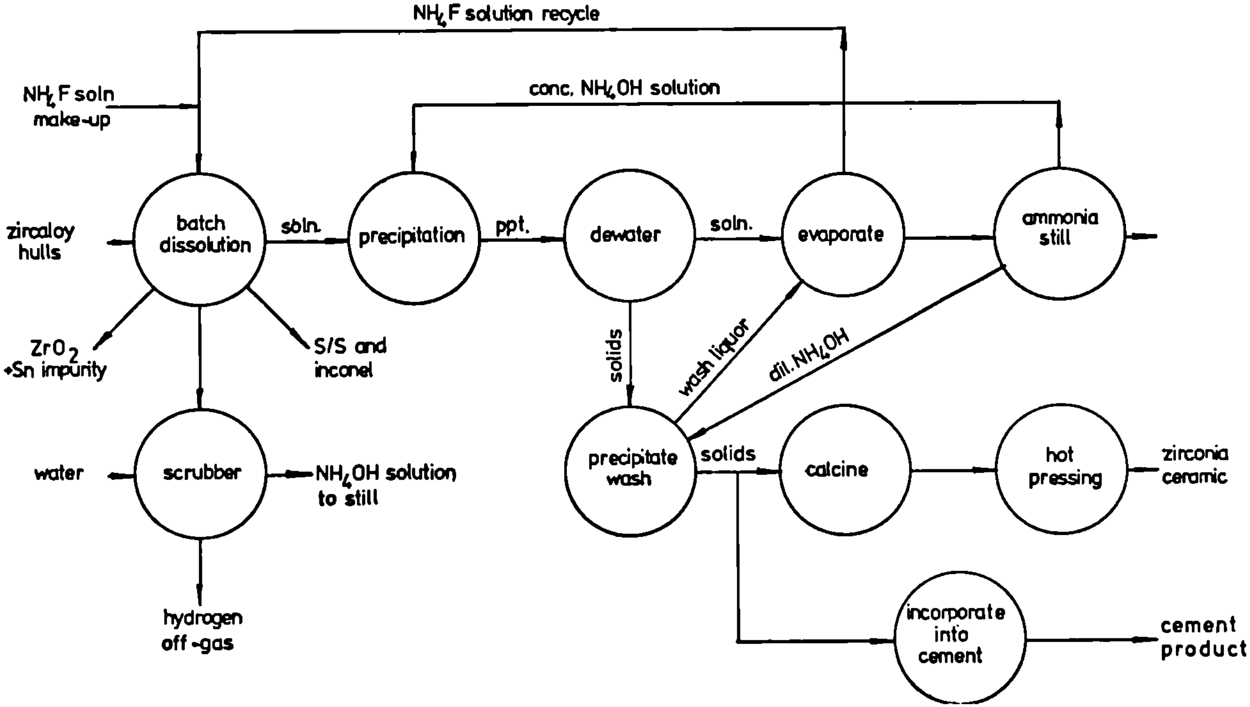


Figure 16 : Zircaloy conversion process flow diagram

5 litres per mole of zirconium in the five stage process, as compared with 12 litres per mole in a three stage plant and 15 litres per mole for single stage batch washing. The multistage batch washing results have been used to determine zirconia/fluoride/ammonia solution equilibrium data.

- Active demonstration

The proposed conversion process has been demonstrated in a fully-active test using a 50 mm long irradiated Zircaloy hull from a 5-year cooled fuel pin. During dissolution of this hull in 3M ammonium fluoride solution, reaction was observed to occur at the cut ends and at the internal surface of the hull only, with no indication of reaction on the outer surface. Dissolution was followed by precipitation of the hydrous oxide using ammonium hydroxide solution. After washing samples of the oxide produced they have been both hot pressed and incorporated into cement blocks, giving immobilised products which have been leach tested.

In order to prevent the build-up of some fission products, particularly caesium, in the ammonium fluoride liquor recycled from oxide precipitation to the dissolution stage, their adsorption from the dissolver solution onto selective ion exchange materials, ammonium hexacyanocobalt ferrate (ACFC) and clinoptilolite, has been studied. The results show decontamination factors for caesium of approximately 70 and 3 using ACFC and clinoptilolite respectively.

- Oxide incorporation into cement

The incorporation of the washed zirconia into cement has been studied and the effect of washing efficiency determined. The work has shown that the compressive strength of the concrete produced is reduced as the concentration of residual fluoride increases. However, washed material with a fluoride to zirconium mole ratio of 1.4:1 produced a compact of strength well above the IAEA transport recommendations. The results also indicated that the strength of the concrete was independent of the ammonium ion concentration.

- Oxide consolidation by hot pressing

  Samples of consolidated oxide have been prepared by uniaxial hot pressing, using graphite dies, and have been subjected to leach tests which have shown the leach rates to be approximately 2×10^{-5} cm/day for the first 28 days. Thereafter, the leach rates became negligibly small due to the formation of a protective oxide layer of pure ZrO_2.

  Studies on the hot isostatic pressing of hydrous zirconia using deformable steel cans for powder containment have demonstrated that, although a ceramic block of a high density could be formed, the product was friable, due possibly to reaction between the oxide and the containing can.

- Process flowsheets and overall assessment

  Process flowsheets, for a Zircaloy throughput of 250 kg/day, have been produced for the conversion routes involving both hot pressing and incorporation into cement. In the hot pressing route there is a secondary waste stream of 1000 litres/day of 3.8M ammonium hydroxide solution, whilst for the cementation route the addition of 400 litres/day of 3.4M ammonium hydroxide solution would be required with no additional waste stream. However the hot pressing route gives a volume reduction of 4 whilst the cementation route gives a volume increase of 8.

  The process information obtained during the course of the work under this contract is now being assembled in a final summary report. This will present preferred flowsheet options and will make a critical overall assessment of the Zircaloy conversion process.

1.2.3. WASTE PROPERTIES AND CHARACTERIZATION

Characterization of the final hulls-concrete product

Contract : 168-80-2 WASD, KfK, Karlsruhe.

Scope and Objectives

The determination of repository relevant properties of LWR clad waste products fixed into concrete. Essentially, the investigations included dynamic leaching tests with irradiated KWO clads as well as gas release tests with inactive and tritiated Zircaloy clads respectively, all of them performed on laboratory scale.

The leachants used were distilled water, saturated sodium chloride solution and quinary carnallite brine. The tests were performed at room temperature and standard pressure.

To determine hydrogen generated by radiolysis, concrete and concrete/ Zircaloy specimens were exposed to gamma-irradiation in the FR2 test-reactor decay basin. The activity release from tritiated single Zircaloy clads fixed in concrete matrix was measured in the argon scavenger gas stream.

Progress and Results

At the end of 550 days of leaching with brine (730 days with H_2O) a medium-independent mean HTO leaching rate of approximately 2×10^{-7} cm.d^{-1} was determined.

The maximum leaching rate of actinides (7×10^{-5} cm.d^{-1}) was obtained with saturated NaCl solution.

Caesium leaching gave values of 5×10^{-3} cm.d^{-1} (NaCl), 3.5×10^{-3} cm.d^{-1} (H_2O) and 1.5×10^{-3} cm.d^{-1} (quinary brine).

The radiolytic rate of H_2 formation of 0.15 cm^3 H_2 g^{-1} cement ($W/C = 0.4$) at 10^{-8} rad did not yield different values for specimens consisting of pure concrete and concrete/Zircaloy clads, respectively.

The typical tritium release characteristic initially follows a degressive course and after about 130 days it becomes proportional with time. Within the latter range relative release rates of $2.3x10^{-7}$ a^{-1} (at room temperature) and $1.3x10^{-6}$ a^{-1} (at 100° C) were evaluated. The H_3-release rate from a WAK waste package containing hulls from the KWO power reactor was $1.5x10^{-9}$ a^{-1} and for Kr-85 $4.3x10^{-3}$ a^{-1}.

Based on these measured release rates and the limit value of admissible concentrations, the air throughput required in a man operated final repository was estimated.

Pyrophoric behaviour of Zircaloy chips and fines

Contract : 246-18-2 WASD, KfK, Karlsruhe.

Scope and Objectives

This experimental program serves to assess the fire and explosion hazards of Zry-fines arising in a reprocessing plant during shearing of fuel assemblies, chopping of fuel pins or compaction of leached hulls. The Federal Institute for Materials Testing of Berlin (BAM) tests non-irradiated Zry-dust and defines the test procedure for the investigations on irradiated Zry-dust to be performed by KWU in the Hot Cells of Karlstein. A comparison between irradiated and non-irradiated Zry-dust will be made.

Progress and Results

- Sample preparation

  No representative Zry-dust from a reprocessing plant will be available for our investigations. It is planned to perform the tests on active Zry-fines generated from Zry-hulls of irradiated LWR fuel with a tool specially developed for this purpose. The same tool, a disk file, has been used to produce Zry-fines from non-active Zircaloy for the tests subsequently carried out by BAM.

- Ignition tests on dust layers

  Investigations have been conducted on fractions of dry Zry-filings exposed to various ignition sources. The coarser fraction has a grain size of > 100 μm, the finer fraction one of < 200 μm. The results show that this material is very easy to ignite. Also sparks from Zircaloy caused by friction and impact may ignite Zry-powder. The minimum ignition temperature of Zry-filings on a hot plate, which is called minimum ignition temperature of a dust layer, and in a hot enclosure, which is called self-ignition temperature, has been determined. The minimum ignition temperature of a dust layer was measured under VDE Regulation 0165 for filings < 200 μm to be 375° C. For the coarse filings > 100 μm dust layers did not ignite up to a temperature of 400° C. The self-ignition temperature has been measured in the Gliwitzky apparatus for the fraction < 200 μm and > 100 μm to be 260° C and 270° C, respectively. The minimum ignition temperature of dust layer and the self-ignition temperature are a criterion for the maximum admissible surface and ambient temperatures, respectively. For the practical purposes one has to keep in mind the dependence of the ignition temperatures on layer thickness and dust volume.

- Ignition tests on dust suspensions

  With the Godbert-Greenwald furnace the minimum ignition temperature has been determined according to the draft of an IEC standard. For the fraction of Zry-filings < 200 μm, the minimum ignition temperature was measured to be 460° C.

- Maximum explosion pressure and rate of pressure rise

  These parameters have been determined in the 20 l sphere. The maximum pressure was 4.8 bars and the maximum rate of pressure rise was 53 bars s^{-1} (both values relate to a volume of 1 m^3). The results can be applied in the design of explosion protection methods on an industrial scale. The active experiments in the hot celles will only be feasible with the 20 l sphere. The data obtained will be applicable to an industrial situation if there is a good correlation with the data of the 1 m^3 vessel for any type of dust. Consequently, intercomparison tests were made and a correction factor was elaborated for the range of dust explosion data concerned.

In practice, the maximum pressure is required if the plant is to be designed to withstand the full explosion pressure of a dust explosion; the maximum rate of pressure rise is used in determining explosion relief and automatic suppression requirements.

- Maximum permissible oxygen concentration to prevent explosion

The experiments were carried out in the 20 l sphere with argon as an inert gas. The criterion of an explosion was a pressure during the ignition tests 0.1 bar above the blind tests and, moreover, the identification of oxidation products of Zry after the experiment.

The results showed that a dust explosion could still be triggered in an atmosphere of 1 part by volume of oxygen and 99 parts by volume of argon. Only in pure argon this was no longer possible. Hence, it follows that the maximum permissible oxygen content when inertizing with argon is 0 %.

The chemical inertness of argon allows the application of the results to irradiated Zry-fines. For any other gas, verification of its effect on active Zircaloy is indispensable.

1.3. TREATMENT AND CONDITIONING PROCESSES FOR LOW AND MEDIUM ACTIVITY WASTE

In this programme action, the main emphasis is placed on treatment processes since only three R&D activities out of eleven are concerned, at various extents, with the conditioning aspects.

Regarding treatment processes which can be regrouped within three main categories (ion-exchange, chemical precipitation – possibly coupled with the use of UF membranes - and particular techniques) significant steps forward and, in some cases, new orientations in the conducting of the researches, were taken in the last period.

Particularly, the good promise of three processes (combination of UF with floc processes, testing of an industrial flocculator prototype and application of the titanium hydroxide particles) was continued by tests on various genuine radioactive wastes.

On the contrary, application of extraction chromatography, as a technique to test the hydroxamic function failed when decontamination of strongly acidic wastes is concerned. Restrictions in the application field of direct use of UF menbranes for the decontamination of various LLLW's arising from a fuel fabrication plant, were also confirmed.

As for the development of very advanced treatment processes such as those based on electrical methods, it was decided to focuss further R&D activities on particulate separation (electro-osmosis) and electrochemical ion exchange since the application of electrodeposition was still fraught with many difficulties.

Due to some delay in the availability of shielded glove-boxes, as well as the break-down in 1982 of the WAK-reprocessing pilot plant, experiments on actinide separation from real MAW-concentrate had to be postponed for about one year.

Concerning conditioning processes, R&D actions were limited to the pursue of parametric studies on cementation and to drying/vitrification experiments on simulated high-level sludges, resulting from the treatment of the MAW-concentrate.

The construction of two conditioning pilot plants, dealing with the PIC and IREP processes was, once again, postponed.

Finally, it has to be mentioned that some modifications occurred in the choice of LLLW and MLLW initially contemplated for study in the framework of this programme action (see annual report 1980). Experimental work on the solvent wash alkaline waste was considerably reduced and even stopped (Harwell), pending the supply of genuine samples.

On the other hand, new real waste streams were added to the programme, i.e. LLLW and MLLW produced at AERE-Harwell and "sol-gel" waste arising from manufacture campaigns of PuO_2-UO_2 fuels.

The following contracts are reported :

1.3.1. PRECIPITATION AND MEMBRANE PROCESSES

Separation of actinides and fission products from MAW concentrate

Contract : 177-81-31 WASD, KfK, Karlsruhe.

Objective and Scope

The objective of this R&D action is twofold :

- to decrease the transportation cost for the MAW-concentrate from the reprocessing plant to the final repository,
- to improve the long term behaviour of the waste product containing the long-lived actinides.

This can be achieved by splitting the MAW-concentrate into three fractions :

- an actinide fraction which could be subsequently solidified in a very stable matrix (ceramic)
- a fission product fraction (containing the main gamma-emitters) which could be vitrified according to well established procedures
- a LAW-concentrate, capable to be transported after conditioning, without further shielding.

Concerning the transportation aspects, the required DF's for the main gamma-emitters have already been calculated (see annual report 1981).

In 1982, the experimental work mainly consisted of optimising the operating conditions for isolating the actinides on the one hand, and the fission and activation products of concern on the other hand. All these experiments were performed using simulated MAW-concentrate, tracered with Ba-133, Ce-144, Cs-137, Eu-152, Ru-106, Sb-125 and Sr-85. Cerium and Europium were used as substitutes for plutonium. Analytical determinations were carried out through atomic absorption spectrometry measurements and gamma-spectrometry for the inactive and active elements respectively.

Progress and Results

- Actinide separation

  It is intended to separate actinides selectively through their coprecipitation at low acidity as oxalate salts in presence of an excess of cerium (0.05 mole/l). Four different operating conditions have been investigated :

  - addition of the Cerium carrier to the MAW-concentrate, followed by denitration with concentrated formic acid HCOOH containing the oxalic acid $H_2C_2O_4$
  - addition of the Cerium carrier to the $HCOOH/H_2C_2O_4$ mixture prior to denitration of the MAW-concentrate
  - pH adjustement of the MAW-concentrate at 0.2 and 0.5 through NaOH dropwise addition.

Results, presented in table 19, showed that minimal entrainments of gamma-emitters along with the oxalate precipitate are achieved either by adding NaOH or by denitrating the MAW-concentrate already containing the Ce-carrier.

radio-nuclides	a) Ce		b) pH	
	Ce added to the feed	Ce added to the concentrate	0.2	0.5
Ba-113	100	90	100	100
Ce-144	*< 2	*< 2	*< 4	*< 4
Co-60	100	35	100	100
Cs-137	100	100	100	100
Eu-152	3	*< 0.2	*< 0.2	*< 0.2
Ru-106	100	76	100	100
Sb-125	100	100	100	100
Sr-85	n.m.	n.m.	100	100

* Detection range limit

Table 19 : Percentage of radionuclides precipitated after acidity adjustment of the MAW-concentrate in case of :
a) denitration with HCOOH b) NaOH addition

When a further denitration is performed, partial precipitation of Co, Sr and Zn occurred in the MAW-concentrate, whereas Co, Sb and Ru remained in the supernate.

On the basis of the Ce and Eu precipitation yields, actinides are expected to be separated to such an extent that the residual alpha-activity of the conditioned MAW-concentrate would not be higher than 100 nCi/g.

- Fission and activation products separation

  This step is carried out using classical reagents after raising the pH of the MAW-concentrate to 8.5 or 11. There are two alternatives for this treatment :

  - two successive precipitation steps at different pH (8.5 and 11)
  - one precipitation step only at pH 11.

  These procedures are leading to reduced volume of flocs. The application of two filtration steps may complicate somewhat the process. Typical figures of 500 and 250-350 for Cs DF's were achieved in case of precipitation at pH 8.5 and pH 11 respectively with preformed nickel-ferrocyanide.

  Further activities will aim at :

  - decreasing the amounts of carrier (Ce) and precipitant reagents
  - performing actinide separation with real Pu and Am.

Decontamination of low activity liquid wastes from fuel fabrication plants by ultrafiltration

PARLEMENT EUROPEEN BIBLIOTHEQUE

Contract : 230-81-35 WASD, Nukem, Hanau.

Scope and Objective

The purpose of this project is to investigate whether ultrafiltration with or without chemical pretreatment of the waste streams concerned, is a suitable method for the decontamination of LLLW arising from a fuel fabrication plant.

Progress and results

It has been previously indicated (see annual report 1981) that direct ultrafiltration was rather unsuccesful since most part of the active contaminant, mainly uranium, is not present as expected in a colloïdal form but under stable soluble complexes. Therefore a pretreatment is required for most of these solutions.

Experiments to set up a suitable pretreatment were performed using a lab-scale unit (Millipore Pellicon, Nuclepore and Nalgene flat sheet membranes, 47 mm diameter) which could be operated with 100 ml samples

In order to determine the DF's by gamma-spectrometry, all solutions most of them simulated, were spiked with 20 mg/l of highly enriched uranium.

These tests confirmed that direct application of the UF technique is useful only for the decontamination of laundry and floor-cleaning wastes. In this case, a D.F. of about 10 was achieved, which is genera ly sufficient. For all the other waste streams (process and decontami nation wastes), different pretreatments were investigated :

- precipitation of $U(OH)_4$ after photochemical reduction
- addition of $K_4 [Fe (CN)_6]$
- coprecipitation with calcium phosphate
- coprecipitation with ferric hydroxide or calcium stearate.

As a whole, the D.F.'s obtained were rather satisfactory (between 100 and 200) provided that no carbonate, oxalate and in some cases fluorid ions are present in the wastes. The most efficient pretreatment may b the photochemical reduction of uranium followed by precipitation of th U(IV) since this is not inhibited by the presence of F^-.

Unfortunately the presence of these complexing anions cannot be avoid for most of the process waste streams. They have to be removed from the solutions prior to the pretreatment, thereby complicating the whol treatment.

However, in all cases, an overall volume reduction factor of 10 to 15 can be achieved by UF with respect to the classical precipitation methods used at the time being.

Active liquid treatment by a combination of precipitation and membrane processes

Contract : 179-81-31 WASUK, UKAEA, Harwell.

Objectives and Scope

The objective of this programme is to develop liquid waste treatment processes giving improved decontamination factors and/or reduced final volumes of active solids, by using ultrafiltration (UF) to concentrate existing or deliberately created particles of colloidal or greater size.

The programme has advanced on two fronts. Small scale feasibility tests have been carried out in order to establish what types of radwastes could be treated by UF/precipitation techniques. In parallel with this, tests have been carried out with commercial types of UF modules in order to obtain the information required to design a realistically sized pilot plant, and to prepare flowsheets for possible UF processes.

Progress and Results

- Small scale feasibility experiments

  Earlier experiments with simulated wastes showed that in principle most of the important radionuclides, including Pu, Am, U, Th, Sr and Ca could be removed by UF/precipitation processes. First experiments have now been carried out with samples of real radwastes and have confirmed the promise of the technique, particularly for alpha activity removal. The real wastes included the Harwell site medium level and low level wastes and ranged in α, β and γ activity from 10^{-5}-10^{2} Ci/m^3. Ultrafiltration of these effluents gave α decontamination factors that in some cases exceeded 10^4. The decontamination factors that in some cases exceeded 10^4. The decontamination factors were some 10-100 times higher than the factors achieved in the conventional established floc processes, emphasising the advantage of the UF technique. In addition, because of the smaller precipitate additions required for the UF processes, higher volume reduction factors were also achieved.

In those case where access to the real waste has proved difficult, further experiments have been carried out with simulated wastes.

. For the solvent wash alkaline waste, some experimental tests, apparently successful, were performed on the decontamination of Zr by means of $Ti(OH)_4$.

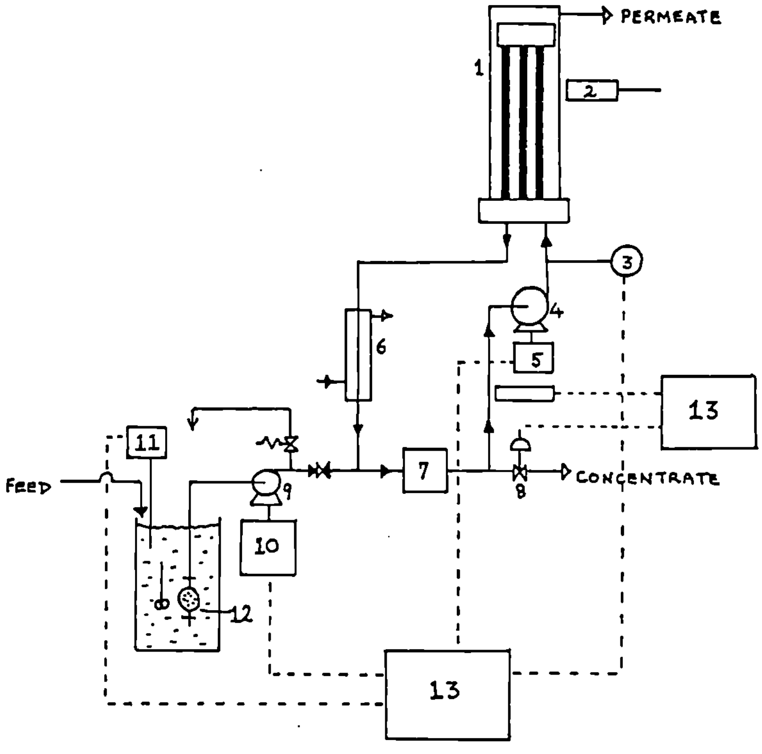
  However, due to the difficulty of preparing representative simula no more work will be carried out until real waste samples are available.

. For the iron bearing alpha-waste, segregation of the alpha activi from the Fe was investigated by adding calcium oxalate to the wast stream. This allows a Pu co-precipitation along with the oxalate salt, Fe remains soluble as oxalic complexes.

Unfortunately, to obtain an adequate alpha DF (> 50), the required amount of CaC_2O_4 to be added is comparable, in terms of weight, to the $Fe(OH)_3$ generated by direct precipitation. Therefore the value of this segragation process appears limited.

- Operation of ultrafiltration plant

Considerable progress has also been made by the operation of differe types of commercially available UF modules, and it now seems quite feasible to envisage the construction and installation, in the comi year, of a demonstration pilot plant treating a real active waste. Small test units were built around two different types of UF module and have been operated for short periods on the same type of simula ted effluent. Comparison of the performance of the two units indicated that the Carbosep tubular module, with its large bore tubula inorganic membrane has significant advantages over the Romicon plas hollow fibre module. The main advantages of the Carbosep system we its greater resistance both to chemical and radiolytic degradation and its greater operational stability and flexibility, particularly in conditions where appreciable fouling of the membranes could be expected.



Key:
1. carbosep module
2. γ counter for membrane deposit
3. pressure alarm
4. centrifugal circulation pump
5. pump motor
6. heat exchanger
7. turbine flow meter
8. solenoid valve
9. gear pump
10. air motor
11. level alarm
12. feed strainer
13. control boxes

Figure 18 : Small scale automated Carbosep test unit.

A small scale automated test unit (figure 18) was built and has been used to remove Sr activity by $Ti(OH)_4$ precipitation from simulat Magnox pond water. It has been operated on a continuous basis at a processing rate of 50-100 litres per day for a period of several months.

The experience accumulated to date has confirmed in a most satisfactory manner that stable performance can be maintained while operating at high volume reduction factors (~ 250). At such high volum reduction factors the UF concentrate stream was a dilute sludge, suitable for direct treatment by a dewatering process such as vacuum filtration.

A membrane flux of over 1m/day and a Sr decontamination factor of 1(have been maintened during the operation of the unit. Techniques ha been demonstrated for chemically cleaning the UF membranes at intervals of several weeks, and for dealing with the secondary waste arisings (i.e. the spent cleaning solutions). Since virtually all t anticipated plant operations have been performed in testing this aut mated unit, much valuable information on volumes and activity levels of all the major arisings (UF concentrate, dewatered filter cake, spent cleaning liquors, etc.) has been accumulated and is being use(to draw up overall process flowsheets.

Specification of equipment items for the pilot plant is under way a a new module end-fitting design, which permits the semi=remote handling of spent ultrafiltation modules has been evolved. A prototype version of this system is currently being tested under cold conditions.

- Conclusions

Ultrafiltration/precipitation processes have now been applied sucess fully, on a small scale, to the treatment of real radwastes. Whe compared to conventional floc sedimentation processes, the enhancement in alpha activity removal achieved by ultrafiltration has been particularly encouraging. Confidence in the operability of ultrafiltration processes has been much enhanced by the construction and sucessful operation for many months of a small automated ultrafiltra tion unit.

In the next phase of the work it is intended to proceed with the construction of a versatile design of a demonstration ultrafiltration pilot plant and to then prove the design through extended operation on real waste streams.

Treatment of low and medium activity liquid waste by flocculation

Contract : 181-81-31 WASF, SENA/Chooz.

Objective and Scope

The treatment of liquid LLW and MLW arising from a pressurized water reactor by flocculation/precipitation techniques.

Progress and Results

The construction of the flocculator prototype (5 m^3/h) has been completed and the first testing campaign started in june 82 with genuine utility wastes. Due to problems encountered in performing these tests, some modifications were made to the installation, such as :

- Increasing the length of the flocculation tube with 50 m to prevent post-flocculation in the treated effluent.

- Replacement of stainless steel by PVC for the injection pipe, to avoid corrosion.

- Setting-up of a distribution system to prevent by-pass of flocs in the settler.

- The main components of the CuFeCy were introduced separately in the flocculator since preformed CuFeCy caused many problems in the metering pumps (nota : Cy = cyanide).

Pre-industrial tests showed (table 20) that the residual activity of the treated waste reached the requirements for direct release into the

				EFFLUENT A TRAITER						SORTIE DECANTEUR (* : sortie filtre HANSON)						FACTEUR DE DECONTAMINATION					
ESSAI	RESERVOIR	DATE	VOLUME TRAITE	β Total	Mn^{54}	Co^{58}	Co^{60}	Cs^{134}	Cs^{137}	β Total	Mn^{54}	Co^{58}	Co^{60}	Cs^{134}	Cs^{137}	β	Mn^{54}	Co^{58}	Co^{60}	Cs^{134}	Cs^{137}
9	266 C	24/08/82	40	5.445	900	358	2.360	962	1.470	503	959	378	206	103	111	10,8	1	1	8	9	13
10	266 C	26/08/82	42	13.370	3.220	701	10.400	1.110	1.820	423	642	220	142	55	64	31,6	5	3	73	20	28
11	266 B	27/08/82	27	7.475	3.730	2.090	4.060	1.190	2.430	637	1.500	955	607	46,7	< 19	11,7	2,5	2	7	25,5	128
12	266 C	30/08/82	23	1.855	643	317	963	234	661	258	669	320	1.940	97,4	147	7,2	1	1	-	2,4	4,
13	266 B	31/08/82	32	9.030	3.670	2.110	3.050	1.810	2.970	711	1.140	958	652	79,3	88	12,7	3	2	5	23	34
14	266 C	02/09/82	22	1.084	477	191	1.240	173	544	164	220	138	217	35	76	6,6	2	1,4	6	5	7
15	266 B	07/09/82	20	4.382	1.600	677	4.610	2.150	2.720	* 166	92	183	197	64	37	26,4	18	4	23	33	73
17	266 B	13/09/82	8	8.975	816	271	1.010	1.690	2.240	288	-	-	-	-	-	31,2	-	-	-	-	-
20	266 B	21/09/82	22	6.701	2.280	792	5.720	1.650	3.840	* 353	27	185	196	63	111	19	84	4	29	26	35
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
22	266 B	07/10/82	15	2.840	223	87,8	372	1.040	1.520	370	223	76,6	134	71,8	105	7,7	1	1,1	3	14,5	14,
23	266 B	08/10/82	34	3.255	591	195	1.220	2.100	3.010	160	83,6	45,6	78,8	21	31,8	20,3	7	4	15,5	100	95
24	266 B	13/10/82	26	2.950	700	91,7	2.200	1.610	2.510	122	78	19	98	51	82	24,2	9	5	22	32	31
29	266 C	23/11/82	20	657	100	< 9	215	85	388	505	-	-	-	-	-	1,3	-	-	-	-	-
31	266 B	26/11/82	27	3.987	61,2	< 13	73,3	1.700	2.300	236	166	15,7	38	84,8	174	16,9	-	-	2	20	13
32	266 B	29/11/82	22	3.500	127	65,6	295	2.020	2.680	224	249	22	217	95,3	232	15,7	-	3	1,3	21	12
33	266 C	01/12/82	50	1.830	672	148	1.260	430	939	213	110	46,6	314	56,3	139	8,6	6	3	4	8	7
34	266 B	03/12/82	45	3.325	63,2	< 12	106	914	1.270	221	58,6	37,2	< 7	14.6	34	15	1,1	-	15	63	37
35	266 B	06/12/82	29	1.996	146	75,9	491	2.370	3.070	37	44,3	< 11	16,1	15,5	44,6	54	3	7	30	152	69
36	266 C	08/12/82	41	680	231	35,8	404	181	548	159	110	< 8	244	51,3	195	4,3	2	5	2	3,5	3
37	266 C	10/12/82	32	2.190	799	262	1.690	285	850	70	71,4	< 13	< 11	< 10	49.2	31,3	11	20	153	28,5	17
40	266 C	16/12/82	25	1.360	406	< 7	< 5	321	1.130	682	516	< 7	< 5	82,6	104	2	-	1	1	4	11
41	266 B	17/12/82	46,5	9.732	2.860	351	12.000	1.880	2.530	191	141	< 11	220	< 10	14,7	51	20	32	55	188	172
42	266 B	20/12/82	31	3.686	196	54,1	807	1.620	2.150	70	90	< 11	144	< 8	< 10	52,7	2	5	6	202	215
43	266 C	28/12/82	38	973	282	-	775	134	522	382	123	-	414	60.7	105	2,5	2,4	-	2	2,2	5

NOTA : Les essais 9 à 20 ont été entachés de problèmes d'injection des réactifs.

Table 20 : Residual activity of treated waste (results on 28/12/82).

river (1850 Bq/l). However, according to the chemical composition of the utility wastes, some modifications had to be made to the standard procedure :

- When the detergent concentration in the waste is rather high (> 100 ppm) flocculation should be performed at a lower pH (7 instead of 8.5).

- $CaCO_3$ had to be injected in the flocculator when the total salt content is too low.

- In presence of chromate, addition of $FeSO_4$ is necessary.

- Stabilization of the pH is of a paramount importance.

The resulting sludges were concentrated by adding an excess of polyelectrolyte. After filtration on a bag filter, the sludges were dried and incorporated into epoxy-resins.

Denitration and chemical precipitation of MAW concentrate

Contract : 178-81-32 WASD, KFA, Jülich.

Scope and Objective

In order to facilitate transportation of the Maw-concentrate from the reprocessing plant to the final repository site, this R&D activity aims at splitting the waste into two fractions :

- a small high level fraction to be added to the HAW
- a large low level fraction requiring no shielding for transportation.

The activity concentration is performed by means of chemical precipitation at low acidity after denitration with a suitable reducing agent.

Progress and Results

Most of the experimental work has dealt with the setting-up of the op rating conditions for denitration and chemical precipitation on simulates.

- Denitration

  In all denitration experiments formaldehyde or formic acide has bee used as reducing agent. Two different procedures have been compare i.e. feeding of MAW into the preheated formaldehyde or formic acid batch and feeding of the reducing agent into the preheated MAW batc In the first case N_2 is the main offgas component beside CO_2, in th second it is NO, as shown in figure 19. The production of N_2 is advantagenous if nitric acid should not be recovered. However, on account of simple process control, the feeding of the reducing agents into the heated MAW will be preferred. A simple method for t detection of the residual nitrate content, suitable for remote hand ling in a hot cell, could not be developed till now.

- Chemical precipitation

  In order to investigate whether the procedure of precipitation coul be simplified for remote controlled hot experiments, laboratory experiments were initiated with one-step precipitation. They were concentrated on caesium, being the crucial element. Using a preformed precipitate of $K_4[Fe(CN)_6]$ and equimolar $Ni(NO_3)_2$ a decontam nation factor of about 100 for caesium and 5 for ruthenium has been found. By comparing this with the required value of about 300 for caesium, it is evident that further optimization of the precipitati is necessary. The required decontamination factor for ruthenium is In this cas it is anticipated that this can be achieved by addin proper precipitants even without accurate pH adjustment or any othe special pretreatment.

- Phase separation

  Once the activity is precipitated, the problem is to separate the high level sludges without carrying over prohibitive amounts of

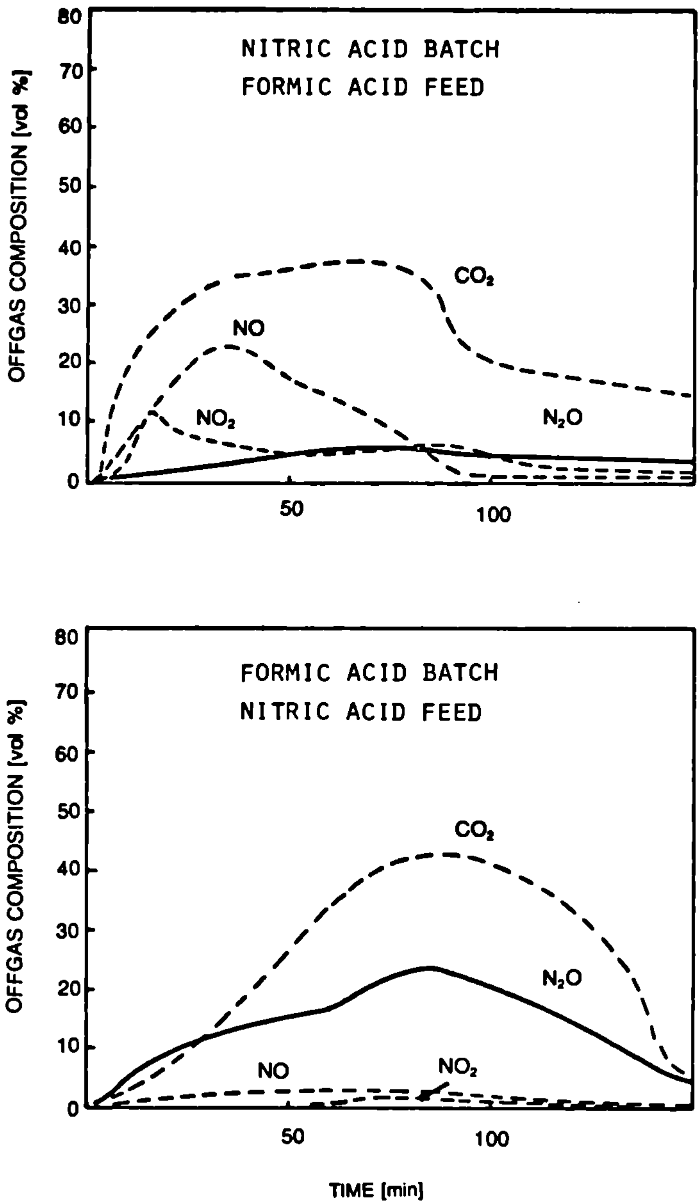


Fig. 19 : Off gas composition for two dinitration procedures of MAW concentrate

sodium nitrate. As a first approach, sedimentation was prefered to filtration. To decrease the settling time, glass powder was added t the MAW-concentrate just before the introduction of precipitants at pH 8.5. In this case, the resulting sludge volume, after 20 minute of settling time, corresponded to nearly 25 % of the total waste volume, which is still too high. Investigations are going on in order to reduce the sludge volume.

1.3.2. EXCHANGE PROCESSES

Inorganic ion-exchangers prepared via a sol-gel process

Contract : 231-81-31 WASI, AGIP Nucleare.

Scope and Objective

Testing of anorganic ion-exchanger particles, prepared in a sol-gel process. for the decontamination of various MAW-streams.

Progress and Results

During 1982 emphasis was put on the investigation of the absorption-elution behaviour of selected radionuclides on fixed bed HTiO IX unit and the decontamination of actinide MAWs generated during (i) americi purification and (ii) refabrication of uranium-plutonium mixed oxide fast breeder reactor fuel.

- Fixed bed column experiments

  Absorption and/or elution tests on fixed bed IX units of Cs^{+}, Sr^{++} and Eu^{+++} carried out under varied operative conditions showed that

  . Sr^{++} and Eu^{+++} are absorbed with very high efficiency for Ph valu of the influent solution in the range of 2.5-11. Relatively high concentrations of alkaline elements (e.g. 1.5 M) do not interfere and high influent feed solution flow-rates are applicable.

. Cs^+ is also absorbed with sufficient efficiency, but alkaline elements, if present, do interfere. Processing solutions of very low salinity only can be treated.

. Dynamic capacities of fixed bed HTiO IX units are high. For radwaste immobilization applications, saturation of the IX particles to 3-5 meq/g HTiO is feasible.

. Within the diameter range of 100-500 microns, the mean diameter of the IX-material has only a secondary effect on the absorption cinetics and the dynamic capacity of the fixed bed IX units. The utilization of larger particles may permit the implementation of simple immobilisation techniques, such as the dispersion of sintered ceramic particles in a glass matrix.

. Quantitative recovery of the elements absorbed on HTiO IX columns is possible by elution with 0.05 M HNO_3.

- Decontamination of actinide MAWs

. Decontamination of solutions generated in the course of americium oxalate precipitation, by means of NH_4OH precipitation of gross impurity elements soluble in oxalic media, filtration and residual americium absorption on HTiO IX fixed bed units, reduces americium concentration in the IX column effluents to levels of maximum permissible concentration in natural water (4.10^{-6} Ci/m^3). Americium concentration in the solutions fed into the IX unit were of the order of 0.1 Ci/m^3.

. Decontamination tests of alkaline Am-Pu effluents generated in the course of mixed oxide FBR fuel preparation by sol gel coprecipitation in NH_4OH showed the possibility to decontaminate these effluents by factors of 50-100. Work in this area is still in progress.

- Various

. Batch extraction tests of Eu from $Eu(NO_3)_3$ solutions of various concentration and pH value adjusted to 3.5 showed a capacity of the IX material of 3 meq Eu^{+++}/g HTiO.

. Batch extraction tests of Ru from solutions of different Ru conce tration, pH and alcaline element content show moderate affinity o HTiO for this particular element.

. During this reporting period a total of 4 kg HTiO microspheres w prepared in support of the evaluation work carried out in the lab ratory and with external organisations.

. The set up of a hot cell laboratory line for immobilisation of TR and/or fission product radwastes in titania based ceramics by mea of : (a) IX loading on xerogel particles, (b) calcining of the ra nuclide loaded xerogel particles (max. temp. of the calcination f nace installed : 1000° C), (c) cold pressing and (d) sintering (m temp. of the sintering furnace installed 1700°), has been complet

. The phase composition of TiO_2-$SrTiO_3$ and SYNROC ceramics loaded w inactive fission product elements, fired at 1350° C under air or Ar-H_2 was confirmed by X-ray crystalography carried out at INE-Kf Karlsruhe.

Decontamination of MLLW by hydroxamic acids

Contract : 175-81-31 WASI, ENEA-Casaccia.

Scope and Objective

This R&D activity aims at testing the performance of the tributyl-acétohydroxamic acid (T.B.A.H., its characteristics are indicated in table 21) with respect to the decontamination of two typical reproces sing waste streams :

- solvent waste alkaline waste;
- acidic raffinate arising during the second and third U-Pu purifica tion cycles.

In the first approach, extraction chromatography was selected as a technique for applying this new cationic exchanger. Two methods wer used to prepare the extraction column :

- T.B.A.H. coating of the inert support with the aid of a wetting agent;
- uniform distribution of the T.B.A.H. within an amorphous porous silica grain.

FORMULA	$CH_3CH_2CH_2CH_2$, $CH_3CH_2CH_2CH_2$, $CH_3CH_2CH_2CH_2$ > C-C(NHOH)=O
MW	243.4
MP	132-33°C
PURITY(COLORIMETRIC METHOD)	98%

SOLUBILITY

ETHANOL	10^3	MMOLES/L
CHLOROFORM	440	"
CARBON TETRACHLORIDE	43	"
BENZENE	76	"
XYLENE	62	"
MESITYLENE	2.3	"
N EPTANE	1.9	"
WATER	0.07	"
HNO_3 1M	NOT DETECT.	

THERMAL AND CHEMICAL STABILITY

IN SOLID FORM AT ROOM TEMPERATURE	MORE THAN 3 YEARS
" " " AT 40 °C	1 MONTH
" " " AT 80°C	1 DAY
" " " AT 21°C WITH 2M HNO_3	6-8 HOURS
" " " AT 21°C WITH 2M HNO_3+0.5M UREA	1 MONTH
0.1M IN CHLOROFORM AT 21°C WITH 5M HCL OR 5M H_2SO_4	MORE THAN 3 MONTHS
" " " " " " " WITH 1M Na_2CO_3 OR 0.5 M $(COOH)_2$	MORE THAN 10 DAYS
" " " " " " " WITH 3M HNO_3	50% DEGRADED AFTER 3 DAYS
" " " " " " " " " " (UREA0.02M)	MORE THAN 1 MONTH
" " " " " " " " 1M HNO_2	ISTANTANEOUSLY DEGRADFO

RADIOLYTICAL STABILITY

0.05 M IN CHLOROFORM AT 30°C IN PRESENCE OF 1M HNO_3 (DOSE RATE 0.5MRAD/H)

WITH 1-2 MRAD	NO EFFECT
WITH 6-8 MRAD	50% DEGRADED

Table 21 : Characteristics of the tributylacetohydroxamic acid

Progress and Results

Batch decontamination experiments showed that a noticeable chemical de gradation of the T.B.A.H. occurred when it is contacted with the acidi waste in absence of large amounts of nitrous acide scavengers, 0.5 M Urea (see table 22). Accordingly, extraction chromatography did not seem to be the most suitable technique for decontamination of the acidic raffinate by means of T.B.A.H. Moreover, the selectivity of the T.B.A.H. with respect to Pu and Fe noticeably decreased in presence of large amounts of other cations.

Support.	SCQ (G)	TEOS (S)
TBAH; mmol /g initial	1.39	~4
After shaking with 2M HNO_3	1.23	0.9
After shaking with 2M HNO_3 (urea 0.05M)	1.28	2.5
After shaking with 2M HNO_3 (urea 0.5M)	1.35	3.9

Table 22 : the stability of the hydroxamic acid on the supports with regard the 2M HNO_3 (contact time : 5 h at 45° C and 16 h at 20° C)

Experiments on the decontamination of the alkaline waste are in progress.

1.3.3. PARTICULAR TECHNIQUES

Liquid waste treatment by electrical processes

Contract : 176-81-31 WASUK, AERE, Harwell.

Scope and Objective

The application of a range of electrical separation processes to the treatment of medium active liquid wastes. The field can be divided into three areas :

- Removal of particulates and colloids by electrokinetic effects including electro-osmosis, electrofiltration and electroaggregation.

- Removal of dissolved ionic material by electrochemically controlled ion exchanges.

- Removal of dissolved ionic material by deposition as metallic elements or as insoluble compounds.

Progress and Results

- Electro-osmosis

  - A wide range of sludges, flocs and colloids have been successfully dewatered - some up to 35 % solids, producing an extract of high clarity (solids retention > 99.95 %). The process may be operated in a continuous crossflow cell.

  - Power consumptions are typically about 0.1 $kWhL^{-1}$ at flow rates of 1 $m^3/m^2/h$.

  - For a genuine site waste, virtually complete retention of α and Co was observed. A retention of 55 % of Cs was measured, which is an improvement on the presently used treatment. A DF of > 300 was obtained for a colloidal suspension of $Ti(OH)_4$ containing ^{85}Sr.

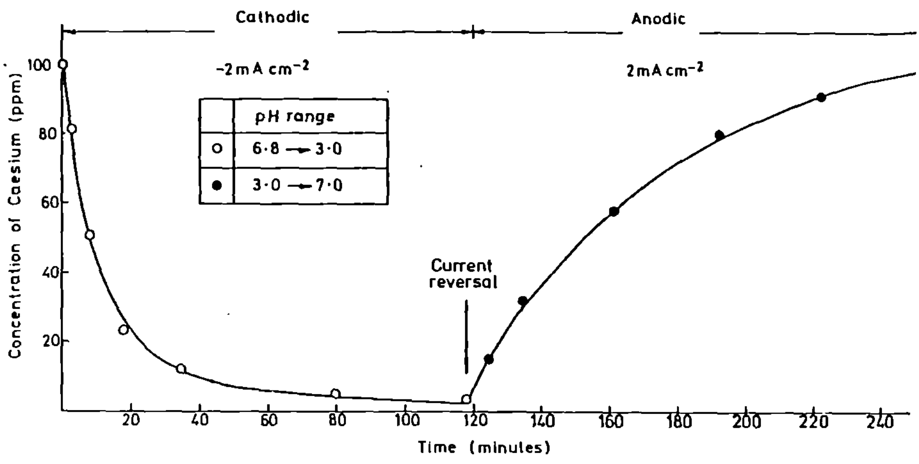
- Dewatering can be achieved at inexpensive cotton membranes, whicl have shown unchanged performance up to 100 MR.

- Electrochemical ion-exchange

  - Electrochemical control of ion-exchange extends the normal capab lities of the exchanger : more rapid adsorption kinetics, wider operating pH range, lower equilibrium free concentration, elution by current reversal.

  - Commercially available weak acid cation exchangers (10 meq/g) an electrochemically activated carbon (1-2 meq/g) have been success fully demonstrated using ^{137}Cs. These can be cycled > 100 times without any significant deterioration in performance.

  - Evidence of selective Cs removal has been observed, even with Amberlite CG50 at pH 4 (fig. 20).



.Fig. 20 : Adsorption of caesium onto an amberlite CG50/Kraton/ Graphite electrode (2nd cycle) from a Cs NO_3 electrol

- Faradaic deposition

  . The deposition of insoluble actinide hydroxides at cathodes by electrochemical reduction of NO_3^- has a low efficiency at pH < 1.5. The process also suffers from Fe^{III} interference. The most adherent U deposits were obtained at concentrations $\leqslant 0.1$ mM.

  . Metallic Ru could not be cathodically deposited from HNO_3 solution due to the stability of the $(RuNO)^{3+}$ complex. However, RuO_2 could be precipitated under more alkaline conditions by anodic oxidation.

  . Deposition of Cs, Sr into mercury cathodes becomes increasingly inefficient in acid solutions due to hydrogen evolution, and in alkaline solutions due to poor selectivity of removal from high Na content streams. It also proved difficult to find a suitable corrosion resistant substrate to support the thin mercury film necessary for acceptable space/time yields.

Catalytic reduction of NO_x into N_2 by ammonia, using a zeolite as catalyst

Contract : 174-81-31 WASI, ENEA, Casaccia.

Scope and Objective

This research activity concerns catalytic abatement of NO_x. The objective is to reduce the amounts of secondary wastes produced by the scrubbing of NO_x containing off gases produced in the radwaste treatment and to decrease the amount of NO_x discharged from the stacks in order to comply with the environment protection requirements.

Progress and Results

The literature review performed at the beginning of the work has shown that the most used method to remove NO_x is by the scrubbing with aqueous solutions, where the efficiency of the removal is controlled chiefly by the NO solubility in the water and the oxidation of NO to NO_2. The NO oxidation reaction can occur slowly, depending on time and temperature, and so the efficiency of the system is strongly influenced by the design of the scrubbing apparatus.

The catalytic abatement of NO_X can be performed in the best way accor ding to literature with ammonia and mordenite as catalyst. The morde nite is a syntetic silicoalluminate having porus structure. In order to investigate the possibility to apply this method in the case of NC produced during the treatment of radioactive wastes, a laboratory sca plant has been built, in which, according to the EUREX bituminization d sign, the flow sheet of the radwastes denitration step before bitumin zation can be reproduced as well as possible, using non radioactive solutions having the same chemical composition as the EUREX radioacti wastes. The produced gases flow through a catalytic reactor made of stainless steel, where they are reacted with ammonia at a fixed temper ture. The control of NO_X catalytic abatement experiences is carried out quantitatively by analyzing the chemicals involved.

The experiments carried out up to now show that the catalytic abateme of NO_X from the gas produced in the denitration reactor can be perfor med at efficiencies higher than 99.5 % and is strongly influenced by the temperature.

In the conditions :

$(NH_3) / (NO_X) = 1.0 \pm 0.1$
residence time = 0.16 ± 0.02 sec
$(NO_X) = 12000 \pm 2000$ ppm
$H_2O = 58 \pm 2$ % v/v

the best results can be obtained at 500° C, as shown in figure 21.

The water vapour negatively influences the efficiency of the abateme At a concentration of 80 vol % the efficiency shows a maximum of abo 93 % of NO_X destroyed at 450° C, and decreases at higher temperature

The work is in progress, and the other parameters involved in the pr cess are being investigated.

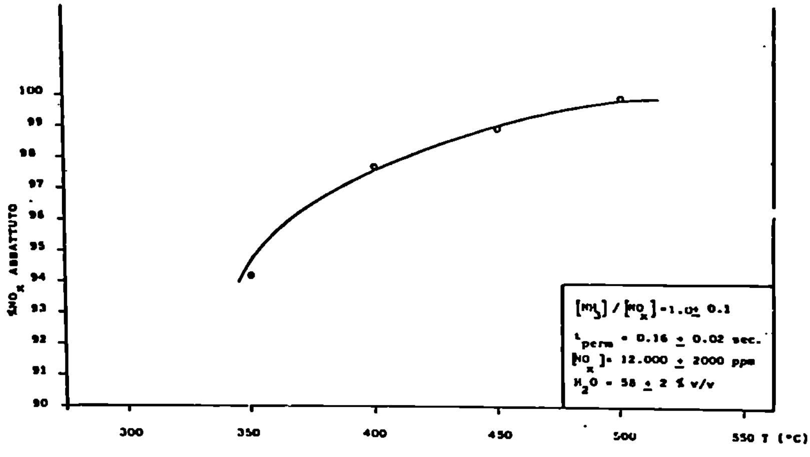


Fig. 21 : Percentage of abated NO_X as a function of temperature

1.3.4. INCORPORATION OF LOW AND MEDIUM ACTIVITY WASTES IN CEMENT

Contract : 166-81-15 WASUK, AEE, Winfrith.

Objective and Scope

This R&D activity aims at identifying procedures, based on commercial cements and mixing techniques, for the incorporation of a wide range of wastes arising from plant maintenance and decommissioning operations in cement.

The programme involves optimising the volume loading of radwaste in the radwaste /cement composites without detrimental effects on the durability (strength, permeability, dimensional changes) and leach-rates.

Progress and Results

- Long term stability testing of cemented simulant wastes

  Cemented simulated wastes containing sodium-nitrate and sodium sulphate have been tested for two years under different disposal modes (shallow land burial and sea-dumping).

  Under normal storage conditions the sodium nitrate/OPC specimens have remained dimensionally stable over this period of time.

  After the fairly rapid changes during the first 28 days, when most of the cement is hydrating, the samples have stabilised and the rate of change is less than 0.02 % in two years of storage. The samples stored under water have gradually expanded, but even for the maximum value recorded (0.72 %) on the samples containing high concentrations of sodium nitrate, the test specimens have remained intact. The sodium nitrate/BFS/OPC matrix test specimens are more stable and show significantly less dimensional changes than the OPC mix; especially for those samples stored under water.

  The sodium sulphate/OPC specimens kept under normal storage conditions have remained stable for two years, although the dimensional changes are greater than for the sodium nitrate/OPC samples. However the sodium sulphate/OPC samples stored under water have disintegrated. This is due to the normal sulphate attack on the cement A significant improvment is obtained by the use of the BFS/OPC matrix and the samples stored under water have also not shown any signs of disintegration.

  With respect to cemented ion exchanger samples, after one year of testing, the dimensional changes and leach rates continue to be very similar to those measured on cemented sodium nitrate wastes.

- Waste/cement mixing equipment

  The high shear mixer is proving to be very successful for the mixing of cement grouts for the encapsulation of solid waste items. This mixer produces a very cohesive type of mix which has the required properties for pumping, eg into an active solidification plant. Th mixer has been used for mixing grouts containing OPC/BFS and OPC/PFA which have been used for the encapsulation of solids at the 220 dm^3 scale.

- Cemented wastes : Plant considerations

The rate of early strenght development in the product was shown very dependent on the size of the waste product blocks. It is quicker in the 200 dm^3 container than in the corresponding cube sample (approximately 5 Nmm^2 at 1 day compared with 1 Nmm^2). After 3 days curing, this rate is approximately the same, but the ultimate strength of the cube sample is higher than the 220 dm^3 bloc.

The influence of the container size on the "centre drum" temperature of nitrate/OPC formulations has also been investigated for containers in the size range of 30 dm^3 to 500 dm^3.

As a result, the difference in maximum temperature is only 30° C for the different sizes of containers, the main difference is the time required to return to ambient temperature. However, it has to be mentioned that the temperature reached in the centre of the container can be considerably reduced by replacing part (at least 50 %) of the OPC by either blast furnace slag (BFS) or pulverized fuel ash (PFA).

- Non-destructive testing of cement samples

Preliminary results indicated that the Grindosonic resonance frequency technique shows promise for comparing the properties of lab specimens of cemented waste with respect to the measurement of the development of mechanical strength (resonance frequency and elastic modulus).

Conditioning of highly radioactive residues by utilizing a drum-dryer

Contract : 180-81-33 WASD, KFA, Jülich.

Objective and Scope

Concerning the high level sludges arising from the treatment of MAW-concentrate (see contract 178-81-33 WASD), this research activity intends to concentrate the sludge by means of a drum-dryer and incorporate the active powder into a borosilicate glass.

Progress and Results

- Drum-drying

  Some modifications have been brought to the drum-dryer installed ir the hot-cells, mainly with respect to the feeding pump, formerly a centrifugal type pump, which has been replaced by a tube type pump order to become more independent of the solid content and viscosit of the high level sludge.

- Incorporation into glass

  In case of direct feed the high sodium content of the sludge is th limiting factor for the incorporation of the waste into the glass. An upper limit of 25 % sodium oxide content of the glass results i 5.5 % waste oxide content. As the total amount of sodium oxide is contributed by the waste sludge, a sodium-free prefabricated glass frit must be used. In case of filtration the waste oxide content be increased to 8-10 %, but the filter cake has to be diluted with fresh water or condensate for further treatment on the drum drier.

  As a sodium-free frit has not been available, glass samples were ma with filtered sludge. In the waste oxide, using a commercially available frit with 30 % alkaline oxide content, a yellow phase separates. This has not been observed using a frit with 9.5 % alkaline oxide and 10 % calcium oxide. These results correspond with those obtained with fission products. It can be assumed that the products can further be optimized on the model of glasses developed for the solidification of fission products.

1.4. PROCESSING OF ALPHA-CONTAMINED WASTE

This action concentrates on the combustible solid alpha-contaminated waste stream, but, in certain processes, incombustible solid material can also be treated.

This waste stream comprises a relatively large volume of materials wi low contaminant concentrations (e.g. room waste) and a small fraction of waste from glove boxes, which will contain significant amounts of

The options for the former are either to immobilize the untreated was or to reduce its volume by destruction of the organic bulk material prior to final conditioning.

For the latter fraction - i.e. the highly contaminated waste - treatments aiming at a decontamination by chemical or mechanical separatio of the main contaminant Pu is a third major treatment option.

The R&D work to demonstrate the feasability of these options comprise studies on :

a) High-temperature slagging incineration for low activity PCM (Plutonium Contaminated Materials)

b) Pyrolytic combustion at temperatures below 700° C

c) Molten salt incineration

d) Acide digestion

e) Decontamination (washing)

for the treatment of the original waste. Complementary projects to extract the plutonium from the residues or liquors of these treatment (except for the high temperature incineration) are also being carried out.

A separate excercice within this action is a comparative test of Pu-assaying and monitoring equipment.

This Round Robin Test on Pu monitoring consists of assaying the same drums with various concentrations and configurations of alpha contaminants by five, possibly six, different measuring devices in four countries of the EC. The compilation and the analysis of the results will be carried out by the JRC Ispra.

Due to the very time consuming transport arrangements for the active standards, the time table for these tests extends over three years.

The following contracts are reported :

1.4.1. INCINERATION AND PYROLYTIC METHODS

Recovery of plutonium from combustible wastes

Contract : 185-81-43 WASUK, AERE, Harwell.

Scope and Objective

An experimental study of plutonium recovery factors, obtained by leaching of the residues of specific waste after combustion or pyrolysis.

Progress and Results

Work has continued on the preparation of plutonium active incinerator ashes for plutonium recovery studies with the emphasis on comparing the effect of different plutonium contaminants. A considerable part of the programme during this period is concerned with treatment of the leach solutions. Methods for selective removal of plutonium and americium from the leach solutions are being investigated. A limited number of washing experiments have been carried out such, that the plutonium recovery may be compared with that obtained from incineration or pyrolysis/char oxidation processes.

- Preparation and leaching of ashes

  Preparation of ashes in the active "model" incinerator has continued. Three typical waste mixes have been used which all contain pvc, polythene and cellulose tissue together with Neoprene, low or high ash Hypalon as the rubber component. The range of plutonium contaminants studied has been extended to include PuO_2 (precalcined at 550 and 800° C), $(U,Pu)O_2$, $Pu(NO_3)_4$ and $UO_2(NO_3)_2/Pu(NO_3)_4$.

The contaminated wastes have been treated by incineration or by pyrolysis followed by char oxidation in the temperature range 550-900° C.

The plutonium can generally be leached more easily at the lower temperatures although in some cases the leachability of the plutonium is at a minimum at about 800° C and then increase again at 900° C. This is because the inactive components of some of the ashes tend to become less soluble and interfere less with the nitric acid/fluoride mixture. However at the higher temperatures the quantity of very insoluble plutonium, which cannot be dissolved even after successive leaching with fresh batches of acide, increases. Generally temperatures of ∿ 700° C give the optimum recovery of plutonium. Typical recoveries are 90 % for a single leach and > 99 % for three successive leachings. Except for materials contaminated with $UO_2(NO_3)_2/Pu(NO_3)_4$ solution the better results are obtained with waste materials treated by pyrolysis followed by char oxidation, than with incineration.

An order of ease of leachability for the various plutonium contaminants for a particular ash is :

$$PuO_2\ (550°C) \sim PuO_2\ (800°C) < Pu(NO_3)_4 << UO_2(NO_3)_2/Pu(NO_3)_4 < (U,Pu)O_2$$

For the mixed uranium/plutonium oxide and nitrate contaminated ashes up to 90 % of the plutonium can be dissolved in 10 M nitric acid alone if the incineration temperature is 700° C or below. At the higher temperatures fluoride ions must be added to obtain ⩾ 90 % recovery.

- Treatment of ash leach solutions

A number of flowsheets have been considered for treatment of the ash leach solutions in order to separate and recover the Pu and Am present in such solutions. Although a tributylphosphate/odourless kerosene (TBP/OK) extraction from ∿ 5 M nitric acid gives a good extraction of plutonium from the leach solutions, the americium containing raffinate requires further treatment. The americium may be

20 % of the α-activity in the original leach solution. Although floc precipitation has been shown to give a very effective decontamination of the americium containing raffinate a large quantity of inactive metal ions also precipitate, even if the pH is carefully controlled.

Although there are some reagents which will extract both plutonium and americium from > 1 M nitric acid they are not yet well established. However at low acidity ($\sim$ 0.1 M H^+) and high nitrate concentration ($\sim$ 5 M NO_3^-) TBP/OK should extract both plutonium <u>and</u> americium. The key stage in the process is the neutralisation of the leach solution to $\sim$ 0.1 M nitric acid. It has been found that if the plutonium is present as plutonium- IV, much of the plutonium is converted to a non extractable species, even if the neutralisation is carried out slowly (e.g. by passing an air/ammonia mixture over the solution). However if the plutonium is oxidised to plutonium - VI prior to the neutralisation, quite good extraction of the plutonium can be achieved. After six extractions the residual level of α-contamination is $\sim 10^5$ α dpm/ml compared to a starting level of 5×10^8 dpm/ml. Quite good results are also obtained if the plutonium is reduced to plutonium - III prior to the extraction. The extraction of americium can be improved by adding ferric or aluminium nitrates to the solution. The extraction conditions are currently being optimised.

- Washing experiments

A limited number of washing experiments have been carried out for Pu recovery comparison with that achievable with incineration or pyrolysis/char oxidation processes. Plutonium recoveries of $\sim$ 90 % can be achieved under favourable conditions but poorer results are obtained if cellulose tissues are present in the waste mixture. Ageing of the waste after contamination also reduces the plutonium recovery. If plutonium recoveries in excess of 90 % are required, incineration or pyrolysis/char oxidation followed by ash leaching is the preferred process. By leaching several times with acid plutonium recoveries of > 99 % can be achieved.

Incineration of plutonium contaminated waste

Contract : 186-81-44 WASUK, UKAEA, Springfields.

Scope and Objectives

The aim of this work is to provide design data for the construction of a prototype inactive demonstration unit for the incineration of plutonium contamined wastes. A two-stage process would be used in which package wastes were first hydrolysed and the resultant char oxidised in the second stage. The volatiles from the pyrolysis would pass into an after-burner, which has been the subject of a separate design study. The design throughput of the unit would be 26 kg/H. The plant would be designed to achieve incineration with minimal carry-over of activity to the off-gas system and a secondary design aim would be to limit process temperatures in order that the residual plutonium should be recoverable from the final ash. The objectives of the experimental programme are :

- to define the rates of decomposition of solid and liquid wastes and the composition of their off-gases during pyrolysis at a scale relevant to a 10-20 kg/H throughput.
- to determine the rate of combustion of the chars produced in the primary pyrolysis process and thus enable future designs to be developed.

Progress and Results

The experimental studies have shown that pyrolysis in an inert atmosphere at 700-800° C is generally to be preferred, because no soot is generated and decomposition occurs at an acceptable rate with no detectable char carry over. Anaerobic pyrolysis, leads to the formation of volatile hydrocarbons (C1-C4), tars and chars in proportions dependent on the source materials, together with other gases, particularly HCL from chlorinated plastics and CO/CO^2 from cellulosics. The relative amounts of these pyrolysis products from individual materials are listed in table 24. The rates of evolution of these products have also been estimated for package sizes relevant to plant applications.

Pyrolysis trials with individual solid PCM wastes and mixtures, in package sizes of to 2.5 kg of 203 mm Ø has shown that the pyrolysis times for mixtures cannot be predicted with confidence, particularly when they contain significant proportions of polythene. The times taken for pyrolysis i.e. when 90 % of the volatiles have been evolved can be illustrated firstly by reference to mixtures of waste which are likely to arise at the dounreay nuclear establishment and also at BNFL and DNE mixtures pyrolysed in about 17 and 40 minutes respectively at 700° C. The pyrolysed times for the 1 kg DNE packages decreased with temperature from about 38 minutes at 800° C to 52 minutes at 600° C. Further, the pyrolysis time is proportional to the package diameter but the proportionality is dependent on the particular waste composition.

Source material	Char	Tar	"non-condensible" hydrocarbons	HCL	CO/CO^2
	<-------------------		weight %	--------->	
PVC	14.7	16.6	35.9	32.7	-
HYPALON	32.5	11.0	36.5	19.9	-
TISSUES	18.4	17.6	29.9	-	34.0
NEOPRENE	25.0	18.6	32.4	23.8	-
POLYURETHANE	5.0	19.2	32.3	-	43.5
POLYTHENE	0	7.0	93.0	-	-

Table 24 : Pyrolysis products

Water, odourless kerosene and lubricating oil additions of up to 150 ml to the 1 kg DNE package only marginally increased the pyrolysis time, but the amount of volatile hydrocarbon increased with the latter two liquids.

The tars generated during pyrolysis are a problem if they back diffuse into the package loading mechanism. This problem can be prevented with a purged slide valve mechanism and minimum surface temperatures of 300° C. The tars will then pass into the after burners together with the other volatile hydrocarbons.

No solids carryover from the char was observed in the pyrolysis process.

The char yields from the PCM wastes have been determined in addition to their oxidation characteristics. The source material of a char determines its initial oxidation rate, but another important factor which can affect the time for complete oxidation is the ash content of the char. Combustion of a bed of char, even at 900° C, is slow if air is passed over its upper surface. The rates can be increased by gentle stirring of the bed as occurs in a slowly rotating kiln. However, carryover of ash increases to greater than 20 % wt. for plant conditions. This problem is intensified by the very fine particle size of the ash.

It would appear that the problem of ash carryover can be limited by passing air or oxygen slowly upwards through a packed bed of char but locally high temperatures will occur. Data now exists from these studies with which to design a continuum incinerator capable of complete ashing. However, the subsequent extraction of the small amounts of plutonium may be difficult because of the relatively high temperatures reached in the char oxidation stage.

High temperature incineration of radioactive waste

Contract : 190-81-42 WASB, SCK/CEN, Mol.

Scope and Objective

The aim of this research is to further develop and run on a test base the FLK-60 high-temperature incineration installation.

Some technical improvements have been carried out, allowing treatment of combustible liquid waste and improving remote control and automation, with the aim of preparing the treatment of Pu-contaminated waste.

In the meantime, the incineration campaign, which had been started at the end of 1981, has been continued successfully. Most emphasis was put on the material and activity balances. A run with spiked waste has been carried out.

Different test runs have given valuable experience in the treatment of various kinds of combustible liquid waste.

Progress and Results

Technical works

- Preparation of sludge

  The thickeners-clarifiers have been tested and adjusted. The installation has been completed.

- FLK-60 incineration furnace

  . Main combustion chamber (FLK)

  On may 10, 1982 the superior part of the refractory lining was damaged and the plant had to be shutdown for disassembly of the furnace and pouring of a new lining. A more heat-resistant material was used for the part which had molten away. This incident caused about 36 days unplanned outage.

  . Auxiliary combustion chamber (ALK)

  The system for feeding the auxiliary burner with combustible liquid wastes is ready for use. It consists of two supply lines :

  ◊ A first line is used for waste oils with flash point above 25° C. It consists of a classical pumping system. The oil can be preheated before injection in the burner.

  ◊ A second line is used for mixtures with flash point under 25° C, such as toluene solutions of liquid scintillators. It consists of two closed tanks from which the waste is to be feeded by nitrogen pressure. Various safety devices have been incorporated.

  Both lines have been successfully tested.

- Granules conveying system

  . Granulator

  On september 21, 1982 the corroded chain of the granulator had to be removed and replaced. The new one was covered with a preventive coating. Since that time a nitrite-based inhibitor is added to the water bath.

  . Conveying of drums to the exit lock

  Pneumatically operated carriages allow positioning of drums under the granulator, air-tight connection and removal of filled drums to a point where they can be taken by the remotely operated overhead crane.

- Gas purification line

  . Water injection cooler

  The four low-pressure spray nozzles are now fed through a separated distribution circuit, which makes the whole device independant of the scrub water network and reduces the probability of plugging events.

  . Bag filters

  The construction of the hot line and of the small house for testing of metallic fiber bags has been started.

  A study about insolubilization of caesium-laden dust in concrete with various additives has been carried out.

  . Gas scrubbing

  The pH-control of the scrub water has been automatized by means of an adjustable-speed metering pump.

  The former steel piping network is being replaced by a new one, made of the more corrosion-resistant material polyvinylidene difluoride (PVDF).

- Nitrogen blanketing of the waste preparation line

  A new flowsheet was adapted to increase the blanketing efficiency and decrease the nitrogen consumption.

- Cooling water

  The secundary cooling loops will be fed with demineralized water to avoid scaling of the plate heat exchangers.

- Cranes and elevators

  The overhead crane in the alpha-hall can be operated from the control room, allowing remotely-controlled conveying of drums from the carriages to the exit lock. A special grasping device for 100 1 drums was designed and constructed.

Waste treatment in the FLK-60 installation

During the year 1982, 16 incineration runs totalizing 1111 working hours have been carried out. To this some 150 hours of test exploitation of the liquid combustible waste system have to be added.

The installation treated about 40 metric tons of mixed solid waste, which corresponds to a mean capacity of 36 kg/h, and some 10 m^3 of liquid combustible waste.

Secundary waste production amounted to about 650 kg of caesium-laden dust, some 20 prefilters and 12 HEPA filters, and about 800 m^3 of scrub water blowdown, which has been treated by chemical flocculation.

Characterization work

The granules and secundary waste streams were submitted to an extensive characterization work aiming at the determination of the physico chemical properties of those streams. Granules appear as tempered glass with typically 50 % SiO_2, 20 % Fe_xO_y, 20 % CaO, 7 % Al_2O_3 and 3 % of other oxides; dust is a mixture of chlorides and sulphates of sodium and zinc and scrub water in a sodium/hydrogen/carbonate solution.

From May 3 to 7, 1982 the feed was spiked with various beta-gamma emitting nuclides, allowing a radioactivity balance to be made. The most important result of it is that at most 0.8 % of the ^{144}Ce contents of the feed escape the furnace and are trapped in the gas purification line. The incorporation of that plutonium simulator in the granules can therefore be considered as quantitative.

Incinerator of alpha-waste in molten salts

Contract : 191-81-44 WASI, Agip Nucleare, Bologna.

Scope and Objectives

The aim of this work was the completion of the studies on the process of incineration in molten salts of alpha-contaminated waste. In particular the program considered the practical demonstration of the feasibitity of the process on the pilot installation (1 to 2 kg/h of uranium-contaminated waste) built in Medicina, Bologna.

Progress and Results

- Pilot installation for uranium-contaminated waste

  During 1982 the installation has been set at work again, after the incident of last year, caused by the deterioration of the gas-post-combustion chamber, which had to be completely rebuilt.

  During this period of idleness the opportunity was taken for making other changes on the installation, suggested by the experience acquired before the incident. Such changes have mainly concerned the the molten salt filter, the fan for the pneumatic conveyance of the granulate waste and the stirrer for the batching of the same to the incinerator.

  Furthermore an equipment for the control of the powders in the gas was installed. This also allows the measurement of their velocity.

  At first the installation has been tested with non-active waste with different compositions, then with waste contaminated by natural uranium.

The possibility to introduce capacitive and own-built self-induction probes into the pilot installation, for measuring the level of molte salt, was experimentally investigated.

On the bench-scale equipment there have been prepared some samples o the melt with a high content of ash and uranium. Such samples have been sent to CEA Fontenay-aux-Roses for testing on the electrolytic recovery of uranium.

In this way was confirmed the potentiality of the project (1 to 2 kg/h), reduction factors of weight and volume of about 5 and 50 respectively, and the good quality of the process gases, whose contents of powder before filtering were less than 20 mg/m^3. Accordin to the Quality Control Plan of the AGN Laboratories, the Operation Manual for the installation, has been drawn up.

- Experiments with plutonium

  At CCR Euratom - Ispra (Va), there has been concluded the expected cycle of experiments on the installation for the treatment of alpha-contaminated waste.

  There was carried out the whole sequence of operations, foreseen for the process on little quantities of synthetic waste containing uranium and plutonium : incineration of the waste, dissolution of ash, electrolytic recovery of uranium and plutonium in the form of oxides The recovery of uranium has been quantitative, that of plutonium more than 90 %.

- Laboratory activity

  As an alternative to the vitrification which has already been tried out, a system for the final conditioning of the ash + salt residues has been tried out with some tests on the granulation of the molten residues and englobing them in a metallic matrix, according to a technique proposed for glass and calcinates.

Recovery of alpha-wastes by molten salt electrolysis

Contract : 192-81-44 WASF, CEA, Fontenay-aux-Roses.

Scope and Objectives

In correlation with the incineration-pyrolysis studies of Agip-Nucleare (see contract 191) this work is concerned with the recovery of alpha-wastes from samples of molten sulphates by electrolysis. As in 1981 the experiments are aimed at the recovery of uranium.

Progress and Results

- Tests on Agip pyrolysates containing 10 % ash without uranium

  The necessary uranium is added at the CEA to these AGIP pyrolysates by sulphuric dissolution of oxide UO_2.

  The electrolyses are carried out at 580° C in cycles (for example a cycle of 18 operations in 112 hours), under constant 1,5 volt tension between two platinum electrodes.

  The deposits obtained, remarkably well-crystallised, are highly encouraging. Though morphologically different they ressemble the deposits laid down earlier with ash-free sulphate baths. The electrolysis technique thus proves efficient for the removal of uranium from these AGIP pyrolysates.

  Spectrographic analysis shows that the purity of the deposits is good, while the "coating salt" content (residual electrolyte) is very low (Na + K < 40 ppm), according to neutron activation analyses. The post-electrolytic washing methods used are therefore satisfactory.

- Corrosion studies

  These corrosion tests are aimed at the definition of a "pilot" laboratory electrolyser. They are carried out in the ternary sulphate eutectic at 600° C for 670 hours with three steels (mild steel, 304 and 316 stainless) and a nickel alloy (Hastelloy X). The main results are as following :

- mild steel, with a weight loss of 60 to 100 $mg.cm^{-2}$, is 10 to 50 times more corroded than the other materials, which show a mass variation between 2 and 6 $mg.cm^{-2}$;
- no appreciable corrosion difference is observed between partially and totally immersed samples.

The thermopile effect, often observed in these media, thus seems very slight.

A micrographic analysis has been carried out.

N.B. This study should help to solve the serious corrosion problems encountered by AGIP in their pyrolysis work.

- Tests on real AGIP Nucleare pyrolysis baths

(about 10 % UO_2 and 10 % ash).

With these <u>real</u> pyrolysis baths, received from AGIP during the second half of 1982, the results confirm the efficiency of electrolysis for the extraction of uranium from such media. The deposits are well crystallised and the extraction yields very high ($\sim$ 95 %). Here the electrolysis is performed in cycles of 12,6 hour periods under a constant 1,5 volt tension. To estimate the electric or faradic yield, the electrolysis is performed in a single operation, lasting about 160 hours. The extraction yield is still good ($\sim$ 95 %), which takes priority in this recovery process, but the faradic yield is only about 10 %. With ash-free baths however the faradic yield under the same electrolysis conditions is high, around 90 %. These results were confirmed both with new ash free AGIP baths (12,3 % UO_2) and with 10 % ash AGIP baths to which uranium was added at the CEA by sulphuric dissolution.

The presence of ash thus seems to have a decisive effect on the faradic yield.

X-ray analysis with these <u>real</u> pyrolysates show a change in nature of the deposits according to the electrolysis time. In fact the lattice parameter "a_0" increases steadly from the start of electrolysis, where U_4O_9 is deposited, until the end where the deposit is UO_2.

1.4.2. WASHING AND LEACHING, CHEMICAL TREATMENT

Conditioning of plutonium-bearing waste by acid digestion

Contract : 187-81-45 WASD, KfK, Karlsruhe.

Scope and objective

The plant ALONA was errected at Mol in 1981 for treatment of the plutonium containing wastes stored at Eurochemic : approx. 1 metric ton of waste,containing approx. 8 kg of plutonium. Inactive testing was started.

Within the framework of preparations for the active demonstration of the process the plant components were subjected to testing during six weeks of permanent inactive operation, the operating parameters set and the operating crew trained for active operation. Besides, investigations were performed with regards to the safety of the chemical process.

Progress and Results

- Inactive test operation

  During inactive test operation all components of the plant were subjected to testing. No significant faulty operations occurred. Contrary to the planned waste throughput of 50 kg/week, 25 kg/week were attained. The deficit is a result of the long cooling time of the digester content of 12 hours and of interruptions in operation due to the lack of operating experience of the staff. In the course of the test operations approx. 150 kg of simulated waste were digested. It was possible to adjust the operating parameters and mode of operation to conform to those of the optimized inactive test plant, e.g. for the specific consumption of media (HNO_3, H_2O_2). Fig. 23 shows the acid balance of the plant.

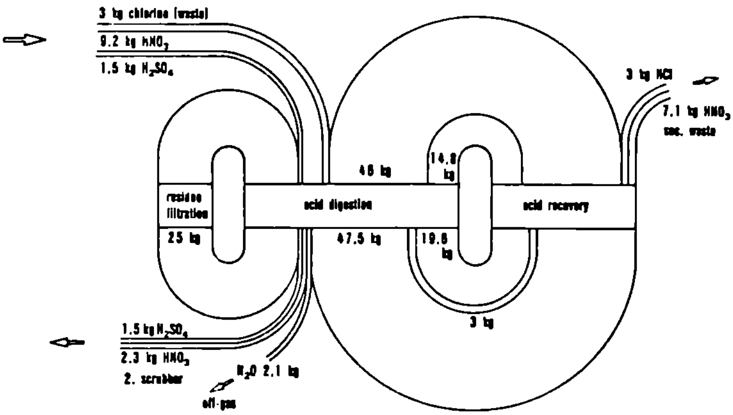


Fig. 23 : Plant ALONA
Material balance of the acids per 10 kg waste digested

- Investigations into the safety of the chemical process

The plutonium containing waste of Eurochemic, which is composed of cellulose, neoprene, polyvinyl chloride and polyethylene, may also contain potassium permanganate, oxalic acid and sodium carbonate. These materials were used to decontaminate gloveboxes and equipment. Most of the plutonium occurs as oxide. It may also be present as nitrate since one of the sources producing waste was the facility for concentrating plutonium nitrate. The presence of specific chemicals in the waste may constitute a potential risk to the plant. To be able to estimate this risk potential, appropriate investigations were performed with inactive materials in a plant comparable to the active plant as regards the process and the throughput capacity.

- Risk potential due to potassium permanganate

The presence of potassium permanganate in the waste can be dangerous. Therefore, tests were performed to obtain quantitative information about the risk potential. According to the results only the presence of cellulose absorbing the potassium permanganate leads to an increase in the temperature of the sludge of 10° C above room temperature (related to a batch of 8 l of sludge of the usual solid concentration). Such a temperature rise lies within acceptable limits.

If the waste containing potassium permanganate enters into contact with the sulphuric acid used in the mixing vessel, a reduction into Mn^{2+} takes place immediately. The formation and accumulation of manganese heptoxide (Mn_2O_7), which may undergo explosive decomposition, can be ruled out because of the presence of organic materials.

- Risk potential during the production of waste sludges

Nitrate ions may be introduced into the system by sulphuric acid contaminated with HNO_3 and by plutonium nitrate. During mixing of the waste sludges this may lead, besides the partial carbonization of the waste, to its partial oxidation as well.

In this case an increase in temperature, gas formation and, dependent on the amount, the buildup of a foam layer on the surface of the sludges are observed. As shown in investigations, the temperature of the sludges increases to 55° C in case 4.5 l of sulphuric acid (96 wt.%) contain 1 mole of nitrate ions. This corresponds roughly to 70 ml HNO_3 (65 %) or about 100 g plutonium nitrate, respectively.

This rise in temperature is counteracted by analysis of the produced acid from acid recycling prior to discharge into the mixing vessel and by limiting to about 20 g the plutonium amount in each batch (this limitation is imposed also to keep low the radiation exposure of the staff).

If in case of failure of the controls the temperature rises in the mixing vessel and a foam layer builds up, cooling is possible (the mixing vessel is provided with a double jacket). Nevertheless, the foam layer may extent itself over the waste post-in system (contents about 20 l) and in the process offgas line up to the first oxidation absorption column. However, this bears no serious consequences on the system.

- Risk potential during wet combustion of the waste

It must be clarified whether the reaction of the waste materials with nitric acid might may produce nitration products on account of the elevated temperature. Literature studies have shown that at a temperature of 250° C and a molar ratio of sulphuric acid to nitric acid of at least 50:1,nitrated samples are not produced. (In ALONA the molar ratio ranges from 50:1 to 100:1). It is rather an oxidation of the organic compound that occurs, during which the C-C-bonds are splitted with the intermediate formation of carboxylic acids (in the last term oxalic acid) to give ultimately carbon dioxide and water.

Investigations were performed into the tendency of formation of volatile nitrated organic compounds leaving the reactor together with the exhaust gas. It was shown that no such nitration products are formed. In these investigations the waste was introduced on the acid surface whilst the waste in the ALONA plant is fed in the partly carbonized condition below the hot acid surface. In this way, it is dispersed immediately and further carbonized in the digester acid followed by oxidation.

During the whole testing phase of the ring digester (about 300 hours of operation) with a simulated waste the combustion of gaseous products has never been observed. Also in case of addition of methanol into the waste sludges subsequent wet incineration the same result was obtained. Similar tests as well as tests extended by imposed ignition,were performed also by HEDL. It was shown that only in the presence of large amounts of ethylene glycol auto-ignition of the gas mixture takes place. However, this liquid is not present in the solid wastes of Eurochemic.

Washing processes for plutonium recovery from solid wastes

Contract : 188-81-44 WASD, Alkem, Hanau.

Objective and Scope

Aim of this R&D programme is to evaluate the potential of mechanical washing processes for the recovery of Plutonium and Uranium from primary wastes, generated during fabrication of Plutonium containing fuel.

Objectives of the R&D programme are :

- to establish a washing process with sufficient decontamination results applicable to the decontamination of solid alpha bearing waste and
- to recover fissionable elements from washing solutions in order to avoid secondary wastes of Plutonium.

After premininary investigation with uranium contaminated wastes for the determination of the processes, the tests were continued with plutonium contaminated wastes for the optimisation of the processes and process parameters. After that it should be demonstrated the efficiency of the washing process on a technical scale.

Progress and Results

During the last year a number of washing experiments using PuO_2- and PuNH-bearing original wastes from MOX fuel fabrication have been carried out in order to study the influence of the primary contamination level and the radiation impacts of Plutonium/recovery/rates.

A small washing machine of 4 litres volume and an ultrasonic bath have been used together with an aqueous solution, HNO_3 and Freon ($C_2F_3Cl_3$) as washing agents. The Plutonium contamination of the waste was measured by neutron coincidence counting before and after washing.

Using water with a foam-suppressing detergent containing EDTA as washing medium and after 1 h washing at 60° C, recovery rates from PuO_2-contaminated organic wastes as shown in tables 25-27 were obtained.

The efficiency of the washing processes depends largely on the age of the contamined material and the degree of the contamination. Shorter contact times with the alpha-emitter means better recovery. Ultrasonic treatment in addition to the chemical waste washing does not improve the recovery rate in case of soft organic material. The application of Freon instead of aqueous solution gives no advantages except of the fact that the synthetic tissues must not be dried after washing.

Current No.	active age	number of wipes per package	Pu-Inv./pack. before washing	Pu-Inv./wipe before washing	Pu-Inv./wipe after washing	Pu-recovery rate R %
1	1 week	8	21,50 g	2,68 g	0,19 g	93 %
2	1 week	8	16,90 g	2,10 g	0,22 g	90 %
3	1 week	10	6,10 g	0,61 g	0,07 g	89 %
4	4 weeks	3	0,83 g	0,27 g	0,10 g	63 %
5	4 weeks	5	1,00 g	0,20 g	0,07 g	65 %
6	16weeks	19	9,73 g	0,51 g	0,13 g	75 %
7	24weeks	2	2,20 g	1,10 g	0,40 g	64 %
8	54weeks	6	2,99 g	0,50 g	0,22 g	56 %

[1] 4 l-machine, water with 4 % "Radiac Wash" as detergent at 60 °C for 1 hour, 2 rinsing steps each 10 minutes

[2] approx. 30 x 30 cm, weight per wipe approx 15 g

Table 25 : Washing of PuO_2-bearing polyester wipes [2] whith aqueous solutions in a small washing machine [1].

Current No.	active age	number of wipes per package	Pu-Inv./pack. before washing	Pu-Inv./wipe before washing	Pu-Inv./wipe after washing	Pu-recovery rate R %
1	1 week	5	6,70 g	1,34 g	0,40 g	70 %
2	2 weeks	7	16,70 g	2,38 g	0,21 g	91 %
3	3 weeks	6	12,00 g	2,00 g	0,22 g	89 %
4	3 weeks	4	0,70 g	0,175 g	0,075 g	57 %
5	3 weeks	10	6,60 g	0,660 g	0,190 g	71 %
6	3 weeks	6	5,30 g	0,880 g	0,420 g	50 %
7	3 weeks	5	5,30 g	1,060 g	0,180 g	83 %
8	3 weeks	5	6,80 g	1,360 g	0,220 g	84 %
9	3 weeks	7	4,70 g	0,670 g	0,200 g	70 %

1) 4 l-machine, water with 4 % "Radiac Wash" as detergent at 60 °C for 1 hour, 2 rinsing steps each 10 minutes

2) approx. 38 x 46 cm, weight per wipe approx. 14 g

Table 26 : Washing of PuO_2-bearing polypropylene-wipes [2] with aqueous solution in a small washing machine [1]

Table 27-28 show also the results using 0.5 M HNO_3 as washing medium for different materials under similarly conditions (60° C, 1 h washing). As shown less pores in the surface improved the recovery rate.

Using Freon for purification of nonporous metallic wastes recoveries of 76-98 % can be achieved.

For porous metallic filters the treatment with HNO_3, for dissolution of UO_2/PuO_2 should be recommended because for washing experiments with Freon and aqueous solution recoveries in the range of 20-70 % only have been obtained.

Current No.	material	active age	aggregate	washing solution	Pu-Inv./pack. before wash.	Pu-Inv./piece before wash.	Pu-Inv./piece after wash.	Pu-recovery rate R %
1	polypropylene wipe	3 weeks	US-bath 6)	H_2O-RW 1)	2,64 g	2,640 g	0,290 g	89 %
2	polypropylene wipe	3 weeks	agitated US-bath	H_2O-RW 1)	3,04 g	0,760 g	0,290 g	62 %
3	polyester wipes	1 week	agitated US-bath	Freon 2)	21,26 g	2,66 g	2,63 g	2 %
4	polyester wipes	56 weeks	US-bath	Freon 2)	1,30 g	1,30 g	1,30 g	0 %
5	cellulose tissues	<6 months	US-bath	Freon 2)	1,70 g	1,70 g	1,30 g	21 %
6	cellulose tissues	<3 days	US-bath	Freon 2)	0,18 g	0,18 g	0,16 g	11 %
7	polyester wipes 3)	5 weeks	4 l-wash. machine	0,5 m HNO_3 1)	3,50 g	0,70 g	0,16 g	77 %
8	polypropylene wipes 3)	5 weeks	4 l-wash. machine	0,5 m HNO_3 1)	0,76 g	0,19 g	0,14 g	26 %
9	polyethylene bottles 5)	20 weeks	4 l-wash. machine	H_2O-RW 1)	2,40 g	1,20 g	0,048 g	42 %
10	rubber piece 4)	>2 years	4 l-wash. machine	H_2O-RW 1)	3,28 g	3,28 g	1,45 g	56 %
11	neoprene-box glove	>2 years	4 l-wash. machine	H_2O-RW 1)	2,50 g	1,25 g	1,00 g	20 %
12	neoprene-box glove	>2 years	4 l-wash. machine	H_2O-RW 1)	0,90 g	0,90 g	0,40 g	56 %
13	neoprene-box glove	4 years	4 l-wash. machine	H_2O-RW 1)	1,21 g	1,21 g	0,51 g	58 %
14	neoprene-box glove	>1 year	4 l-wash. machine	H_2O-RW 1)	0,97 g	0,97 g	0,67 g	31 %

1) 1 hour at 60 °C, 2 rinsing steps each 10 minutes
2) 1 hour 20 °C, 2 rinsing steps each 10 minutes
3) wipes contaminated with PuNH
4) rubber container of a centrifuge
5) Ø 5 cm, height 10 cm
6) D x W x L = 15 x 15 x 30 cm

V = 6,7 l, 80 watt HF-net efficiency

Table 27 : Washing of organic PuO_2-bearing waste materials at different conditions

Current No.	material	active age	aggregate	washing solution	Pu-Inv./part before washing	Pu-Inv./part after washing	Pu-recovery rate R %
1	Alu-box	1,5 years	US-bath	Freon 1)	21,00 g	0,58 g	98 %
2	Alu-box	1,5 years	US-bath	Freon 1)	19,00 g	0,58 g	97 %
3	Alu-box	2 years	US-bath	Freon 1)	1,64 g	0,13 g	92 %
4	Alu-box	2 years	US-bath	Freon 1)	2,12 g	0,50 g	76 %
5	metallic filter	> 1 year	US-bath	Freon 1)	5,30 g	1,66 g	69 %
6	metallic filter	> 1 year	US-bath	Freon 1)	13,57 g	10,18 g	25 %
7	metallic filter	> 1 year	US-bath	Freon 1)	1,04 g	0,81 g	22 %
8	metallic filter	> 2 years	US-bath	0,5 m HNO_3 2)	11,80 g	0,40 g	97 %
9	metallic filter	> 2 years	US-bath	0,5 m HNO_3 2)	1,20 g	0,50 g	58 %
10	porcelain frit	5 years	4 l-wash. machine	2 m HNO_3 3)	4,06 g	1,81 g	55 %
11	porcelain frit	5 years	4 l-wash. machine	H_2O-RW 4)	3,70 g	2,80 g	24 %

1) 1 hour at 20 °C, 2 rinsing steps each 10 minutes
2) 20 minutes at 20 °C, 2 rinsing steps each 10 minutes
3) 20 hours at 20 °C, 2 rinsing steps each 10 minutes
4) 1 hour at 60 °C, 2 rinsing steps at each 10 minutes

Table 28 : Washing of anorganic PuO_2-bearing waste materials

1.4.3. ALPHA-MONITORING OF WASTES

Measurements on standard waste drums

Contract : 182-81-42 WASF, CEA, Cadarache.

Scope and Objective

Work in this and the following two contracts are concerned with a round-robin test on plutonium monitoring of a number of drums, containing cemented Pu-contamined waste. Participants are CEA-Cadarache, UKAEA-Harwell and KfK-Karlsruhe.

The aims of this round-robin test are :

- the comparison of the measurement and analysis results on a same set of waste drums
- the exchange of information on the different methods, techniques and instruments used to get these results
- the drawing up of a conclusion on the state of the art including the limitations, the uncertainties and if necessary a proposed development programme.

CEA-Cadarache and KfK-Karlsruhe are charged with the manufacture of the waste containing drums.

Progress and Results

- Intercomparison of the contaminant samples

  90 contaminant samples have been measured in the same configuration, for comparison, by the two passive techniques : VDC spontaneous fission neutrons detection and gammametry. These results are correlated with the contaminant masses measured during the fabrication phase.

- Reference calibration

  10 contaminant samples of different sizes and natures have been calibrated by the Bureau National de Métrologie, Office des Rayonnements

Ionisants, Laboratoire de Métrologie des Rayonnements Ionisants SACLA'

Three types of measurements were used : calorimetry, gammametry and neutron detection to get :

- the Pu isotopic composition
- the number of heavy nuclides
- the number of emitted neutrons
- the number of (α, n) neutrons.

- Matrixes preparation

The polyethylene foam matrixes (8 items) have been machined to drill the longitudinal holes for spatial contaminant variation studies. In the same time, aluminium guide tubes were prepared. One concrete matrix with four longitudinal holes has been built in two axial halfs tc facilitate the handling.

- Waste drum set build up

Four synthetic modular drums were filled with a drilled foam cylinder and the contaminant sample(s) can be introduced at different positions to get the wanted configurations.

Four synthetic sealed drums were filled with a drilled foam cylinder, the contaminant samples fixed in non communicated positions, then th drums were top covered and sealed.

The concrete drum is a modular one.

Two real waste drums were prepared in an independant laboratory with identified materials.

For the modular drums a table giving the contaminant positions in the different configurations will be send to the other participants i the round robin test.

- Measurements

Eighty-two pre-defined configurations have been measured on the BANC(prototype device.

BANCO allows the simultaneous measurements in passive mode of :

- spontaneous fission neutrons

- gamma spectrum integrated during an axial gamma scanning with a rotating drum.

The spontaneous fission neutrons detection is made by a VDC technique associated with one ring of 24 He^3 counters.

The gammametry is performed with a HP Ge planar detector, with a special radial and axial collimator, moved in parallel to the axis of the drums in an axial slit machined in the neutron detection block.

In addition a neutron active method has been applied on two configurations : 200 1 drums with 0.3 g/cm^3 polyethylene foam and concrete.

The activation is produced by a Cf source and the delayed neutrons are detected.

- Results

Raw experimental results will be analysed in 1983.

The elaborated results will be reported with no diffusion to the other participants before the end of the experimental phase of the round robin test.

Comparison of different monitoring techniques for alpha-bearing waste

Contract : 183-82-41 WASUK, UKAEA, Harwell.

Measurements at Harwell on these drums started in 1983.

Comparation measurements on waste drums

Contract : 184-81-43 WASD, KfK, Karlsruhe.

Measurements at KfK-Karlsruhe will start after reception of the drums from UKAEA-Harwell.

1.5. TESTING AND EVALUATION OF SOLIDIFIED HIGH ACTIVITY WASTE FORMS*
(joint annual report)

The joint test programme-involving the laboratories of AERE Harwell, CEA Saclay and Marcoule, SCK/CEN Mol, the Frannhofer Institut Würburg, the Hahn-Meitner-Institut Berlin and the University of Leiden, - was continued during 1982. The reference test materials, essentially borosilicate classes, which are the same as during 1981, are presented in table 30.

	UK 209	UK 189	C 31/3	VG 98/3	SON 45	SON 58	SON 60/20	SON 60/30	SON 61	SON 61a	SON 62	SON 64	SON 64/G3	SON 65	SAN 60	SM58 LW11	SM58 LW11
Fission product oxides	9.75	9.50	15.20	15.54	24.76	22.70	14.09	24.14	13.04	24.76	13.14	13.14	13.00	15.68	1.21	(SCK) 6.06	(F1) 2.82
Waste oxides	◊	◊	*	+		✱	A		ᴗ	□	◦	∘	∇		Δ		●
Fe_2O_3	2.73	2.68	1.47	0.70	0.66	0.60	5.44	0.73	5.07		5.07	5.07	5.90	0.60		1.17	1.71
Cr_2O_3	0.56	0.55	0.42	0.24	0.13	0.20	0.47	0.05	0.43		0.43	0.43	0.50	0.10			0.28
Ni O	0.36	0.36	0.23	0.21	1.00	0.10	0.26	1.05	0.24		0.24	0.24	0.20	0.68		0.11	0.43
Mg O	6.34	6.23		0.40	0.24			0.16						0.18			
Al_2O_3	5.11	5.03			1.78	0.10	1.69	1.62	1.70		1.70	1.69	0.20	4.83			0.94
U_3O_8	0.06	0.058	0.46	1.21	3.84	3.60	0.48	3.87	0.45		0.45	0.45	0.90		0.02		0.12
Na_2O																3.67	3.37
Also : ◊ 0.1% SO_4, 0.4% ZnO, 0.23% P_2O_5, * 2.2% Na_2O, + 0.60% P_2O_5, ∇ 0.4% P_2O_5, 5.9% Gd_2O_3, Δ 0.15 F^-, 0.62 SO_4^{--}, 0.33 Fe_2O_3, ✱ 0.6% P_2O_5, ∘ 0.36% P_2O_3, 0.43% ThO_2, A 0.38% P_2O_3, 0.46% ThO_2, □ 2.83 AmO_2, ● 0.55 SO_3, 0.77 F_2																	
Glass formers			ϕ														
Si O_2	50.88	41.51	34.75	41.84	37.16	43.60	45.11	48.27	44.96	50.82	43.41	47.16	44.20	45.24	43.41	56.87	56.87
B_2 O_3	11.12	21.87	4.14	10.48	13.44	19.00	16.50	13.09	18.43	13.39	22.11	18.42	17.30	21.98	17.00	12.28	12.28
Na_2 O	8.30	7.68	1.12	22.25	20.65	9.40	15.04	8.05	14.74	8.25	12.60	12.53	11.50	8.68	10.67	4.63	4.63
Li_2 O	3.99	3.69	0.98												5.00	3.74	3.74
Al_2O_3			10.28	1.20											18.09	1.16	1.16
Ca O			3.84	2.32											3.50	3.83	3.83
Ba O			14.48														
TiO_2			2.80	3.52												4.45	4.45
MgO			1.44													2.05	2.05
Also : ϕ 0.8% ZrO_2, 4.88% ZnO, 0.48% As_2O_3																	

Table 30 : Composition of reference test materials in weight %.

* The presentation of chapters 1.1 and 1.5. is slightly different from the other chapters, where reporting is done contract by contract.

The joint annual report of the R&D work performed during 1982, is presented under the following headings :

The above mentionned contracts refer to the following laboratories, titels, etc. :

121-80-53 WASUK, AERE, Harwell, "Evaluation of properties of materials for immobilization" (see pp. 134, 146, 147, 149)

122-80-53 WASD, HMI, Berlin, "Characterization of comparison of HAW-products" (see p. 132)

123-80-55 WASF, CEA, Marcoule, "Testing of the radiochemical resistivity of glass products" (see p. 143)

124-80-55 WASB, SCK/CEN, Mol, "Physico-chemical characterization of conditioned radioactive waste products" (see p. 140)

125-80-53 WASNL, Univ. of Leiden, "Testing and evaluation of ceramic materials for HAW-immobilization" (see p. 150)

232-81-53 WASD, Fraunhöfer Institut, Würzburg, "Corrosion mechanisms of HAW containing glass" (see p. 135)

268-81-55 WASF, CEA, Saclay, "Migration study on actinides and fission products in HAW-glass matrices" (see p. 137)

The main efforts during 1982 were devoted to :

- Study the basic leaching mechanisms by complementary analyses of the leachate and of the sample surface.

- Continuation of testing of the radiation stability of samples dope with 238 Pu during the first programme 1975-79
- Complementary parametrical studies with emphasis on the two Belgia reference glasses
- Research on the retention capacity of various hollandite phases fo Cs and Sr.

A considerable amount of work under this programme was presented at t Fifth International Symposium of the Materials Research Society co-sponsored by the Commission and held on 7-10 June 1982 in Berlin*.

1.5.1. CHEMICAL STABILITY

- Basic leaching mechanisms
  . Hydrothermal leaching of simulated HLW glass

Contractor : Hahn-Meitner-Institut Berlin (122-80-53 WASD)

The hydrothermal leaching of simulated high level waste borosilicate glass C-31-3EC was investigated in water, rock salt und KCl-$MgCl_2$-CaC $MgSO_4$ solutions (Q und Z solutions) at 200° C. Surface layers were investigated by Scanning Electron Microscopy (SEM) and Electron Probe Microanalysis (EPMA). The samples were glass beads having size and shape comparable to beads,which will be produced in the German prototype vitrification plant PAMELA.

Leaching with NaCl, Q and Z-solutions leads to the formation of sur face layers of different compositions and complex structure. From th composition of the layers and concentrations of the elements in the layers (fig. 25) it must be assumed that the layers do not represent partially leached glass phase and are formed by instantaneous precipi tation of insoluble compounds, formed upon leaching.

* See Seminars nr 2.

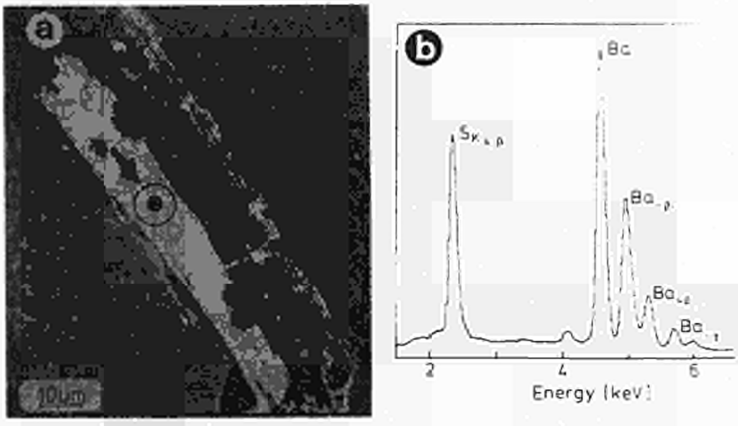


Fig. 25 : (a) SEM photomicrograph of a cross-sectioned glass surface leached one year at 200° C in quinary brine.
(b) EDX spectrum of the phase, indicated by the black point in figure (a).

The surface layer of the one year leached sample adhered very strongly to the surface and could not be removed, while on the contrary layers peeled off more readily after short leaching time. Longer leaching periods yielded denser surface layers. Obviously, with increasing leaching time, the mechanical stability of the surface layer increases, but the layer does not become thicker after 30 days. The specific weight loss after one year was about 5 to 6 $mg.cm^{-2}$, the same as after 3 - 10 d leaching. The leaching rate slowed down close to zero. Hence, the release of matter was discontinued, but the surface layer became increasingly impervious for both the leachants and leachates.

From the changes of surface composition and the changes of the leachant composition, it was concluded that a stationary state was not reached after one year of leaching.

The drop in the leach rates suggests that the surface layer protects the underlying glass against further attack.

Although the surface layers formed in the various leachants are different in nature and composition, the protective property for the underlying glass can be assumed to be a common feature.

Contractor : AERE, Harwell (121-80-53 WASUK)

The studies on glass UK189 have now been extended to temperatures up to 60° C. At all temperatures, Na, Li, B and Mg were found to leach congruently (i.e. at a rate proportional to their concentration in the glass) while Si, Sr and Al were released more slowly. The silicon leach rate decreased with time at the higher temperatures, whereas at 20° C it was time independent. In the longest experiment, it was found that, after an initial settling down period, the amount of Li leached at 20° C was proportional to $\sqrt{(\text{time})}$ for up to one year, indicating a diffusion-controlled mechanism.

A series of experiments has been started in which glass granules are leached to saturation in a small volume of water. Samples of granules are sealed in PTFE containers of 8 ml capacity and placed in a water-bath for various times. The two glasses UK189 and UK209 are being used each in two size fractions such that the surface area/volume ratios are 7.8 and 19.0 mm^{-1} respectively. Preliminary results for UK189 show greatly reduced leach rates. In experiments at 45° C the following results were obtained.

Leach time (days)	S.A./V (mm^{-1})	Volume of water (ml)	Si Conc. ppm	Total Si mg	Glass equivalent leach rate ($g.cm^{-2}/day^{-1}$)
79	7.8	3.35	46.3	155	3.9×10^{-8}
70	19.0	3.43	65	223	2.5×10^{-8}

In unlimited water the leach rate would be ca. 3×10^{-5} $g.cm^{-2}$ day^{-1}. Since the concentrations of major elements are far below saturation after this short test, it is thought that the high pH is the major cause for the reduction in leach rate. Unfortunately there was insufficient leachate to measure pH exactly, but it was certainly in excess of 10. More samples are in course of preparation, and results for longer times will become available over the next 6 months.

Contractor : Fraunhofer Institut, Würzburg (232-81-53 WASD)

The Fraunhofer-Institute für Silicatforschung, Würzburg, has undertaken a part of the investigations concerning the chemical durability of certain glasses provided for the storage of high level waste (HLW) in the Federal Republic of Germany. The test conditions - i.e. the application of temperatures $\leqslant 200°$ C, pressures $\leqslant 130$ bars, and the so-called Q-solutions as leachate - correspond to the concept of waste storage in rock salt deposits. The glass investigated during 1982 is the so-called SM 58 LW 11. Its composition in wt.% is 57 SiO_2, 12.5 B_2O_3, 1 Al_2O_3, 4.5 TiO_2, 3.5 Li_2O, 4.5 Na_2O, 2 MgO, 4 CaO, and 11 (simulated, i.e. inactive) waste.

Experimental

SM 58 LW 11 samples were corroded in Q-solution under hydrothermal conditions for periods between 6 and 360 days. In order to obtain the overall kinetics of the corrosion process, the weight losses of the samples were determined. Concentration changes occurring in the surface region of the glass were investigated by the ESCA (electron spectroscopy for chemical analysis) method. By the application of Ar ion milling and hydrofluoric acid etching techniques, depth profiling was carried out. Some of the samples were heat treated for crystallization. Some crystallization properties were determined by optical microscopy.

Results

The complex corrosion mechanism mainly consists of three individual mechanisms :

- During corrosion a heterogeneous reaction layer was formed on the glass surface. It was at least partly crystalline, had a poor mechanical stability in itself and a very weak connection to the residual glass. The boundary between reaction layer and residual glass was very sharp. The layer was removed before further investigations (e.g. weight loss measurements, ESCA) were carried out.

- During corrosion the glass matrix was dissolved. This effect could be measured gravimetrically (comparing the mass of the glass before the test with the mass of the residual glass). The weight loss data showed little or no pressure dependence. They were enhanced when the surface area to leachate volume ratio was small. Temperature dependence was very strong : a comparison of 30 days tests carried out at 120 and 200° C, respectively, revealed an increase in weight loss by a factor of 25. Very recent results from tests at 120° and 160° C indicate that, after an initial period of about 30 days, the kinetics of the dissolution mechanism changes towards a time law with an exponent well below 0.5.

- After corrosion the concentrations of elements in the near surface region of the residual glass were found to be different from those in the bulk, i.e. concentration profiles were built up. Temperature had a strong influence on this process. As to the time dependence : the profiles of many elements seem to reach a stationary form even after eight days. This is, however, not the case for sodium and hydrogen, which

In addition to the experiments with homogeneous glass samples, corrosion tests with crystallized samples were carried out. Crystallization severely deteriorated the chemical durability of the glass. It is however questionable, whether crystallization properties of the inactive model glass are valid for the active glass.

Outlook

The results obtained so far give an insight into the corrosion behaviour of the SM 58 LW 11. At the same time they show the need of further investigations especially in two fields. The reasons for the change in the dissolution kinetics have to be discovered (the change may be due to the reaction layer or the corrosion profile formation process or to both of them). Moreover, the question whether the Na- and H-profiles will reach s steady state or not, has to be answered. Appropriate experiments are projected.

. Surface analysis of hydrated glass

Contractor : CEA, Saclay (268-81-55 WASF)

The aim of this work is to follow the behaviour of actinides (Np, Pu, Am, etc.) and other interesting elements (H, Na, Al, Si, rare earths, etc.) in the gel layer, developed at the surface of an hydrated glass, versus leaching conditions (temperature, pH and nature of the leachant, etc.) corresponding to a real storage configuration.

This study will contribute to a better understanding of the basic principles which govern the leaching mechanisms, and to obtain scientific data concerning the efficiency of nuclear waste glasses.

Experimental methods

The experimental devices used to leach, to check and to prepare α spiked glass samples before their analysis, were set up and tested.

Concentration profiles, induced in the near surface region of glasses by the aqueous leaching, are measured in a non-destructive way, using analytical techniques especially developed.

Two methods seem particularly adapted :

- the direct observation of resonant nuclear reactions to determine light elements (H, Na, Al, etc.);
- Rutherford backscattering of helium-4 ions to study heavy elements (actinides, rare earths, etc.).

The eventual distortions of such profiles, consecutive to the variation of the hydrated layer composition versus depth, are notably reduced using a FORTRAN computing program especially built for this purpose.

An adapted experimental set up, needed for the examination of glasses containing actinides, using the analytical techniques previously described, has been installed near a 2 MV VAN DE GRAAFF accelerator.

Moreover, a nuclear microprobe allows on one hand to perform some particularly interesting punctual observations, on the other hand to explore thick layers (concentration profiles on typical depth in the range 10 → 500 μm).

Results

The experimental devices and the analytical techniques briefly presented have been tested with simple borosilicate glasses containing cerium and thorium.

The results obtained show that the acidity (resp. the basicity) of the leachant, but also the presence of ionic species (Al^{3+}, Fe^{3+}, CO_3^{2-}, ...) in aqueous solution, strongly influence the behaviour of the two heavy elements, mentioned above, in the hydrated layer.

Some experiments, performed with the nuclear microprobe, illustrate the possibilities allowed by this new analytical tool in the field of the hydrated glass surface studies.

Main conclusions are the following :

- the eventual secondary effects like ionic migration during sample bombardment are practically negligible;
- the concentration profiles of more than ten elements (Na, Si, Ca, Mn, Fe, Ni, Zn, Sr, Zr, Mo, Ce, Th, U, etc.) are simultaneously determined on a depth from 10 μm to several 100 μm, with a lateral resolution around 2 μm.

Fig. 26 constitutes an application example of the use of this new analytical device for the observation of the superficial region of hydrated glasses.

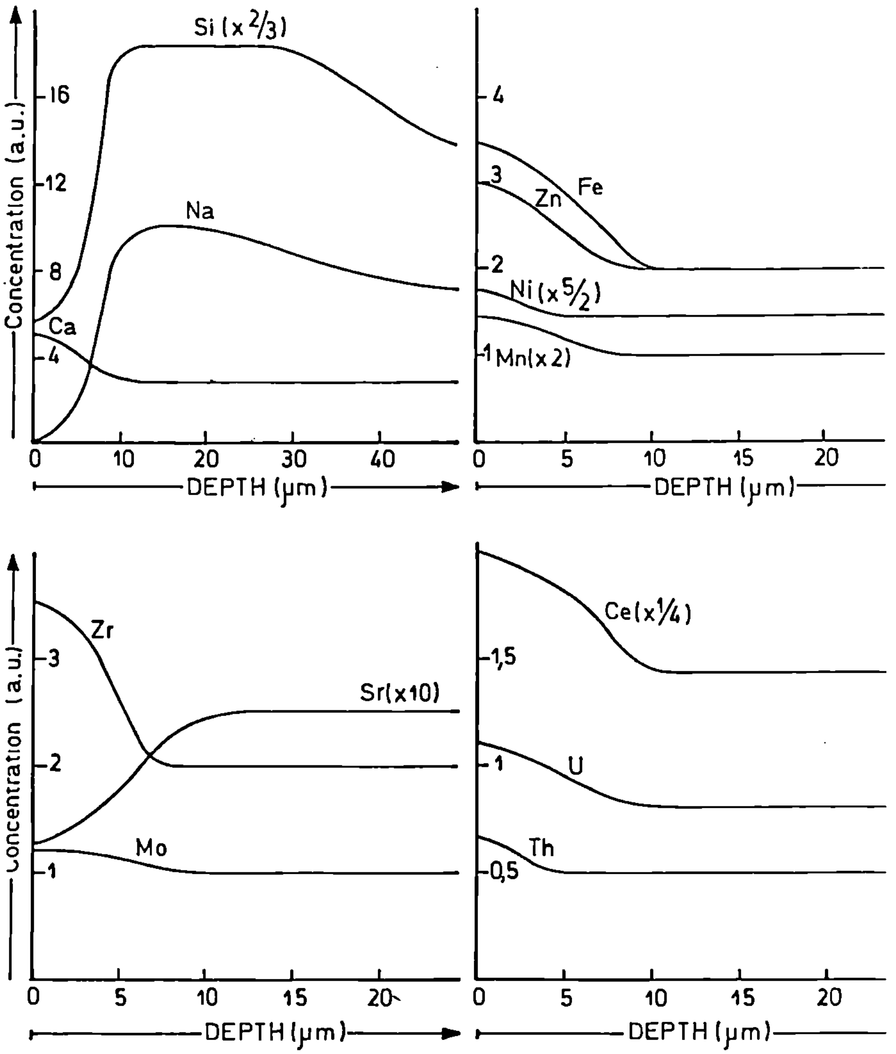


Fig. 26 : Elemental concentration profiles determined in the near surface region of glass sample SON 68 18 17 leached at 90° C during 14 days in deionized water (SA/V = 0.5 cm^{-1}), using nuclear microprobe.

- Parametrical studies

Contractor : SCK/CEN, Mol (124-80-55 WASB)

The objectives of this research programme are twofold :

a) Characterization of two glass compositions developed for the Eurochemic waste, by Soxhlet leach tests and by static leach tests at temperatures of 40, 70, 90, 120, 150, 200° C. Both cast and devitrified glasses will be investigated. Effects of pH are studied at 90° C.

b) Evaluation of the behaviour of the two "Eurochemic" glasses and of four reference waste forms in conditions representative of a clay repository. Static leach tests in clay-derived water environments will be carried out at the various temperatures given under (a).

Progress and Results

Characterization of glasses SM58LW11 and $SAN602519L_3C_2$ (see table 31).

	SAN 60	SM 58
SiO_2	43.41	56.87
B_2O_3	17.00	12.28
Na_2O	10.67	8.30
Li_2O	5.00	3.74
Al_2O_3	18.09	1.16
CaO	3.50	3.83
TiO_2	-	4.45
MgO	-	2.05
Fe_2O_3	-	1.17
FP ox*	1.21	6.06

*Fission product oxides

Table 31 : Main components of the glasses SM58LW11 and $SAN602519L_3C_2$ (in wt.%)

The Soxhlet corrosion rate of glasses SM58 and SAN60 are (41.7 $\pm$ 1) x 10^{-5} and (56.8 $\pm$ 11) x 10^{-5} g cm^2 d^{-1}, respectively, and compare well with the corrosion rates for the more resistant borosilicate glasses investigated thus far (e.g. UK 209). A surface layer forms on both glasses, which is enriched in Fe, Zr, Ti (when present) and lanthanides, and which cracks upon drying. The investigation of the thermal stability of both glasses, in terms of the identification of the crystalline phase formed after annealing and of the influence of the annealing treatment on the Soxhlet corrosion stability is in progress.

Parametric study of the corrosion stability of six HLW forms (glasses SM58LW11, SAN602519L_3C_2, SON641920F_3, SON583020U_2, UK209 and glass-ceramic C31.3EC).

- Corrosion in distilled water at 90° C

As reference condition a static leachant is used with a surface area to solution volume (SA.V^{-1}) ratio of 1 cm^{-1}. From weight loss measurements, the corrosion rates are found to decrease sharply with time (between 2 minutes and 8 months). Increase rates of leachant pH are largest at the beginning of corrosion (e.g. first 2 hours). Infrared reflection spectroscopic (IRRS) analyses suggest that the specimen surfaces roughened during the initial period, indicating some matrix dissolution (see e.g. SON 64, in fig. 27). The strong decrease of the corrosion rates with time can be related to saturation effects in the leachates for elements such as Mg, Ca, Sr, Cs, Fe, Al, U, and even Si (see also fig. 27). A relationship between the equilibrium concentrations of Al and Si is suggested. The elemental leaching behaviour of the glass-ceramic C31.3EC differs from that of the glassy waste forms. The evaluation of the elemental concentrations as a function of distance from the specimen surface and of the corrosion time, using Auger electron spectroscopy, is in progress.

The influence of SA.V^{-1} was investigated in additional experiments at 0.1 and 2 cm^{-1}. After 3 days of corrosion, the SWL's were already larger at 0.1 than at 2 cm^{-1}. The differences increased with increasing corrosion time. A screening test was also conducted at a constant flow rate of 2 cm^3 d^{-1}, so that no saturation effects are expected.

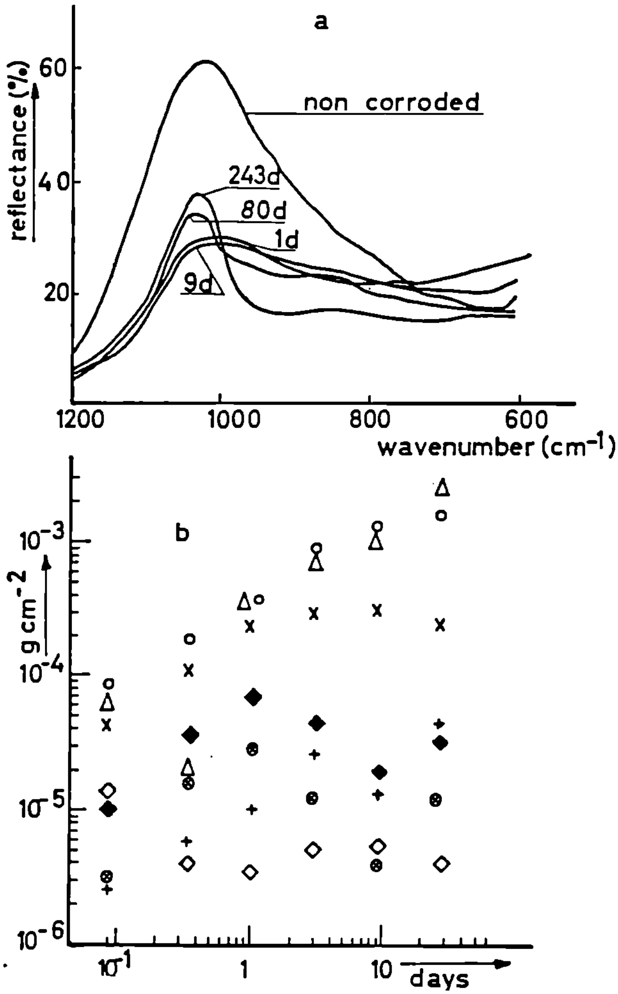


Fig. 27 : SON641920F$_3$; IRR spectra (a) and NSWL (b) as a function of the corrosion time (H_2O, 90° C, 1 cm^{-1})

X Si; O B; Δ Na; ◇ Sr; ◆ Cs; ⊕ Al; + U.

- Influence of pH

  Corrosion experiments in water, buffered at pH values 9.5 and 5.7 are underway (90° C, 0.1 cm^{-1}).

- Influence of the corrosion medium (clay-water mixture, wet clay)

  The corrosion experiments were conducted under oxidizing conditions at 90° C and 1 cm^{-1}. After 3 months, SWL's are 2 to 15 (clay-water mixture) or 8 to 55 (wet clay) times larger than in distilled water. The pH of the clay-water mixture does not change markedly during corrosion. The major reason for the increased corrosivity seems to be the smaller influence of saturation effects in the leachate, due to the sorption capacity of the clay particles. Some corrosion experiments are in progress in reducing clay media.

- Influence of temperature (40, 70, 90, 120, 150, 200° C)

  The dependence of the SWL's on time and corrosion medium observed at 90° C is also valid at 40 or 70° C. The temperature dependence, however, is very complex since the slopes of Arrhenius plots between 40 and 200° C are not constant, and, moreover, change with corrosion time.

  The interpretation of the autoclave experiments at 200° C, in the different corrosion media, in terms of surface and leachate analysis is in progress.

- <u>Optimization of the AVM glass</u>

<u>Contractor</u> : CEA, Marcoule (123-80-55 WASF)

During the year 1982, the works were conducted in order to complete the previous ones carried out in 1981 to investigate the effect of various parameters upon the leach rate of radioactive glasses.

Time dependance at room temperature was evaluated on two different glasses, one SON 61 30 14 doped with 241 Am. The other, SON 58 30 20 U2 was a non radioactive replica.

Both were leached with tap water under a static mode with SA/V = 0.6 cm^{-1}. The alpha doped glass was subjected successively to three runs, 109, 161 and 459 days duration. Daily water renewal was applied on the first and third runs. The same leachant remained during the end run. The leach rate measured for the third run was as small as twice the one observed for the first run. The leach rate relating to the second was decreased by a factor 30 as compared to the first one.

The non-radioactive sample has been leached for 365 days under daily tap water renewal. The leach rate, based on weight loss, could not be determined because a weight increment was observed at the end of the test, probably due to the physical state of the hydrated surface layer the thickness of which is about 100 micrometers (see figure 28).

Temperature dependance was investigated on a radioactive (beta, gamma) glass block son 60 20 18 F3 and on two replicas son 64 19 20 F3 and 60 20 18 F3 under the following conditions : temperature range 25 to 150 (5 variants) tap water, weekly renewal, SA/V = 0.6 cm^{-1}. The radioactive glass block was submitted successfully to various temperature, on the contrary the non radioactive samples were renewed each time the temperature changed.

Owing to the technical impediments which occurred the results relating to the radioactive block are difficult to interpret. From the non radioactive samples, it was found out : Sr released is governed exclusively by temperature. A change of slope of the L = F(1/T) curve between 70 and 100 displays a change of leach mechanism.

The effect of pressure (up to 200 bars) at room temperature, with tap water, static leaching and weekly renewal investigated by means of a radioactive (beta, gamma) glass block, was negligible.

The effects of various types of water are approximately the same. The involved leachant were tap water, siliceous water, granitical water, sea water and argilaceous synthetic water.

The effect of the leach mode was investigated on a radioactive (beta, gamma) glass block son 64 19 20 F3 G3 at room temperature with tap water.

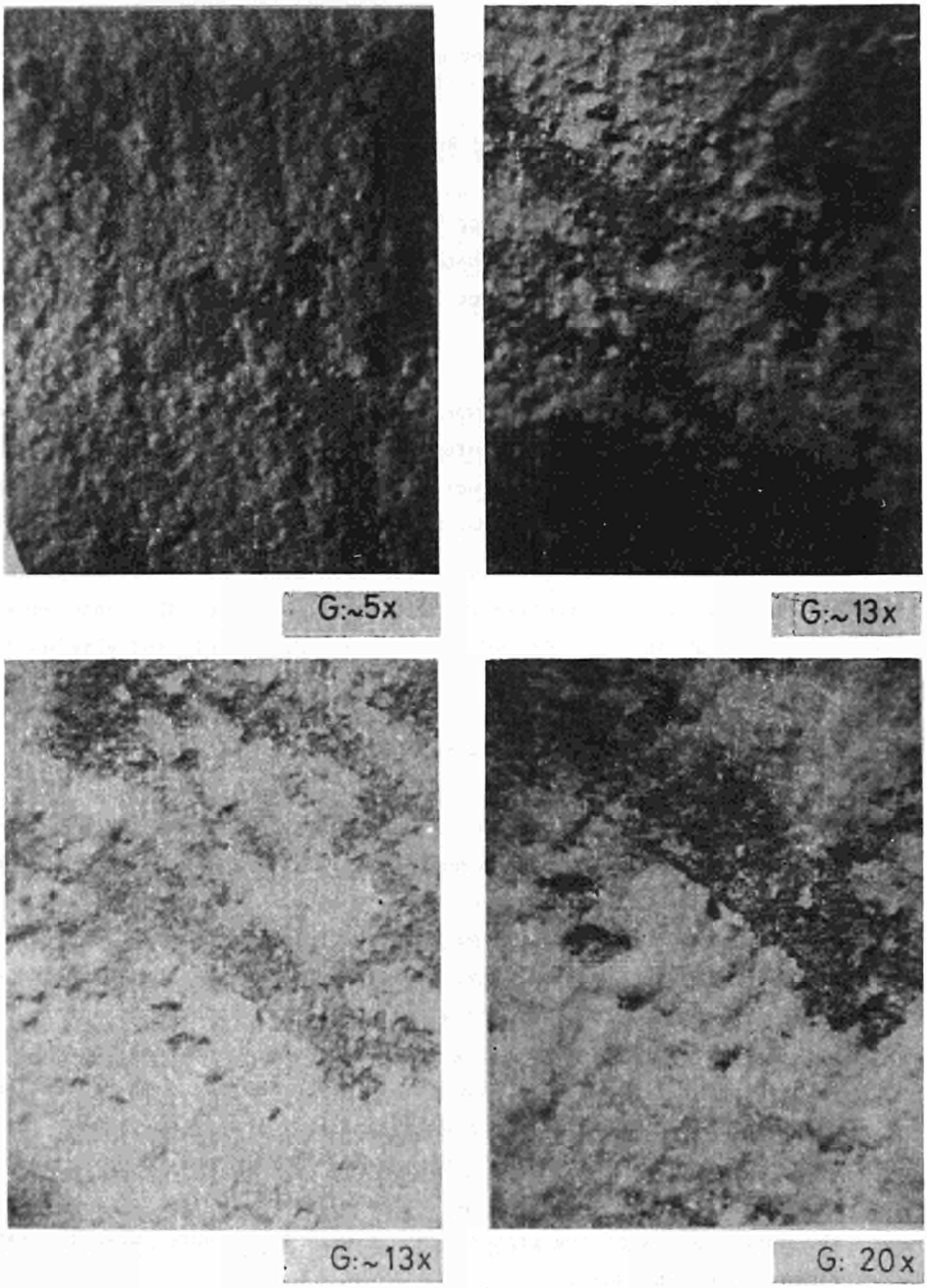


Fig. 28 : Surface of inactive glass after 1 year leaching at room temperature (glass SON 58.30.20 U2)

It was pointed out that :

- Cs and Sr leach rates are not modified when flowing leachant is applied after a static one
- Static leach rates of Ce and Ru are much lower than the flowing ones.

These findings can be explained by the fact that Cs and Sr are considered as very movable on one hand, and, on the other hand Ru and Ce could be present in the surface layer in the form of mechanically weak physicochemical species.

It can be concluded that the most important parameters as regards as the glass leach rate are temperature and renewal frequency. The apparent americium leach rate, as well as the cerium one, decreases largely if the frequency decreases. Cerium and ruthenium are little sensitive to a rise in temperature.

- Repository simulation

Contractor : AERE, Harwell (121-80-53 WASUK)

Repository simulation experiments have been carried out in which specimens of doped glass have been held in a 1.5 ml sample chamber at the top of a water filled column of granite at 60° C. The only flow past the specimen occurred when 1 ml samples of leachates were removed at monthly intervals for analysis; the replacement water had been in contact with the granite for many weeks before it reached the sample chamber. The resulting leach rates were very much lower than those obtained in the flowing water experiment, even for the more mobile isotopes, e.g. ^{99}Tc : 50x lower for UK189 and 150x lower for UK209. The results for UK209 are shown in figure 30. The extent to which the isotopes have been absorbed on the Teflon walls of the apparatus and on the upper layers of the granite column will be measured when the experiments are concluded.

Leaching at low flow rates

Flowing leachant experiments at flow rates of 1 ml/week have continued with glass specimens containing a full spectrum of non-active fission product isotopes, but spiked with one of the active isotopes ^{90}Sr, ^{137}Cs, ^{99}Tc, ^{237}Np, Pu or ^{241}Am. For glasses UK189 and UK209 very little change in leach rates occurred over the year for which the experiment was continued, but the parent glass of the glass-ceramic G B1/3 showed a marked drop in leach rate over the first 80 days, for reasons which are not yet clear.

After over a year, the experiments with UK189 and UK209 were concluded and the weight losses from the specimens were measured. These agreed within a factor of two with those deduced from radiological measurements of the total amounts of the various isotopes in the leachates, adsorbed on the walls of the apparatus and in gel layers on the surfaces of the specimens. The actinides were strongly retained in the gel layers, particularly for glass UK189, for which over 99 % of the Pu and Am was held there.

1.5.2. RADIATION STABILITY

Contractor : AERE, Harwell (121-80-53 WASUK).

Samples of six glass compositions were doped with ^{238}Pu for correct simulation but subjected to increased dose rates with what is potentially the most damaging type of radiation, i.e. the α-decays of incorporated actinides. After a dose of about 2×10^{18} decays per gram, changes in density, which are less than 1 %, suggest that the effects are approaching saturation. This dose would take many thousands of years to build up in the real case, the exact time depending on the source and concentration of the waste in the glass. The leach rates of some compositions has increased slightly - by 4x in the worst instance - but others were almost unaffected.

The sample of the glass VG 98/3 was annealed isochronally after a dose of 2.29×10^{18} α-decays per gram. In this technique, the sample was

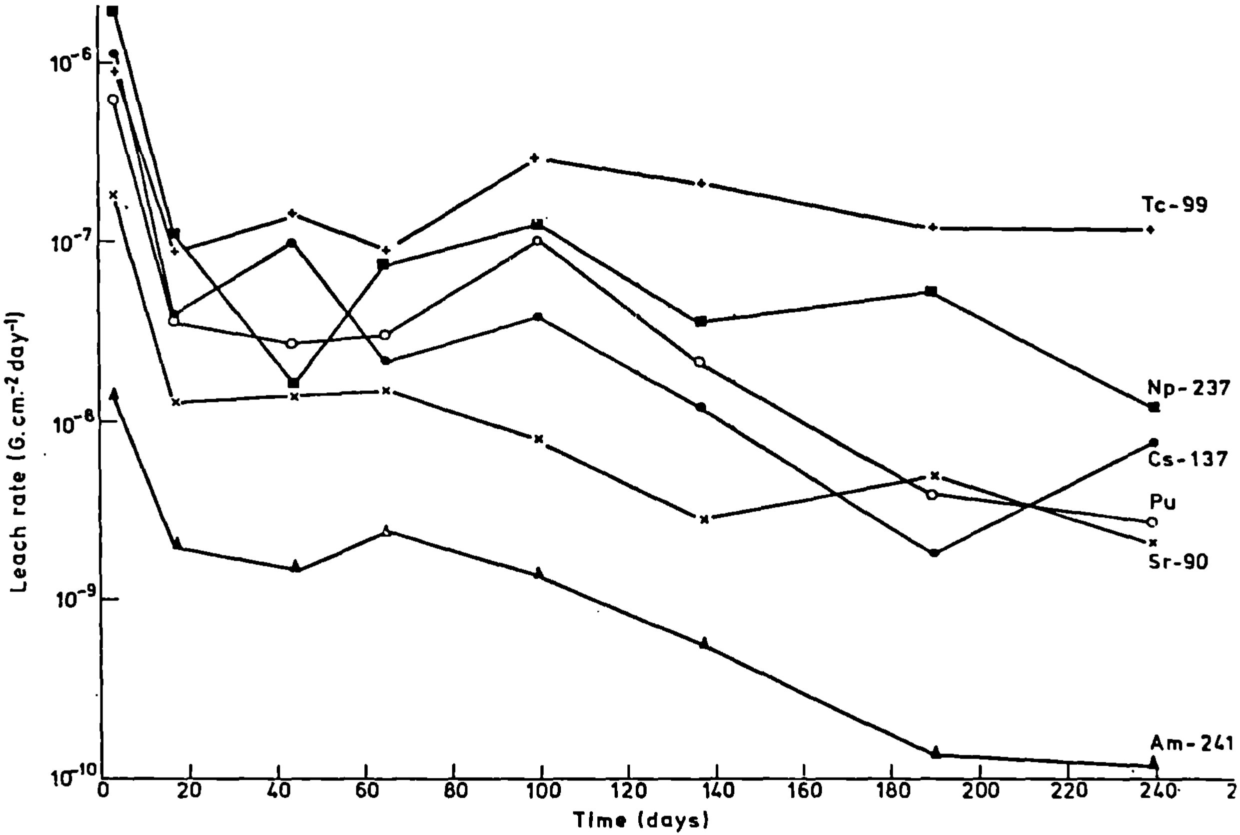


Fig. 30 : Leach rate of UK209 at 60° C in repository simulation

heated to successively higher temperatures, spaced at about 25° C intervals, for a constant time (here, 16 hours) and the density was measured (at room temperature) between each annealing.

The values of the recovery rate from the isochronal annealing experiments on VG 98/3 are extrapolated to 4×10^{-8} sec^{-1} at 25° C. Damage for this case will never build up in a real situation.

1.5.3. MECHANICAL STABILITY

Contractor : AERE, Harwell (121-80-53 WASUK)

The canisters used in these experiments are of an 18/9/1 stainless steel, internal dimensions 0.25 m diameter, 0.75 m long, wall thickness 5 mm. The furnace used has two heat zones, controlled separately. Six thermocouples are fastened to the outside of the canister, equally spaced along the length of the glass. Two melting and cooling runs have been completed, a third is in progress at the time of writing. Glass frit is melted in the canister to a depth of ca. 0.6 m and allowed to stand at 950° C for at least 24 hours to clear any bubbles.

In the first run, the furnace was switched off and the glass allowed to cool as rapidly as possible to ambient temperature. In the second run the glass was first cooled to 520° C, allowed to stand for 24 hours to come to thermal equilibrium, and then cooled to ambient temperature at the same rate as that for the first run. The third run is to be exactly the same as the second, but internal thermocouples have been fitted to measure actual temperature profiles.

The containers were removed to discover the amount of cracking. Calculations have shown that the heating effect of the radioactivity will produce a radial temperature profile, and hence a stress distribution, that can be simulated by a faster cooling rate.

Contractor : Hahn-Meitner-Institut, Berlin (122-80-53 WASD)

The characterization of mechanical properties of nuclear waste glasses is important, because the leaching rate is proportional to the total surface area of the materials exposed to the liquid.

In choosing methods for testing the crack propagation and strength behaviour of nuclear waste glasses the special test conditions in a hot cell were taken into account.

In order to measure fracture stresses the Hertzian indentation test was chosen and in order to measure the velocity of crack extension the double torsion method with variable load was selected.

Critical stresses were measured in the glasses VG 98/3, F-SON 58, UK 209, UK 189, C-31-3 and the glass ceramic B1-3. Additionally a soda-lime-glass (mirror glass) was tested for comparison.

The results for the surface fracture stress measured by the Hertzian indentation test showed similar behaviour of all glasses. According to the double torsion results, the waste glasses seem to be less susceptible to slow crack growth.

1.5.4. CERAMIC MATERIALS FOR HAW-IMMOBILIZATION

Contractor : University of Leiden (125-80-55 WASNL)

The aim of this research is to prepare model compounds and study their thermal stability, phase relations, crystallographic properties and behaviour in water with 10 % NaCl at elevated temperature (300° C under pressure). The model compounds are the hollandite and perovskite phases containing Cs, Rb, Sr and Ru.

The composition of the hollandite phase

The general formula of hollandites is $A_xB_{4-p}C_pO_8$, A = Ba, Sr, Pb, Cs, Rb, K; B = (Si), Ce, Ti, Ru, Sn; C = Al, Ga, Cr, Fe, Zn. The structure of the hollandite phase is presented in fig. 31.

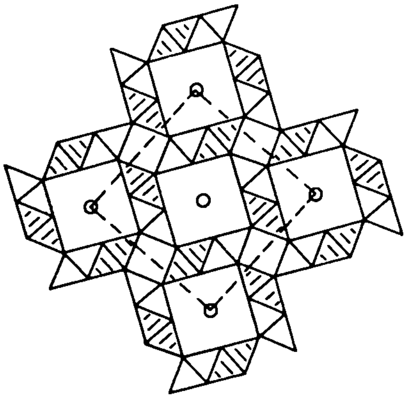


Fig. 31 : Hollandite structure. Double chains of edge-sharing octahedra share corners to produce square tunnels occupied by large A ions. The body centered unit cell is outlined.

The big ions A are in the tunnel, but not all available sites are occupied. The size of the A ion is such that in general not more than 2 out of 3 tunnel sites can be expected to be filled with small B and C ions.

Table 34 gives a number of hollandites for which the phase-widths are found.

Ba(Cs) hollandite phase, $Ba_{x-y}Cs_{2y}Ti_{4-2x}Al_{2x}O_8$

For low Cs content (20 %) there is no indication up to now that the phase-width has changed from the value found in table 34, when compounds were tried to synthesize with tunnel filling (x + y) > .64. This results in the formation of $CsAlTiO_4$.

A	B	C	x_{min}	x_{max}
Ba	Ti	Al	.58(1)	.64(1)
Ba	Ti	Ga	.585(5)	.65(5)
Ba	Ti	Cr	.563(5)	.674(5)
Ba	Ge	Cr	.575(5)	.70(1)
Ba	Sn	Cr	.675(5)	.691(5)
Ba	Sn	Zn	.678(5)	.732(5)
Ba	Ru	Cr	<.60	>.67
Sr	Ge	Cr	.618(5)	.668(5)

Table 34 : Phase-width hollandite $A_xB_{4-2x}C_{2x}O_8$

When this is not enough to reduce the filling to the maximum, not only all the Cs is incorporated in $CsAlTiO_4$, but in addition other phases are formed and the hollandite has the formula $Ba_{.64}Ti_{2.72}Al_{1.28}O_8$.

Leaching properties of Ba(Cs) hollandites

The results of the leaching experiments (300° C, 2 kbars, 1 week) are at this moment not interpretable. In some experiments the Cs in the liquid phase is not detectable, in other experiments about 20 % of the Cs is leached.

System $SrO-TiO_2-Al_2O_3$ (1300° C)

A hollandite phase in this system with good stability in water at elevated temperature and pressure was reported, but it was impossible to synthesize the mentioned phase. The phase diagram, fig. 32, was investigated except for the strontium rich part.

The compounds TiO_2, $SrTiO_3$, $SrAl_{12}O_{19}$ and $SrTi_3Al_8O_{19}$ are stable in water at 300° C and 2 kbars. All other compounds decompose under these conditions.

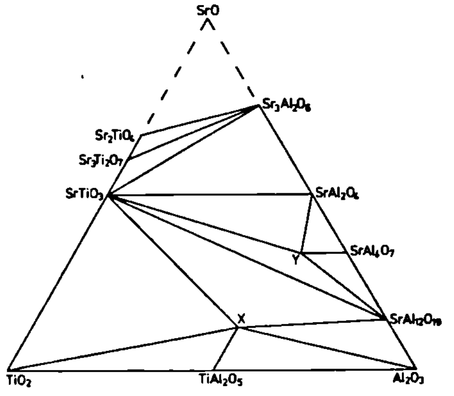


Fig. 32 : Composition diagram of the system $SrO-TiO_2-Al_2O_3$ at 1300° C.
$X = SrTi_3Al_8O_{19}$
$Y = Sr_3TiAl_{10}O_{20}$

1.5.5. THE ACL ROUND ROBIN TEST*

Contractors

AERE, Harwell	(278-82-53 WASUK)
Hahn-Meitner Institut, Berlin	(277-82-53 WASD)
Fraunhofer Institut, Würzburg	(292-82-53 WASD)
CEA, Grenoble	(279-82-55 WASF)
CEA, Cadarache	(283-82-55 WASF)
ENEA, Casaccia	(282-82-55 WASI)
RNL, Risø	(281-82-53 WASDK)
SCK/CEN, Mol	(280-82-55 WASB)
University of Amsterdam	(293-82-53 WASNL)

The tenth laboratory which participates is JRC Ispra. The test material is the UK209 glass. The test was designed to develop - complementary to the US/MCC 1 test - a similar test for leaching temperatures between 100° and 200° C, suitable for the quality control of HLW vitrification processes. The test results will become available by the end of 1983.

* ACL = autoclave leach (test) see fig. 33.

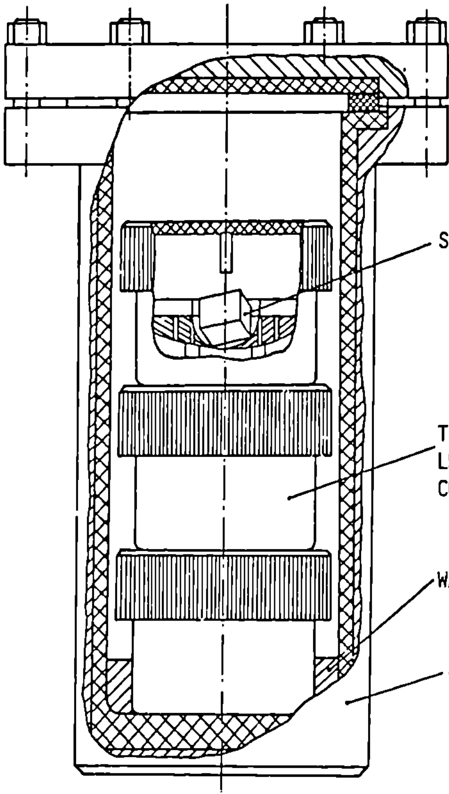


Fig. 33 : Leaching apparatus

The characteristics of the test are :

. mode : static conditions
. use of teflon lined autoclaves
. leachant solution : deionized water
. surface/volume ratio ; 400 mm^2/40.000 mm^3
. test temperature : 90°, 110°, 150°, 190° C - 3 temperatures are compulsory
. exposure time : (3), 7, 14, 28, (56) days (and longer)
. measurement and analyses :
  - sample surface and solution
  - pH
  - weight loss
  - elements measured : Si, B, Cs, Sr, Nd, (Na), (Al), (Ce), (Mo), (Fe) (Cr) and F in a blank test*.

Experimental problems, like loss of leachant and sample material, temperature control and sample suspension, will be identified in order to define the requirements for a quality control standard test.

1.6. IMMOBILISATION AND STORAGE OF GASEOUS WASTE

The radioactive gaseous wastes considered under this chapter mainly arise from the reprocessing of nuclear fuel and in particular from the dissolution of the fuel at the head end of the process.

The research activities concern the typical volatile radio-nuclides Krypton-85, Iodine-129, Tritium and Carbon-14 as well as the management of aerosols.

Eight different research projects are comprised under this chapter and were all continued in 1982. A substantial part of the supported research concerns the immobilisation of Kr-85. Three projects are dedicated to this problem. They deal with the krypton inclosure into a metallic matrix and into the porous structure of zeolites.

The former process of krypton incorporation in metals by ionic sputtering of deposits has reached an advanced state towards application and is going to be tested with real radioactive gas.

The second process, the krypton capture and inclosure in zeolites, has undergone further development on laboratory scale in view of improving the identification of the material and operating characteristics.

On 29 June 1982 an E.C. specialists seminar was organised by the Commission on "Methods of Krypton 85 Management". It gave a review of the state of the art based on a study report drawn up jointly by CEA Fontenay-aux-Roses and the University of Pisa*.

Retention of tritium from aqueous effluents is studied in laboratory experiments at technical scale. The tritium is concentrated in the aqueous effluents by a combined isotope separation process using electrolysis and catalytic gas/liquid phase exchange. Process development has further advanced into the state of hot (active) testing and into the construction of a pilot installation for representative detritiation runs.

* see Seminars nr 4.

As to assessment of Iodine-129 and Carbon-14 management, two desk studies have been continued and should be terminated at the end of the year. Whereas the former is focussed on the refinement of the radiological aspects of iodine, the latter gives a comprehensive review of all questions, technical and radiological ones, that are relevant to carbon-14 management.

Finally experimental work has been carried on for two projects in the field of improved aerosol filtration. They both deal with the development of cleanable porous prefilters to be used upstream of the so-called HEPA-filters in order to extend their operational life-time. One of the projects has been terminated at the end of the reporting period.

The following contracts are reported :

1.6.1. IMMOBILIZATION OF KRYPTON-85

Incorporation into a metal matrix by ion-sputtering

Contract : 157-80-8 WASUK, AERE, Harwell.

Objective and Scope

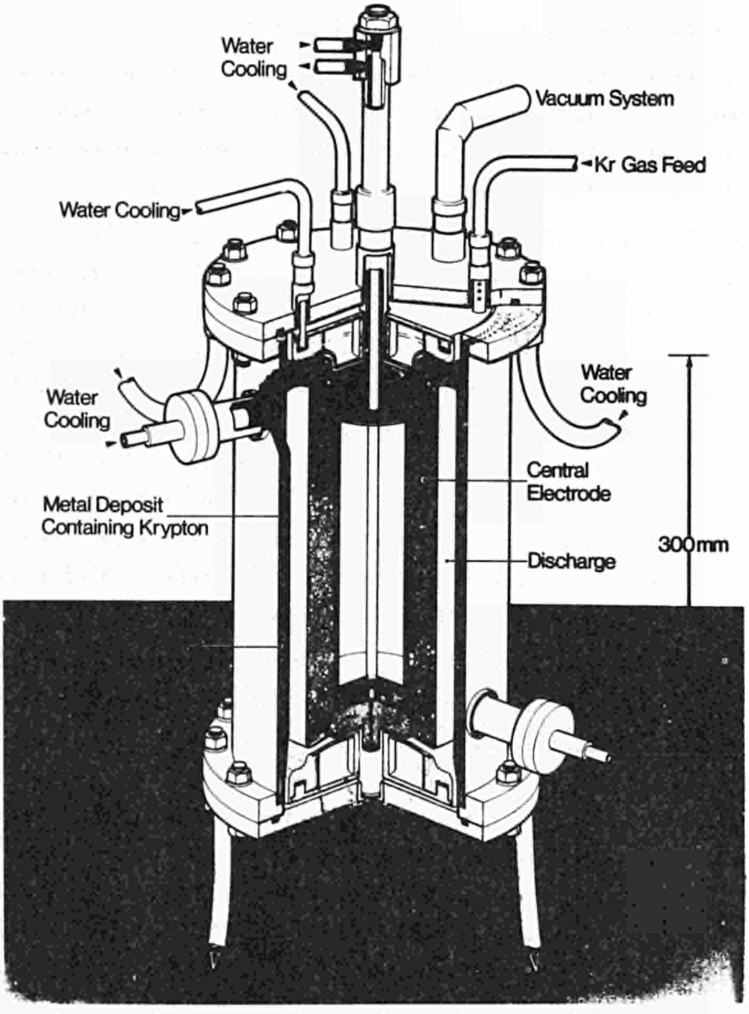
A process for the immobilization of Krypton in a metallic matrix by combined ion implantation and sputtering is being developed at AERE Harwell. In the first European Community's R&D programme a half scale inactive pilot plant was designed, built and operated to demonstrate the process on a scale representative of an industrial plant (fig. 36). A copper deposit 22 mm thick containing over 300 litres of gas was built up and its properties determined.

The primary aims of the current programme are to assess potential candidate metals for the long term containment of Krypton arising from the reprocessing of nuclear fuel, to test a full-scale vessel and to carry out a design study for an active test rig.

Progress and Results

- Preparation of candidate materials

  Last year a survey of possible storage and disposal locations was made, candidate metals identified, and the active test rig design study carried out. Work was started to prepare samples using matrices of stainless steel 316L and Incoloy 825. Thin deposits were laid down successfully, but when attempts were made to prepare depo-


Water
Cooling
Vacuum System
Kr Gas Feed
Water Cooling
Water
Cooling
Water
Cooling
Central
Electrode
Metal Deposit
Containing Krypton
300mm
Discharge

sits which were more than about 0.5 mm thick the deposit tended to flake from the substrate electrode. A series of tests has been carried out in an attempt to identify the cause and to find a remedy. The poor adhesion of the alloys was found to be due to contamination on the electrodes which had not been removed during precleaning, together with high intrinsic stresses within the deposit, particularly for the alloys where swellings of 5 % were observed.

In initial tests with nickel it was found that the process efficiency was much higher than that with copper. Nickel also seemed likely to have the necessary thermal stability and corrosion resistance for containing Krypton.

A layer of nickel 9.5 mm thick, weighing over 7 kg and containing over 107 litres of gas, was laid down in a series of experiments using a vessel of outer diameter of 200 mm and an effective length of 200 mm, with a central electrode fabricated from Nickel 201. Efficiency and gas concentration measurements showed that the process efficiency to give a deposit containing 150-170 litres of gas per litre of metal, was 0.017 litres/kWh. This is significantly greater than for copper, where the efficiency is 0.010 litres/kWh for a deposit containing the same amount of gas. This improvement represents a reduction of 40 % in both the power requirements for a reprocessing plant and also in the number of process units required in a plant of given size.

A sample of the "glassy" alloy Ni-10 % La was also prepared, since Tinsey and McClanahan at Battelle Pacific Northwest Laboratories have shown that this gives a very high gas incorporation efficiency. However the efficiency of the process was not markedly better than that achieved with nickel and the discharge was not as stable. The deposit has not yet been examined.

- Assessment of gas filled material

The long term measurements of the release of gas from the thick copper samples, held at various temperatures, were continued. Results from samples held for up to one year, show that the amount of gaz released increases with the square root of time and has an activation energy of 1.2 eV. At 300C 0.3 % was released in this period. The amount likely to be released during storage for 100 years is therefore expected to be negligible at an initial storage temperature of 150° C. Laser interferometry was used to measure the variation of the thermal expansion coefficient of gas-filled copper with annealing. Preliminary results showed that the expansion coefficient varied with the gas bubble size and internal gas pressure in accordance with a theory being developed.

Samples of the nickel matrix have been sectioned and prepared for assessment. In comparison with the thick copper deposit, the nickel is more brittle and cracks easily when cut. The average Krypton concentration across the deposit, measured by a scanning electron probe, was 5.2 atomic % and agreed well with the measured gas input. The density of the deposit was 93 % of that of bulk nickel. The lattice parameter of nickel deposits was about 0.5 % larger than that of normal nickel. Samples of nickel have been prepared for long term release measurements. Rapid heating measurements indicated that the gas is released from nickel between 670° C and 730° C, compared with 550° C to 650° C from copper. For both copper and nickel the release from samples prepared on a substrate heated to about 150° C occurred at a temperature 100° C higher than those prepared on a cooled substrate.

- Tests on full scale vessel

A vessel 1 metre long and 0.26 m diameter has been built in order to determine the operating parameters of a full-scale vessel. The central electrode was fabricated from mild steel plated with copper. Preliminary measurements indicate that the operating conditions are similar to those of the half-scale vessel.

- Process development

Halfway through the deposition of nickel the effect of impurities in the Krypton gas feed was determined by changing to a Krypton gas mixture containing 15 % of argon, xenon, nitrogen and hydrogen. The total gas flow rate and pumping efficiency remained unchanged and mass spectrometry indicated that all the gases were pumped at equal rates.

A MINC computer, based on a PDP 11/23 microprocessor has been coupled to the plant. The plant is now routinely operated under full automatic control. A routine enables operational parameters to be altered over a preset range of values to obtain experimental data and to optimise the settings of the plant while it is running unattended.

The data recorded during the deposition of the nickel has been used to calculate the concentration of gas in the deposit as a function of depth. This is in good agreement with the measured concentration in the deposit.

Long-term storage of radioactive Krypton by fixation in zeolite 5A

Contract : 158-80-8 WASD, KfK, Karlsruhe.

Scope and objective

The objective of this research programm is to develop a process for the long-term storage of ^{85}Kr by fixation in zeolites. It is based on a laboratory study in which it was shown that in the temperature range 520-650° C and at pressures of a few hundred bar, krypton can be trapped efficiently in zeolite 5A by a transformation of the original crystal framework into an amorphous state of the solid substrate.

Progress and Results

- Fixation of radioactive krypton

  To verify the process and obtain a product for observing the long-term effects of decaying radioactive krypton, several hot samples have been prepared. The employed equipment, shown in fig. 37, is simple. It consists essentially of a one liter storage cylinder, a pressurization vessel and a autoclave (1 cm^3), containing the zeolite. With this equipment five hot samples have been prepared, having specific activities in the range 0.02 - 28.3 (mCi/g zeolite) and loadings of the order of 20 $\pm$ 1 (cm^3 STP/g). These first measurements lead to the following observations and conclusions :

  . the fixation of radioactive krypton can be carried out by remote operation,

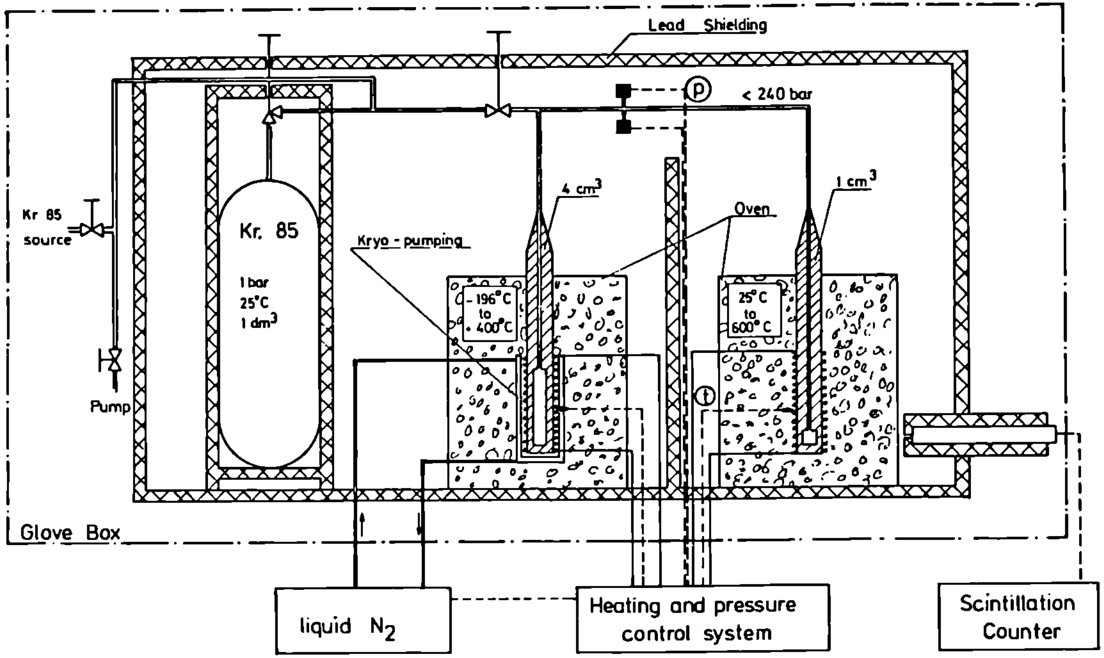


Fig. 37 : Small scale test facility for the fixation of radioactive krypton in zeolite

. the previously postulated trapping mechanism, i.e. sorption/desorption/chemifixation can be verified from measurements of the radiation emitted during noble gas encapsulation,

. the loading of the pellets can be estimated from their specific radioactivity,

. radioactive aerosols have not been detected when the autoclaves are opened after completion of a fixation

. the samples were found to be qualitatively and quantitatively stable for a period of now almost 8 months.

- Leach tests

Leach tests were carried out with zeolite 5A samples containing krypton. The leach rates from loaded pellets stored in distilled water, tap water, Q-solution, salt solution, etc. having pH values as low as 5 were examined for a period of up to 10 months. The observed krypton release rates were found to be very small.

- Facility to demonstrate the immobilization of Kr in zeolites

A demonstration facility is presently under construction, gas densification will be achieved by sorption/desorption either at 4.5 bars and room temperature or at 1 bar and - 20° C. The facility will provide information on large scale pretreatment, heat transport, material behaviour, energy consumption, operation time, loading homogeneity, safety devices, etc.

- Microprobe analysis of noble gas encapsulates

Electron microprobe analysis was employed for the first time to investigate gases immobilized in zeolites. Because in all samples the density of the noble gas follows exactly the density of the aluminosilicate framework, it is concluded that the noble gas is homogeneously distributed in the zeolitic material and not present in the form of bubbles. It was shown that each of the noble gases Ar, Kr and Xe can be specifically monitored in the presence of the two others.

Occlusion and storage of krypton in solids

Contract : 291-82-8 WASB, University of Antwerp.

Scope and Objective

This alternative immobilization method for gases in solids is based on the gas absorption in zeolites, followed by a structural modification, resulting in a narrowing of the zeolite pores. The adaption of the pore size, in a controlled way, is potentially important for different industrial applications such as : (a) occlusion effects in order to encapsulate and to store gases and (b) controlled pore size reduction, in order to separate gases with a high efficiency by changing the sieving properties.

Progress and Results

- The separation ability of modified zeolites by pore-size engineering

  Using the modification procedure described in annual report 1981 and based on the controlled change in the zeolite pore size, very efficient gas separations were established. Starting from Ar/Kr, N_2/Kr, O_2/Kr, N_2/O_2/Kr and $CH_4/N_2/H_2$ gasmixtures, respectively Ar, N_2, O_2, N_2/O_2, Kr and CH_4 were isolated with high separation efficiencies.

- The homogeneity of the Kr encapsulation in modified zeolites

  An electron microprobe analysis has been tested as a method to investigate the homogeneity and loading capacity of encapsulated Kr in modified zeolites. With this method a fast analysis of Kr in Kr-loaded mordenite samples was possible. Furthermore, the density of the Kr follows exactly the density of the aluminosilicate framework, so that it can be concluded that the occluded Kr is homogeneously distributed in the zeolite material.

- The stability towards gamma-irradiation, acids and mechanical grinding

  Stability tests towards environmental effects (H_2O, pH, mechanical grinding) and gamma-irradiation were carried out with very satisfactory results. These observations indicate that this chemical modification procedure for pore size engineering is a valid alternative for both Kr-85 isolation and storage.

1.6.2. RETENTION OF TRITIUM

Separation of tritium from aqueous effluents

Contract : 159-80-8 WASB, CEN/SCK, Mol.

Scope and Objective

Under the first Community programme on radioactive waste management and storage, SCK/CEN has performed (contract : 090-78-7 WASB) laboratory studies on the ELEX process for the removal of at least 90 % of tritium from the aqueous effluents of a commercial reprocessing plant (tritium content : about 100 Ci/m^3).

The ELEX process is a combination of the tritium enrichment effect of water electrolysis and of tritium exchange between hydrogen and water using a hydrophobic catalyst, produced according to a Belgian patent.

The objective of the present research is the further development of the ELEX process, including the construction and exploitation of an integrated bench scale detritiation unit and the design and construction of a pilot detritiation installation.

Progress and Results

- Catalytic tritium exchange studies

  Additional tritium exchange experiments in a counter-current packed bed column confirmed the high over-all tritium exchange rate. Up to 100 mol s^{-1} m^{-3} were obtained by combining a more porous catalyst with a more efficient packing material and a wetting procedure before start-up. The addition of oxygen to the hydrogen further increased the over-all exchange rate. The addition of carbon monoxide poisoned the catalyst.

From a preliminary evaluation it follows that the amount of catalyst required by an alternative bithermal tritium separation process, that would work under the conditions studied up to now for the exchange part of the ELEX process, would be at least two orders of magnitude larger than the amount for an equivalent ELEX process.

- Process demonstration and optimisation at bench scale (fig. 38)

The maximum tolerated tritium inventory of the bench scale ELEX installation was increased to 100 Ci. In this 10 $mol.h^{-1}$ minipilot three active and long duration experiments were carried out at feed concentrations of 20 mCi tritium per dm^3 water for the first and 100 mCi per dm^3 water for the second and the third run.

The ELEX process was successfully operated in the detritiating of more than 1 m^3 of water, containing up to 100 mCi tritium per dm^3, which is the feed concentration to be expected for the application of the process in a reprocessing plant. The process decontamination factor was always higher than 100. The reduction factor for the water volume increased linearly with time and for the 1000 to 1500 hours of operation it lay between 10 and 15. Higher volume reduction factors will become possible with a new, low-volume electrolyser. The over-all tritium balance fell within the experimental errors of the various measurements. The technical availability of the installation was high and there were no tritium contamination problems.

- Pilot detritiation installation

Based on the previous experiences a pilot detritiation installation has been designed and is being constructed, which may be considered as a last step before industrial application. This pilot consists mainly of a 80 kVA electrolyser and a 10 cm diameter exchange column with an enriching and a stripping part, installed in a ventilated second enclosure. In this loop, which will have a total tritium inventory of maximum 1000 Ci, demonstration of the ELEX process is aimed with the following design data :

. throughput	0.15 m^3 H_2O (HTO) per day
. feed concentration	100 Ci tritium per m^3

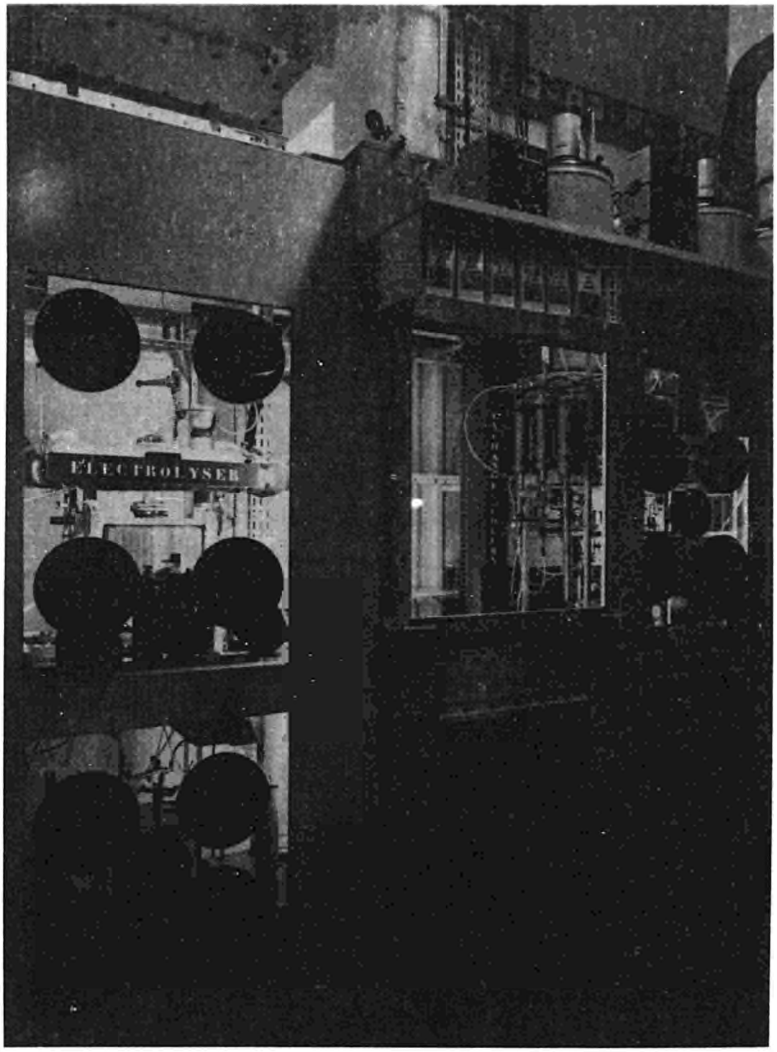


Fig. 38 : Partial view of the bench scale ELEX installation

. volume reduction factor 100

. process decontamination factor 100

- Evaluation

The costs of detritiation, by means of the ELEX process, of the aqueous effluents of a small reprocessing plant with a capacity of 60 ton LWR fuel per year, were estimated on the basis of the present mini-pilot results and on the basis of extrapolated pilot plant costs.

1.6.3. ASSESSMENT OF I-129 AND C-14 RELEASE

Radiological assessment of waste management modes for Iodine-129

Contract : 161-81-8 WASUK, NRPB, Chilton.

Scope and Objective

In a joint study forming part of the 1975-79 CEC programme on Waste Management and Storage, UKAEA and CEA studied the technological aspects of the feasible options for the management of iodine-129. NRPB evaluated their radiological impacts using existing models of the behaviour of iodine in the environment. The objective of the present research is to continue and conclude the work, particularly in the areas of radiological modelling and in assessing the relative merits of waste management options for iodine-129, technologies and costs, which were defined in the preliminary study.

Progress and Results

- Modelling Iodine-129 in the global iodine cycle

The half-life of iodine-129 is so long (16 million years) that any disposal method will ultimately release iodine-129 into global circulation. A satisfactory model for calculating this contribution to the total radiological impact is therefore required. A report on the environmental behaviour of iodine has been prepared by experts from the Agricultural Research Council and the Natural

Environment Research Council, and has been used in reviewing and revising a global iodine model, first proposed by Oak Ridge National Laboratory (USA). The structure of the revised multi-compartment model is shown in fig. 39. Particular attention has been given to the behaviour of iodine-129 in deep ocean sediments and in soils; the latter is also important in determining the radiological impact of the initial dispersion of atmospheric discharges (see below).

General conclusions from the revised model are that ocean sediments are a major reservoir for iodine-129, but do not constitute a permanent "sink" since 99 % of the uptake is returned to the oceans on a 105 y timescale; and that the main contribution to global-circulation doses comes from iodine-129 evaporated from the oceans and deposited onto the soils, in which it can persist and enter food-chains for thousands of years before returning to the oceans.

- Initial dispersion of iodine-129 after disposal

  Each of the many disposal options for iodine-129 leads to a charateristic mode of initial dispersion into man's environment, in each case leading to a different magnitude and time-distribution of the initial radiological impact. Existing models for initial dispersion have been reviewed and if necessary revised, and by combining the results with those of the model for the subsequent global circulation the total radiological impacts have been calculated as functions of time for the following disposal options : atmospheric discharge, liquid discharges to a river or to coastal waters, and disposal as a solid in the deep ocean bed or in a deep geologic repository at an inland or a coastal site.

Assessment of Carbon-14 waste management

Contract : 163-81-8 WASUK, UKAEA/NRPB, Harwell.

Scope and Objective

An assessment study of the options for carbon-14 waste management was completed in 1982.

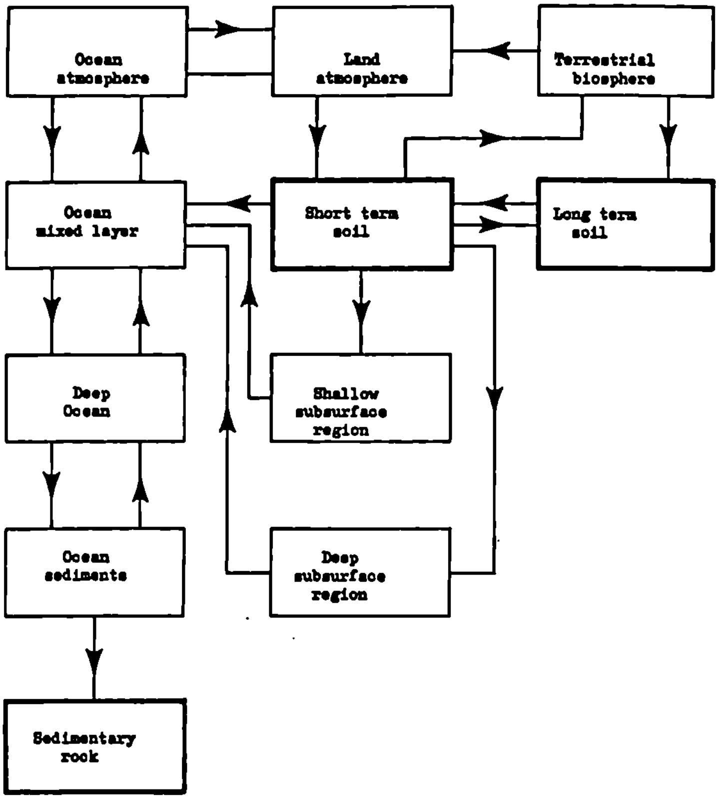


Fig. 39 : Model for the global circulation of iodine, into which releases of iodine-129 may be superimposed

Progress and results

Carbon-14 is formed by neutron activation reactions, mainly involving the common nuclides ^{14}N, ^{13}C, and ^{17}O, and is therefore present in a variety of waste streams both at reactors and at reprocessing plants.

A reliable picture of the production and release of carbon-14 from various reactor systems has been built up for the purposes of this study. It is based on a critical analysis of reported calculations and measurements and some new calculations in the case of AGRs and Magnox reactors. Generally good agreement exists between various sources of data.

Analytical methods for the measurement of carbon-14 at nuclear facilities have been reviewed. Adequate methods exist but they are not generally suitable for on-line application.

A possible management strategy for carbon-14 might be the reduction of nitrogen-14 impurity levels in core materials, since the activation of ^{14}N is usually the dominant source of carbon-14. Only reductions of about a factor of five in arisings could be achieved in this way, because of the contributions of other activation reactions. A proper assessment of this option is not possible because the sources of nitrogen in fuels and other materials are not adequately known.

The key problem in carbon-14 management is its retention in off gas streams, particularly in the dissolver off-gas stream at reprocessing plants. In this stream the nuclide is present as carbon dioxide, and is extensively isotopically diluted by the carbon dioxide content of the air. The size of plant required for retention, and the quantities of solid waste produced, are therefore determinated by the air flow-rate through the dissolver.

Processes for trapping carbon-14 from these off-gases must be integrated with the otherprocesses in the overall off gas treatment system, and should provide for conversion to a stable solid compound of carbon, suitable for subsequent immobilization and disposal.

Three alternative trapping processes, that convert carbon dioxide into insoluble carbonates, have been suggested :

. The double alkali process. Carbon dioxide is absorbed by sodium hydroxide solution. The resulting liquor is treated with calcium hydroxide to form calcium carbonate and to regenerate sodium hydroxide for recycle.

. The direct process. Carbon dioxide reacts with an aqueous slurry of calcium hydroxide to give calcium carbonate directly.

. The barium octahydrate process. Carbon dioxide reacts with a fixed bed of solid barium hydroxide octahydrate to give barium carbonate.

It is probable that calcium or barium carbonate, produced in the above processes, could be incorporated into cement or bitumen matrices to provide satisfactory immobilised waste forms. However, the stability of such waste forms to prolonged irradiation and to leaching remains to be investigated.

A number of disposal options for solid carbon-14 wastes have been identified. The radiological impacts of some of these, together with those of discharges to the atmosphere, to rivers and to coastal waters, have been calculated. None of the options considered need to be rejected on the grounds of potential radiation doses to individuals. The acceptability of the various options will be determined by the ALARA principle i.e. that all exposures should be as low as reasonably achievable, economic and social factors being taken into account. Cost-benefit analysis provides a method of taking account of the economic aspect as an aid to decision making. Such calculations are subject to methodological as well as parametric uncertainties, whose resolution is beyond the scope of this study.

The results obtained show that :

(a) The collective dose commitment over infinite time is not materially affected by the manner in which carbon-14 is discharged (i.e. to atmosphere, rivers or coastal waters), although there are differences in the first few centuries.

(b) Conversion to a solid waste followed by disposal to a geologic repository could, in some circumstances, substantially reduce the collective dose commitment, relative to that arising from discharge.

(c) Disposal as a solid in geologic repositories or in the ocean bed could provide a substantial postponement of collective doses.

1.6.4. IMPROVED AEROSOL FILTRATION TECHNIQUES

Removal of solid and droplet aerosols on a packed fiber mist eliminator (PFME)

Contract : 162-80-8 WASD, KfK, Karlsruhe.

Scope and Objective

By means of a remotely handled packed fiber mist eliminator it is intended to remove liquid droplets < 10 µm with a removal efficiency ≥ 99 %. Moreover, it is to be used as a prefilter for particulates in reprocessing off-gases so as to increase the service life of the following HEPA filter.

The demister consists of packed glass fibers of about 20 µm diameter with a statistically vertical orientation.

Progress and Results

- Salt loading and cleaning of the PFME

  To determine the aerosol distribution on the fiber packing, a 5 % Mn-56 $(NO_3)_2$ solution was sprayed into the gas stream and subsequently the radioactivity was measured at specific points on the filter housing by means of a dose rate meter. A relatively constant load in the whole circumference of the filter was measured at the respective levels.

  For simulation of salt loading in PASSAT, 130 g of sodium nitrate ($\dot{V} = 75\ m_N^3 \times h^{-1}$, $t = 50°\ C$, r. h. = 100 %, $\dot{m} = 4\ g \times m_N^{-3}$) were sprayed onto the fiberglass packing. This quantity roughly corresponds to a salt loading of the filter in a reprocessing plant under a gas flow of 130 $m_N^3 \times h^{-1}$ and a loading with an assumed 10 mg x m^{-3} of solid particles within four days and without interim self-cleaning as a result of high air humidity and impinging droplets. Short spraying of flushing water (approx. 30 l) onto the filter packing dissolved most of the salts and, after a drainage period of three hours, the original differential pressure was restored.

To quantify this recleaning and study the behaviour of the droplet aerosols embedded in the fiber packing during flushing and their removal, a Ba-139 $(NO_3)_2$ solution was sprayed into the gas stream. After loading, different rinses were carried out and the behaviour of the radioactivities discharged as a function of time was measured in the condensate pipes (fig. 40). The radioactivity was measured by collimated scintillation detectors shielded with lead (NaI).

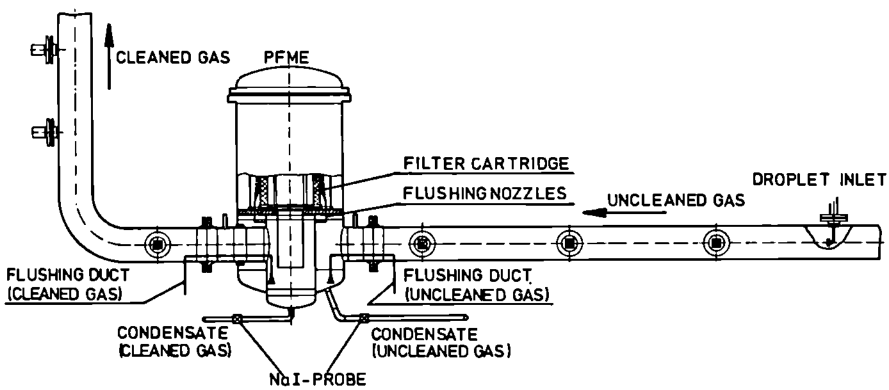


Fig. 40 : Test procedure for the investigation of loading and cleaning

Fig. 41a shows 15 minutes flushing with a total of 75 l of H_2O. This amount is sufficient to flush out the in the fiber packing embedded radioactivity (within the limits of detection). Fig. 41b shows several recleaning steps with periodic flushing and drainage times, respectively. Comparison with once-through flushing indicates that, although the cleanup effect is the same, the water consumption is higher in periodic flushing (105 : 75 l). Periodic flushing however, offers the advantage that the pressure drop associated with recleaning

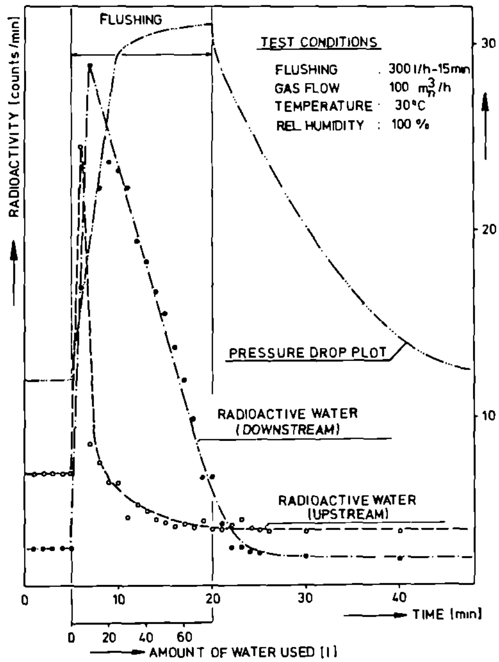


Fig. 41 a.

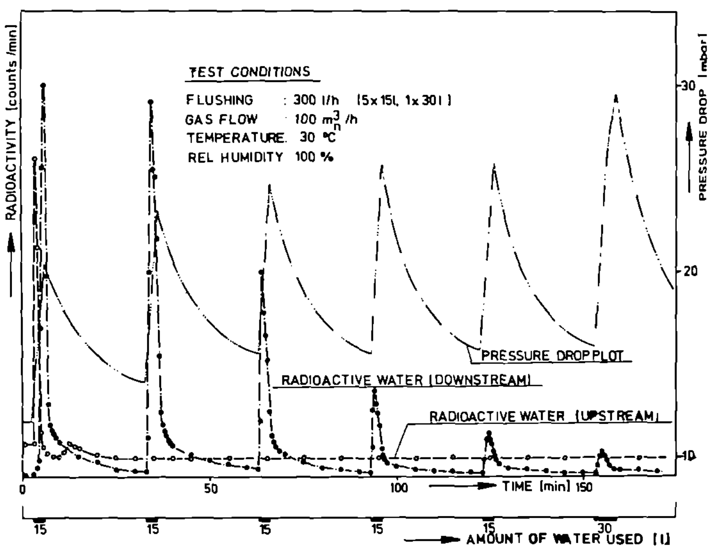


Fig. 41 b.

Fig. 41 : Cleaning characteristics of the PFME loaded with Ba-139$(NO_3)_2$ aerosols. (41a) Once-through flushing (41b) Periodic flushing

is about 20 % lower. Moreover, this diagram shows that radioactivity is removed on the untreated gas side only at the beginning (for approx. 5 minutes) of the first flushing step. This is largely due to the washed out radioactivity adhering to the caisson of the filter cartridge. In subsequent flushing steps no further radioactivity was detected in the untreated gas condensate.

It will be necessary in the dissolver off-gas filter line to rinse the filter element of the mist separator through the fiber packing as soon as a higher differential pressure has been reached, or to replace it by a new element. If even flushing cannot reduce the differential pressure from 4000 Pa at 150 std. m^3/h flow, the filter cartridge must be replaced remotely.

In order to avoid contamination of the cell by spilling solution in this process, the fiber packing is dried in a preheated air stream before replacement.

Aerosol filtration at elevated temperature by regenerative metal fibers

Contract : 228-81-8 WASB, SCK/CEN, Mol.

Scope and Objective

The aim of this study is the development of fibre metallic prefilters with high dust loading capacities and which could be in-situ regenerated in order to extend their operational lifetime. They should retain most of the aerosol charge of the gaseous effluent, should withstand the nature of the process stream and its temperature in the case of high temperature processes (incineration or vitrification).

High porosity mats and sintered webs composed of stainless steel fibers, have been firstly tested on their filtration performance at room temperature. This screening study, using monodisperse latex aerosols, has been described in annual report 1981 and has led to the choice of three filter designs.

The filtration performance for polydisperse methylene blue aerosols and the regeneration by washing techniques has been studied with two filter configurations : a candle type filter and a flat type filter.

Since a candle type filter with small diameter appeared to be not well suited for regeneration by spray washing; the flat type filter configuration has been chosen for test in a high temperature unit with the filter operating at 400° C. The filtration performance of the three filter designs and the regeneration by spray washing has been studied for an aerosol formed by calcination of a simulated waste solution.

Progress and Results

- Comparison of candle and flat type filter configurations

  The filtration performance of the three filter designs and the regeneration by washing has been studied at room temperature using a submicronic methylene blue aerosol (MMAD = 0.6 μm) at low concentration (1 to 4 mg/m^3) as challenge aerosol.

  The characteristics of the different filters tested at the same flow rate of 15.6 m^3/h are given hereafter.

DESIGN I	DESIGN II	DESIGN III
5 layers of Bekipor porous mats with fiber 4 μm in diameter	1 layer of sintered web Bekipor ST10AL2	3 layers Bekipor 12 μm 3 layers Bekipor 8 μm 3 layers Bekipor 4 μm
3 candles Ø int. = 52 mm Ø ext. = 90 mm height = 250 mm	3 candles Ø int. = 52 mm height = 250 mm	flat filter Ø = 280 mm height = 17 mm

The main observations drawn from these tests were :

- the filter efficiency is higher with the porous mats than with the sintered web, when the aerosol loading of the filter is low;
- the trapped aerosol is distributed in the mass of the filter (exponential decrease with depth) for the porous mats and on the filter surface for the sintered web;

- the performance of the sintered web improves rapidly by formation of a dust cake on the filter, which causes also an increase of the pressure drop;
- the regeneration of the porous mats requires a good wetting of the mass of the filter, so that a washing from both sides of the filter is required to have a complete removal of the trapped dust;
- the regeneration of the sintered web is very easy since only a filter cake removal is required to regenerate the filter;
- the washing of candles with small diameters and great length is only possible from outside to inside; moreover a great number of nozzles per candle is necessary. Therefore, it is easier to use a flat type filter configuration with gas flowing upwards so that the outlet side of the filter can not be polluted by the washing solution.

- Flat type filter test at high temperature and regeneration

A high temperature test unit was built to test the filter material in conditions representative of a calcination process.

In a stainless steel calciner operating at 700° C, a simulated nitric acid waste solution containing nitrate salts of Na, Fe, Cr, Al, Mn, Cs, Sr, Ba, Ce, Zr, Mo, Rb, Y and La and tagged with ^{134}Cs isotope is fed and by calcination generates an aerosol containing soluble and insoluble compounds.

The off-gasses of the calciner contain air, 10 to 16 % water vapour and about 0.15 % of NO_x. The aerosol loaden off-gases pass through the filter tested at a temperature of about 400° C. The particle size distribution of the aerosol is determined with a cascade impactor and the filter efficiency is determined by activity measurements of glass fiber sampling filters placed up and downstream of the tested filter.

Three runs have been made with the filter designs I, II and III. The following observations can be drawn from these tests :

- with the challenge aerosol used (median aerodynamic diameter from 2 to 5 µm and concentrations from 100 to 500 mg/m^3), the pressure drop and the filter efficiency depend on the formation of a filter cake on the filter surface. For the porous mats, a fraction of the dust is distributed into the filter mass, whereas for the sintered web only a dust cake is formed on the surface;

- the regeneration of the filter by spray washing is possible for porous mats and sintered webs. For the porous mats, washing of both sides of the filter is necessary, whereas for a sintered web washing of only the filter cake is sufficient.

2. WASTE STORAGE AND DISPOSAL

2.1. SHALLOW LAND BURIAL OF SOLID LOW ACTIVITY WASTE

Shallow land burial is a method already applied on an industrial scale for the disposal of low-activity solid waste. Therefore, the research in this field is mainly oriented to the improvement of the disposal techniques in order to ensure a better protection for the man and his environment. More specifically, the following three topics are convered :

- Status of existing experience
- Improvement of burial techniques
- Radionuclide migration and safety aspects.

During 1982 one new research contract on radionuclide migration research has been concluded. Therefore a total of six study or research contracts (cfr. annual report 1981) were running at the end of 1982.

The first study contract, covering the first sub-heading of this chapter, aims to review the state-of-the-art of the shallow land burial in the Community.

The research carried out under the second subheading considers improving shallow land burial techniques. One contract aims to find methods and materials to reduce the permeability of soils, whereas the other contract is concerned with the design and development of improved waste units, placed closely together below ground.

In the third subheading, radionuclide migration is the subject of research performed under two contracts. This comprises the development of a mathematical model for the calculation of the dispersion of radionuclides in heterogenous sand-clay-soil systems and an experimental investigation of chemical reactions and complex formation of some radionuclides with organic substances in top soil.

A third contract is concerned with an assessment study of the radiological protection aspects of shallow land burial.

The progress achieved in the studies and research is reported contract by contract and covers the following contracts :

2.1.1. STATUS OF EXISTING EXPERIENCES

Present situation and prospects for the burial of low activity solid waste at shallows depth within the Community

Contract : 267-81-6 WASF, CEA, Cadarache.

Objective and Scope

The analysis of the state of the art and the prospects in the EC member States concerning low-level waste burial constitutes the main objective of this study. Review of subjects such as regulations, selection criteria, operation of burial sites, characteristics of buried waste and economic aspects is included in the scope of the study.

Progress and results

The partial analysis carried out up to now shows that disposal of low level waste by shallow land burial is currently practised on a large extent only in France and the United Kingdom. In the past (1956-1972) this disposal method has taken place also in the Netherlands on a very limited scale.

In France, low and medium level waste have been disposed of by shallow land burial at the La Manche disposal centre since 1969.

Two types of manmade structures are used for the disposal of conditioned waste :

- monoliths, located below the original ground level, for waste whose initial conditioning has to be completed by immobilization in a concrete structure;
- tumuli, above the original ground level, for waste whose initial conditioning does not necessitate any supplementary immobilization.

The whole is covered with a thick layer of clay to protect both structures and waste packages from rain water.

The disposal centre occupies an area of 12 hectares and has a disposal capacity for about 400.000 m^3 of conditioned waste. About 200.000 m^3 waste has already been disposed of.

In the United Kingdom, two disposal sites are in operation at Drigg and at Dounray.

The Drigg site of approximately 300 acres is owned and operated by BNFL. Waste is disposed of in trenches, which are 700 m long, 15 m wide and 4.5 m deep and are covered with at least 1 m of soil. It is estimated that approximately 150.000 m^3 of waste has been buried at this site since it started operation in 1971.

The burial site at Dounray is being exploited by UKAEA since 1972. There 200 l steel drums, containing conditioned waste, are piled up in pits which are 7 m deep. Six pits exist at present. The first four have a volume of 6000 and 14.000 m^3 respectively. The empty space between the drums inside the pits is filled with polythene materials. The pits are then covered with earth.

A detailed analysis of the other subjects, included in the scope of the study, is in progress.

2.1.2. IMPROVEMENT OF BURIAL TECHNIQUES

Improvement of the radioactivity confinement by soil barriers

Contract : 196-81-6 WASF, CEA, Fontenay-aux-Roses.

Scope and Objective

The aim of this research is to find fillermaterials which can be incorporated in the soil. Reduction of the quantities of radionuclides entrained by the percolating water is obtained by means of reducing permeability of the soil or by increasing its adsorption capacity.

The fillermaterials are cement-based or chemical fillers. Two filling techniques are investigated :

- cutting a trench around the installation and filling this trench with a low-permeability material
- injection of a delayed-setting material into holes in the soil.

The study is divided in two phases : bibliographic research and experiments.

Progress and results

- Bibliographic research

  This has been carried out basically with the Soletanche company. A schematic presentation of the bibliographical document is given in table 41.

Section \ Technique		Trench cut in soil	Injection
1st group (studies and parameters)	A	Conventional calculation which links the stability of the trench and the density of the soil and presentation of various parameters	Theories of flow in powdered media and fissured media. Stresses on the soil during injection and the consequences thereof.
	B	Optimum geological conditions for application	Parameters characterizing a soil and methods of analysis using these parameters. How to select a filler to achieve the best possible impregnation
	C	Various applications (use of self-hardening soil). Description of the drilling and soil-working equipment. Checks carried out during the working of the soil.	Different injection processes, equipment required and how to check the quality of the work.
	D	Investigation and analytical methods used in the SOLETANCHE laboratory. Study of the constituents of the fillers. Rheological characteristics and their changes with time. Study of the hardened filler.	Investigation and analytical methods used to detail the rheological, mechanical and hydraulic properties of the fillers. Detailed study of cement fillers, chemical-based fillers and special fillers. Effect of outside agents and adjuvants intended to modify certain chemical properties.
2nd group (experiments)	E	List of the 12 sites (including more than 30 outside France) treated between 1962 and 1981. Data on wall thickness, surface, depth and cost for each site. Average cost : 400 (easy terrain) to 750 (difficult terrain) francs per m2	List of the 427 sites (including 85 outside France) treated between 1973 and 1980. Number of drillings, quantity of filler and cost are given for each site. Average cost : 140 (rock) to 450 (alluvial) francs per m3 of soil treated.

Table 41 : Schematic presentation of the bibliographic document, showing the researched area's

. Preliminary results of the bibliographic study

Fillermaterials for sealing can be classified according to their permeability, see table 42.

Permeability m/s	Filler
1 to 10^{-3}	Cement-based filler, bitumen emulsion
10^{-3} to 10^{-5}	Silica gels
10^{-5}	Resins

Table 42 : A classification of fillermaterials as a fonction of their permeability

The permeability of a screen in relation to that of the soil which it may replace is often reduced by a factor of 10^4 to 10^6.

In the case of injection the permeability of the soils treated is reduced by a factor of 400 to 10.000 in a powdery medium and from 5000 to 10.000 in a fissured rocky medium.

In addition, following treatment, the resistance to simple compression may improve by a factor of 10 to 500.

- Laboratory experiments

Six groups of samples of filler of various types were prepared for the tests (three are normally used for the production of watertight screens and three for injection). These samples were of small dimensions (being 25, 50 or 100 mm in height and having a diameter of 80 mm) and they were tested for permeability and retention capacity with respect to Cs-137 and Sr-85.

. Measurement of permeability

The first tests comprised percolation of the water through the samples so as to check the claimed permeabilities. If the water did not percolate at atmospheric pressure, an apparatus enabling the pressure to be increased by several bars was used.

- The results show that, for screening fillers, permeabilities varying from 10^{-7} to less than 10^{-11} m/s can be achieved. Permeabilities lower than 10^{-11} m/s can be achieved for the injection fillers.

. Measurement of the retention of Cs-137 and Sr-85

The tests consisted of percolating water with a pre-determined concentration of Cs-137 and Sr-85 through the samples and measuring the concentrations in the water after percolation; five of the six samples were tested in this way.

In the case of Cs-137 retention, it was established from the very first cm^3's that the concentration is either unchanged or only 2-4 times lower than the initial concentration, dependent on the filler.

In the case of Sr-85 retention, the results obtained so far are generally better than for caesium, except in the case of one of the fillers used as a screen, where the retention was zero (as it was for caesium), while with the other fillers the ratio between initial concentration and concentration after percolation varies between 20 to 50.

It has not been possible to continue the tests since the permeability of most of the fillers reduces with time and the water does not continue to percolate.

It is intended to complete these tests on mass-retention with some surface-retention tests.

- Conclusion

The preliminary results indicate that the fillers are not particularly effective for the retention of caesium-137 in particular, but they can nevertheless improve the qualities of the soil barrier because of their very low permeability as claimed by the manufacturer after tests in the field and confirmed by laboratory tests.

Development of a waste unit for use in shallow land burial

Contract : 195-81-6 WASDK, RNL, Risø.

Scope and Objective

The aim of this project is the developement of a waste unit, to be used in a waste storage, and the design of such a storage. The waste units are made of a specially strong and dense concrete, called "Densit". They are designed for low- and medium level waste. The properties of the unit, which are important in respect of waste storage, e.g. strength and long-term stability, are investigated.

Progress and Results

- Material developement

  The studies of diffusion of various species (tritiated water, ^{134}Cs, and ^{36}Cl) in concrete and Densit have been continued. The rate of diffusion in Densit is much lower than in ordinary concrete. Further studies have been made of properties governing corrosion of iron embedded in Densit.

- Properties of waste units, test facilities

  A series of empty hexagonal waste units have been cast and will be used in a test burial and for various other investigations. Preparations have been made for testing the waste units for leaks by applying a slight internal overpressure on a waste unit and then measure the evolution of this pressure for some months. Preparations have been made for testing the strenght of the unit by applying an overpressure up to about one hundred bars, and by a fall test in accordance with the transport regulations.

- Design of waste disposal

  Three different conceptual designs have been made for waste disposals with these waste units. The facilities are placed 2, 10, and 20 m below ground level, respectively.

The waste disposal 10 m below ground level is seen on fig. 46.

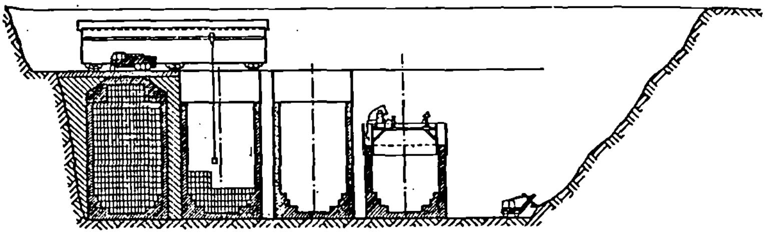


Fig. 46 : Vertical section of burial site with waste units during various stages of manufacture and loading

- External radiation

The external radiation from waste units containing reactor waste will, after decay of short-lived activity, practically only be due to the content of ^{60}Co, ^{137}Cs and ^{134}Cs.

Radiation doses from standard units containing 1 Ci of these isotopes, solidified in cement or bitumen, has been calculated. The dose rates at 1 m distance from the surface of various types of standard units are given in table 43. The calculated values give an idea about the radiation protection problems involved in handling the units. The dose rate near the surface of the units will probably be about a factor 10 to 15 higher than at 1 m distance.

It is seen from the values in table 43 that only the type A_1 units can be regarded as low-level waste with radiation level less than 0.2 R/h near the surface. Type A_2 units will require remote handling and additional shielding during transport. Type A_m units represent the situation which would result if it was technically possible (and desirable) to homogenize the waste so that the activity was distributed evenly in all the units. The result would be an increase by a factor 4 or 5 of the external radiation from the 2000 low-level units necessary per GWyear. The use of such a dilution method for the elimination of the 200 high radiation units is therefore questionable as seen from the point of view of minimizing the doses to operating per-

Type of unit		A_1	A_2	A_m	B
% of waste units with		90	10	100	100
% of activity		20	80	100	100
Container diameter	cm	57.2	57.2	57.2	63.5
Volume	L	216	216	216	285
Waste Volume	L	200	200	200	285
Number of units per GW year or 440 m^3		2000	200	2200	1544
γ emitters Ci/unit at t = 0	^{60}Co	0.02	0.80	0.091	0.130
	^{134}Cs	0.05	2.00	0.227	0.323
	^{137}Cs	0.05	2.00	0.227	0.323
Specific external radiation in R/h at 1 m distance from face of unit containing 1 Ci of the isotope					
Cemented waste Density : 2.35 g/cm^3	^{60}Co	0.131			0.152
	^{134}Cs	0.088			0.114
	^{137}Cs	0.033			0.043
Bituminized waste Density : 1.20 g/cm^3	^{60}Co	0.326			0.344
	^{134}Cs	0.207			0.222
	^{137}Cs	0.076			0.079
Actual radiation in mR/h at 1 m distance from surface of unit					
Cemented waste	^{60}Co	2.62	104.8	11.9	19.7
	^{134}Cs	4.40	176.0	20.0	36.8
	^{137}Cs	1.65	66.0	7.5	13.9
	Total :	8.7	350	39	70
After 30 years :		0.9	35	4	7
Bituminized waste	^{60}Co	6.52	260.8	29.7	44.7
	^{134}Cs	10.35	414.0	47.0	71.7
	^{137}Cs	3.80	152.0	17.3	25.5
	Total :	20.7	830	94	142
After 30 years :		2.0	81	9	14

Table 43 : Calculated dose rates at 1 m distance from the surface of various types of the standard unit

sonnel. Additional shielding during transport of A_m units will be required at least for fresh material.

The radiation from type B units has only been calculated for evenly distributed activity. The increased radiation from these units is mainly due to the higher waste volume and therefore the higher activity content in each unit. A minor part of the increase in radiation is due to the decrease in thickness of the concrete wall (Compare type A_m and B).

The use of cemented waste instead of bituminized (or polymer-solidified) materials gives for the same activity concentration a reduction in dose rate of a factor 2.4 for the type A units and 2.0 for the type B units.

2.1.3. RADIONUCLIDE MIGRATION AND SAFETY ASPECTS

The influence of ground heterogeneity on the dispersion of radionuclides

Contract : 193-81-6 WASNL, Soil Mechanics Laboratory, Delft.

Scope and Objective

The scope of the study covers the migration of non-interactive ions as well as adsorbed species in a generic shallow burial site as defined in the 1981 annual report. No actual field data are available at this moment and therefore the study is entirely theoretical.

Progress and Results

In order to evaluate the performance of the various mathematical models, certain bench marks are needed. These would consist of detailed field studies of contaminant concentration patterns, water flow patterns and soil structure patterns such as the exact size, position and properties of any inclusions, lenses, horizons, etc. This all for a migration field of about 500 m to 1000 m around an actual shallow burial site.

This information is not available at this moment. The first step is thus to construct artificial bench marks by calculating in an as advanced as possible way the migration patterns for a predetermined soil configuration, recognising that the choice of the configuration is somewhat arbitrary, but hoping that the techniques and results of the evaluation will have some wider generality. In fact several configurations were chosen, reflecting roughly sand-clay, clay-organic soil, and sand-organic soil mixtures. The migration patterns were then calculated using a numerical approximation to the convection-dispersion equation contained in the Institutes code VERA. The use of such a model for this heterogeneous system is of course open to question and in order to verify the mathematical implementation of the code, several (new) analytical solutions of limiting cases of the problem were constructed. It was found that the code accurately matches these exact solutions for both the homogeneous case and the single macro clay lens case (see fig. 47 for a typical illustration of this match).

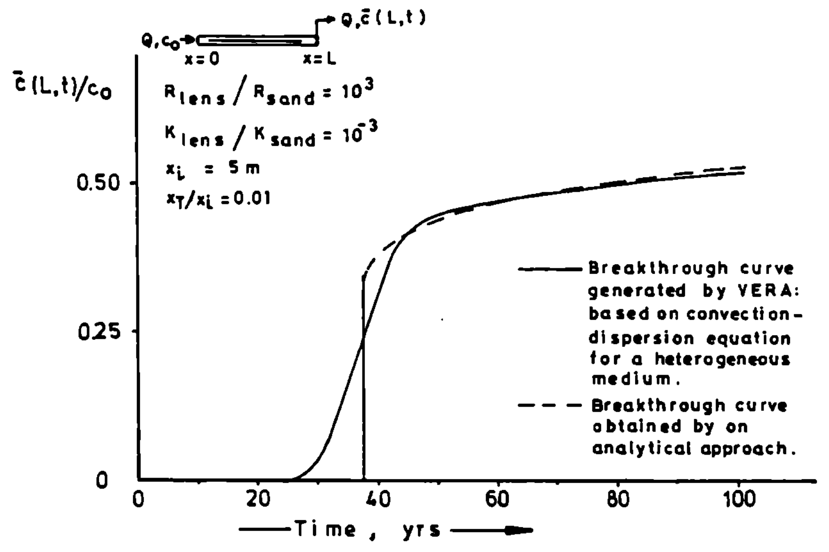


Fig. 47 : Breakthrough curve of one-lens-system

As part of the bench marks phase of the program a systematic study was made of the case of macro clay lenses in a sand system.

The clay / sand ratio was kept constant at 25 %, but the length and thickness of the lenses was varied from 400 m to 50 m and 8 m to 2 m. Both the interactive and non-interactive radionuclides were considered. Illustrative results are shown in fig. 48, which gives the breakthrough curve just downstream of the clay-sand system. The following conclusions can be drawn from these results :

- The shape of the breakthrough curve strongly deviates from that expected from any homogeneous model. In particular there is early breakthrough at low concentrations and long tailing at the higher concentrations. In practical terms this means that critical pollution levels will be reached more quickly and reduction of these levels by ground-water wash-out will occur less effectively than expected.

- Although sooner or later the expected adsorption of an interacting component occurs, there is no significant role of the retardation effect in the important area of the early breakthrough. In other words for the case of the generic site considered large clay lenses do not contribute significantly to the site safety.

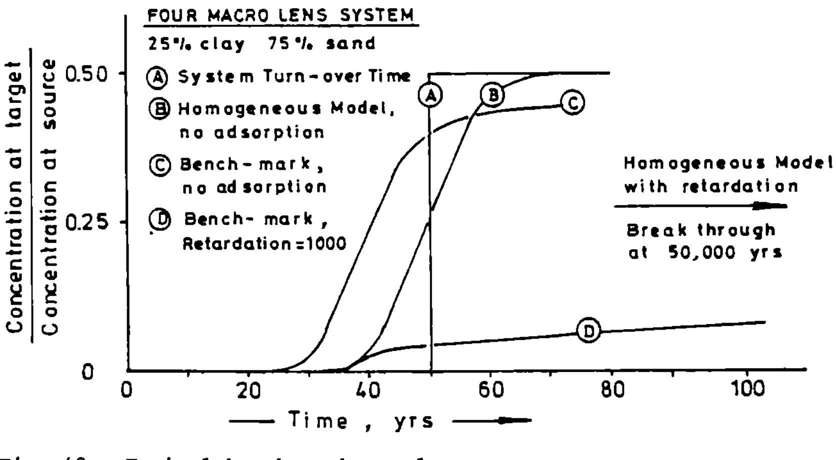


Fig. 48 : Typical bench mark results

Basic geochemical research for migration studies

Contract : 194-82-6 WASDK, RNL, Risø.

Scope and Objective

The aim of the study, initiated in 1982, is to investigate the possible interaction between selected radionuclides ($^{134}Cs^{+}$, $^{60}Co^{2+}$, $^{85/89}Sr^{2+}$, $^{154}Eu^{3+}$) and organic substances commonly found in top soil, including carboxylic acids, amino acids and humic acids. The study is expexted to provide data on the complex formation of the radionuclides with the mentioned ligands; the complexes may play an important role in the possible migration of the radionuclides with ground water.

Progress and Results

The theoretical part of the work has been concerned with two different approaches to the determination of stability constants : a) potentiometric titration, and b) dialysis. The theory of potentiometric titration has been elaborated to handle interactions between metal ions and any poly-basic acid, amphoteric or not. In the case of the polymeric ligands, i.e. humic acid, a technique based on simple dialysis has been developed to determine stability constants as well as complexing capacities, the latter being unknown in the case of humic acid in contrast to the well-defined monomeric species.

In the experimental part interactions have been investigate for the following systems (the derived log β values are given in parentheses) : Cobalt-aspartic acid 1:1 (5.78), Cobalt-aspartic acid 1:2 (10.10), Strontium-aspartic acid 1:1 (2), Strontium-cysteine 1:1 (2), Strontium-humic acid 1:1 (3.32, pH=7)), Cobalt-humic acid 1:1 (5.68, pH=7) and Europium-humic acid 1:1 (5.86, pH=4.5).

In cases where comparison with previously reported data is possible, excellent agreement is observed.

In the forthcomming period the complex-chemistry work will be continued. A study on the influence of chelating agents on the migration of radionuclides through column systems will be conducted. Only sparse and preliminary information on the latter study is available presently.

In the case of low molecular weight organic acids the experimental work is nearly completed. The remaining period will be devoted to the subsequent calculational work.

Assessment of radiological protection aspects and review of siting principles

Contract : 233-81-6 WASUK, NRPB, Chilton.

Scope and Objective

The aim of this study is to assess the radiological impact of disposal of three different waste types by calculating potential doses and risks to individuals, both during the operational period and during the period when the site has been closed and no further wastes are placed in it. The results of these calculations will allow preliminary conclusions to be drawn about the types and quantities of wastes potentially suitable for disposal, site selection, burial facility design and the period of time for which restrictions should be placed on the use of the site after disposal operations have ceased.

Progress and Results

- Release mechanisms and exposure pathways

  The only release mechanisms considered in the assessment are releases by trench fire during the operational period, contact of the wastes by water and human intrusion for building purposes after the site has been closed and restrictions on land use have been lifted.

  Both fully and minimum engineered burial facilities have been considered and a different generic site has been defined for each of the two types (see annual report 1981). At the fully engineered site, groundwater transport of radionuclides may lead to contamination of both the soil zone and nearby streams and hence doses may be received if the site is farmed or from use of the streams. At the minimum engineered site there should be no groundwater transport of radionuclides to the soil zone and only exposure pathways resulting from use of the nearby stream need be considered.

All wastes buried in the fully engineered trench are considered to be non-flammable and it is therefore appropriate to calculate the consequences of release by trench fire for the minimum engineered facility only.

- Probabilities

The radiological impact of shallow land burial is a function not only of the doses which might result from each different release mechanism, but also of the probabilities that these releases will occur and that the doses will in fact be received. During this assessment contact by water is considered certain to occur as an initiating event, but time-varying probabilities have been calculated for each of the resulting exposure pathways. Release by trench fire and human intrusion are treated entirely probabilistically. By assuming that restrictions on site use are lifted as soon as disposal operations have ceased the radiological impact of disposal can then be calculated as a function of time. Results have been calculated in terms of both individual doses and risks for the first 1000 years after closure only, since it becomes increasingly difficult to calculate the probability of the site being excavated for building or farmed at greater times.

- Radiological protection criteria

Two ways of using radiological protection criteria, to determine the period for which restrictions should be placed on use of the site, have been defined. The first of these methods uses the criterion that the maximum annual individual dose arising from disposal should not exceed $5\,mSv\,y^{-1}$ (i.e. the dose limit recommended by ICRP for members of the public) and the second that the maximum risk to an individual should not exceed $5 \cdot 10^{-5}$ in a year. Here, risk is defined as probability of death; $5 \cdot 10^{-5}$ is approximately the risk associated with receiving a dose of 5 mSv.

- Disposal of resins and sludges arising at Magnox reactors

  A preliminary assessment of the radiological impact of disposal of magnox sludges and resins in a fully engineered facility has now been completed. The results of the calculations indicate that the highest risks and doses to individuals during the first 1000 years after site closure arise only from excavation of the site for construction of buildings. At early times after closure (10-50 y) the total dose from excavation is effectively due to external irradiation by ^{137}Cs and inhalation of ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{241}Am. However, at later times (i.e. > 500 y) this total dose is effectively due to inhalation of ^{239}Pu, ^{240}Pu and ^{241}Am.

  In the very long term (i.e. at times greater than 10^4 years) farming and use of the stream give rise to the highest individual doses. The most important radionuclide during this period is ^{237}Np.

  The results of the calculations show that for this type of site and facility, the total individual risk associated with disposal of magnox resins and sludges falls below $5 \cdot 10^{-5} y^{-1}$ at approximately 15 y after closure. In contrast, the calculated maximum annual individual dose falls below $5 mSvy^{-1}$ at about 220 y after closure. Once the calculated risk or dose has fallen below this limit it does not exceed, or indeed approach, the limit thereafter.

- Disposal of LWR operating wastes

  A preliminary assessment of the radiological impact of disposal of LWR operating wastes is now nearing completion. The results of the calculations indicate that the highest risks and doses to individuals during the first 250 years after site closure arise from excavation of the site for building purposes and that the dose received during this period is very largely due to external irradiation by ^{137}Cs. From 250 to 1000 y after site closure the risks and doses arise primarily from farming and from use of the stream and the dominant nuclide is ^{14}C. Later on (i.e. at times greater than 10^4 y) ^{237}Np also gives rise to doses through these pathways.

  The results of the calculations show that for this type of site and facility, the total individual risk associated with disposal of LWR operating wastes remains below $5 \cdot 10^{-5}\ y^{-1}$ from a few years after site closure onwards and that the calculated maximum annual individual dose remains below 5 mSv y^{-1} from 625 y onwards.

- Disposal of general low-level wastes

  Work is now underway to determine the individual risks and doses associated with shallow land disposal of general low-level wastes in a minimum engineered facility. Results will be interpreted within the same general framework as those from calculations for the fully engineered facility.

2.2. STORAGE AND DISPOSAL IN GEOLOGICAL FORMATIONS

This part of the programme is concerned with all R&D work to investigate the possibility of safe disposal of nuclear waste, essentially high-level waste and alpha-bearing waste, at depth in stable geological formations. Three continental formations are studied in the CEC programmes : clay, salt and granite; a fourth line of research is concerned with sub-seabed disposal.

From an operational point of view, the results are presented under the following sub-headings :

Each of the above paragraphs starts with an introduction, which also lists the reported contracts. Progress achieved in the contractual works is thereafter reported contract by contract.

2.2.1. DEEP DRILLING PROGRAMMES

No deep explorating boreholes were drilled in 1982 in the framework of the EC programme.

However, hydrogeological/geological investigations on already existing boreholes were carried out in the UK and in Belgium.

Reported contracts :

Investigations on the hydrogeology of the Mol area

Contract : 144-80-7 WASB, Part 1, CEN/SCK, Mol.

Scope and Objective

Hydrogeological data acquisition for subsequent regional groundwater flow modelling.

Progress and Results

An extensive network of boreholes for piezometric survey and water testing was already completed.

Very important field activities concerned the "in situ" determination of hydraulic parameters of the different aquifers : piezometric head and transmissibility. The manual piezometric head measurements are performed periodically (every 14 days) and automatic data recording is foreseen for each test location.

Determination of the transmissibility is done by slug tests and/or by single well pumping tests at all locations where observations wells penetrate the Boom clay. The latter tests will last until mid 1983. Water sampling for ^{14}C-age determination and for supporting chemical analysis is also performed by appropriate devices and pumps.

All these measurements are used as input data as well as calibration references for the hydrogeological modelling of the Mol area.

In close co-operation with the Ecole des Mines of Paris, the updated version of the numerical model (NEWSAM) has been adapted to simulate the regional groundwater flow in the neogenic sands, the Berg sands and the Brussel sands. In the present conceptualisation of the model a drainance through the confining Boom clay and Asse clay is assumed. An other assumption made was, that all neogene deposits compose one single aquifer. Indeed, recent field observations in about 100 wells argue for this. The periodic piezometric survey of the area learned that no significant piezometric head differences exist between the different lithological subunits of the neogene. Several simulation runs with the NEWSAM-model have already been performed, aiming at testing several hypotheses for calculated and calibrated conditions. Figure 50 represents the calibrated and calculated piezometric contour map of the Berg aquifer, drafted on the basis of the computations by the NEWSAM-model. As expected westwards flow results, mainly due to the constant head distribution along the outcropping borders.

Also for the neogenic sands and the Brussel sands a westward flow was obtained by simulation.

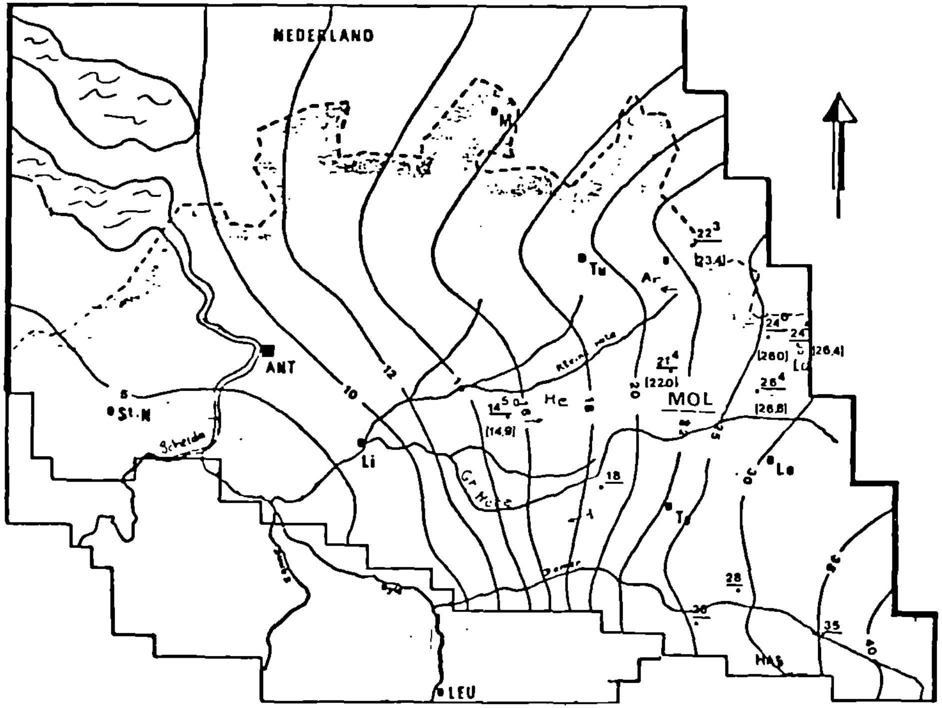


Fig. 50 : Simulation of the Berg sands aquifer

X^y observed piezometric heads (m)
[ ] equivalent piezometric heads (m)
x equipotentials (m)

Geological assessment of the crystalline rock formation at Altnabreac

Contract : 128-80-7 WASUK, Part 1, NERC-IGS, Harwell.

Objective and Scope

The research programme aims at assessing the feasibility of the disposal of high-level waste into crystalline rock formation, with special attention paid to geological and hydrogeological studies.

The programme has continued with the study of the disposal of highly radioactive wastes in crystalline geological formations in the United Kingdom, begun in 1976/77 under contract number 01-76-7 WASUK and continued in 1978/79 under contract number 059-78-1 WASUK.

Progress and Results

The original concept of the programme was that it would involve both the selection and appraisal of research sites and some of the background research, necessary to demonstrate that containment of wastes over long periods of time is feasible. In the event the work at research sites was curtailed by the British Government in December 1981 and during 1982 the programme has concentrated on completing work at Altnabreac in Northeast Scotland; work which was projected in 1982 at further research sites has not been initiated.

The work at Altnabreac was focussed on hydrogeological investigation using the existing boreholes, with additional supporting studies.

- Groundwater sampling and dating

  In May 1982 groundwaters from all the shallow narrow boreholes at Altnabreac in Caithness (except in Al 18, where the hydraulic conductivity is too low) were sampled using a small diameter submersible pump, which was developed inhouse by IGS. Two boreholes which had yielded declining tritium groundwater contents through previous sampling programmes were continually sampled during protracted abstraction (> 9 borehole volumes). Nearly tritium-free water was obtained indicating all water components to be > 30 years old. Three other boreholes have also yielded a tritium free sample. All such boreholes occur in similar situations near the base of long gentle inclines with a pronounced break of slope below them. This supports the flow-modelling conclusions that water movement is essentially horizontal, with flow paths controlled by topography, and that groundwater age is essentially a function of depth.

In July 1982 a repeat groundwater sampling programme was organised to abstract large volumes (up to 18 inter-packer volumes) from zones in the deep boreholes at Altnabreac where old groundwater components had been identified. The aim was to eliminate the effects of mixing of recent waters, as well as to assess the constancy of chemical parameters. It was possible to compare the samples obtained by the modified hydraulic equipment (essentially a gas lift pump) with those abstracted by siphon in one zone in borehole Al B at 129-133 m depth. Mixing with water in the borehole volume around the packers is a problem which tends to be enhanced by protracted pumping and ages of mixed samples cannot be unequivocally interpreted.

Nevertheless at depths to 300 m in the Altnabreac crystalline rocks, groundwaters with ages of up to around 10^5 years have been encountered. These groundwaters are only slightly different in composition from much younger waters and the increase in dissolved material from weathering reactions is minimal after the first few years. Total dissolved solids content never exceeds 500 mgl^{-1} and is dominated by bicarbonate. This seems to be due to the non-leachability of chloride in the Altnabreac rocks and partly reflects the fairly low whole rock halide contents and also the way in which halides are located within minerals. These factors have probably both been influenced by previous hydrothermal episodes, which have effected these very old rocks.

A groundwater evolutionary sequence from rainfall input, through surface processes of evapotransporation and soil zone CO_2 uptake, to calcite dissolution and limited weathering reactions has been established. A satisfactory data base for modelling corrosion of containers, leaching of waste glasses and transport of radionuclides now exists for this geological environment.

- Supporting investigation

In-situ stress measurement by hydrofracturing of rocks at depth has been attempted in one borehole at Altnabreac in the Strath Halladale Granite. An acoustic borehole televiewer was used to study the frac tures in the borehole before and after hydrofracturing. It was also run in the complete uncased lengths of two deep boreholes for comparison of the technique with conventional core fracture logging and with other geophysical methods of fracture analysis. Although the hydrofracturing results obtained were inconclusive, because of the breakdown of part of the equipment, the technique has shown to be a viable method of measuring stress at depth in boreholes. When runned slowly the televiewer proved to be an extremely accurate method of measuring the orientation and position of fractures intersecting the borehole wall.

2.2.2. UNDERGROUND EXPERIMENTAL ROOMS AND SHAFTS

The aim of such exploratory works is to obtain an in-situ, full-scale picture of the geological features and of the geomechanical behaviour of the rock formation investigated at depth.

In addition large-scale in-situ tests can later be performed in these "laboratories", to calibrate and validate predictive models.

Two main tasks were performed as regards clay formation. Firstly, the elevation of the horizontal gallery at 225 m depth in the Boom clay, underneath the MOL site, was initiated; secondly, the process for selecting a suitable site for an underground laboratory in Italian clays, as well as the preliminary design of experiments and instrumentation was continued in Italy.

In salt, the German and Dutch works in the Asse-II salt mine (FRG) were continued* .

Reported contracts :

* see also the speciale note on page 213.

Construction of an underground laboratory in the Boom clay underneath the Mol-site

Contract : 129-80-7 WASB, CEN/SCK, Mol.

Objective and Scope

This contract foresees the excavation of an underground experimental room in the Boom clay, which permits the testing of excavation techniques in plastic Boom clay and subsequently the performance of in-situ experiments.

Progress and Results

The construction of the underground experimental facility was continued. The inner concrete lining was poured upward after the completion of the crossing chamber.

Simultaneously to the pouring of the internal concrete lining, the water-tight polyethylene sheet was placed between the two linings of the shaft in order to protect it against an inrush of water from the water-bearing formations.

Because of creep phenomena of the frozen clay body during the digging operations the crossing chamber, at the bottom of the shaft, was build smaller than foreseen. Moreover it has been reinforced by horizontal steel rings placed against its inner wall in such a way that the additional stresses due to the swelling of the clay body during the freezing period could not produce a failure of the concrete lining.

For the construction of the horizontal gallery, 45 freezing boreholes have been drilled from the crossing chamber in order to install a divergent bundle of freezing pipes of about 20 meters long each.

Such a bundle allows to carry the clay body at a temperature of about - 20° C with two freon freezing groups installed at the surface and with calcium chloride as brine. After a period of one month of continuous circulation of the brine in the freezing pipes the digging of the gallery was begun.

An opening was first made in the concrete lining of the crossing chamber. Then a small rectangular access gallery (1.5 m x 2 m usefull section) was dug in the clay over a length of 4 meters, with joined steel frames as supporting lining.

After the pouring of an intermediate concrete ring at the end of the rectangular part, a first portion of six meters long circular gallery (3.5 m diameter) was dug and lined with cast iron segments, bolted together. Figure 51 gives a partial view of this construction.

A second concrete intermediate ring was poured at the end of this first portion of circular gallery.

A second construction phase will start next year after the completion of the drilling of a new bundle of freezing boreholes from this second concrete intermediate ring.

This second construction phase will comprise 20 meters of circular gallery and a final concrete plug.

During the construction of the first phase of the horizontal gallery the extraction of some vertical freezing pipes was undertaken around the shaft.

At the end of the year six pipes (on a total of 32) were removed without serious problems, with the help of a special 100 tons jack. The remaining openings were filled with a bentonite mud or a cement gel.

The measurements for the geotechnical campaign have been carried on as the construction of the shaft and the first part of the gallery proceeded. The total pressure cells (Glötzl), placed in the clay during the digging of the shaft, have continued to deliver radial, tangential and vertical pressure measurements in the clay in the vicinity of the external lining of the shaft.

Some of these cells, however, have been damaged by the creep phenomenon in the clay during the construction of the shaft.

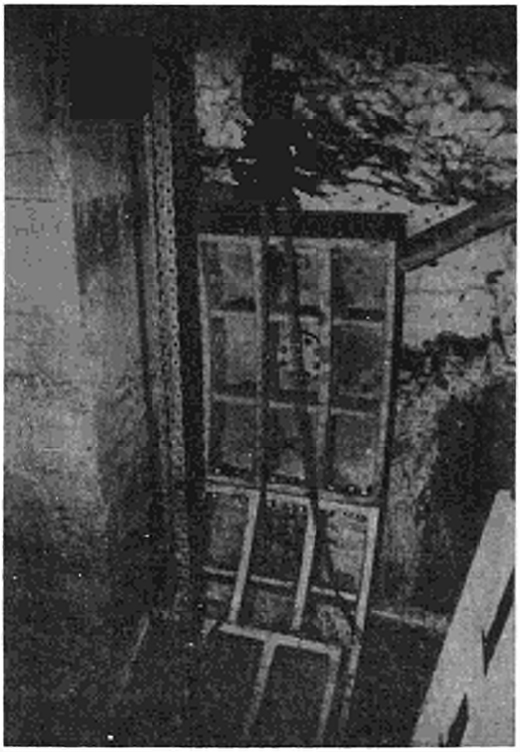


Fig. 51 : Experimental gallery
Emplacement of the first cast iron segments in the circular part of the gallery at - 223 m.

After the completion of the inner concrete lining of the shaft some interstitial pressure cells have been placed in the clay at different levels and at different distances from the lining. These hydraulic pressure gauges, coupled with thermistances, allow to follow the progressive thaw of the clay body and the build up of the interstitial pressures around the shaft.

Though the greater part of the clay body in the vicinity of the shaft is still frozen, some interstitial pressure measurements already done in both frozen and non frozen clay show that the cells work satisfactorily.

At different levels along the shaft and at its bottom several series of slotted tubes, allowing pressiometric tests in the clay (MENARD), have been installed.

Certain test have already been done in the frozen clay.

The inner part of the shaft lining has been equipped with different types of devices allowing to measure the deformation and the convergence of the concrete wall (inductance variation deformeter).

Numerous measurements have been already done with these devices, but still not enough to be in a position to draw valuable conclusions.

Use of an underground cavity as a test facility for radioactive waste disposal in clays

Contract : 140-80-7 WASI, ENEA, Casaccia.

Objective and Scope

The aims of this program are the following :

- selection and technical evaluation of a deep experimental cavity in a clay formation;
- construction of an underground laboratory in the selected cavity;

- design of heating and convergence experiments;
- design of experimental instrumentation.

Progress and Results

The work towards setting up an underground laboratory in clay has consisted mainly of site selection and preliminary design of the experiments and the required instrumentation.

- Site selection

  As a result of two desk studies and other informations a number of potentially interesting sites have been identified.

  Each site has been the subject of reconnaissance and sampling. At the end of the siting work six sites have been considered potentially suitable for siting the underground laboratory.

  The two sites considered to be most favorable are :

  - the service gallery at Orte (105 m deep),
  - the ramp at the mine of Pasquasia (170 m deep).

  The results of the siting work will need to be completed by core-drilling at the site which is eventually selected.

- Preliminary design of experiments and instrumentation

  It is anticipated that the initial experiments to be carried out in the underground laboratory will investigate the mechanical behaviour of the argillaceous materials and the thermal and hydraulic effects of localized heating.

  The rock mechanics experiments will consist of :

  - stress measurements before, during and after excavation of the experimental room;
  - closure rate measurements in boreholes drilled in the floor of the experimental room.

  The other investigation will be carried out in the thermal field, produced by a single heater. Temperatures and pore fluid pressures will be measured.

Special note

The following contractual reports are devoted to the research programme carried out in the German Asse-II salt mine, with a view to evaluate the suitability of salt formation for disposal of high-level waste. Works are jointly carried out by the GSF and KfK (FRG), and the ECN (Netherlands) under three contracts :

Thermophysical in-situ investigations on HLW-disposal in rock salt

Contract : 130-80-7 WASD, part 1, GSF, Braunschweig.

Objective and Scope

Three in-situ field heating experiments are performed or planned in the Asse salt mine :

Simulation experiment in the older halite, Na2 (temperature test 4);

Investigation of geological boundary conditions (temperature test 5);

Hexagon heating test (temperature test 6).

.he main objective of temperature test 4 and 5 is the investigation of heat ind:ced water and gas release from rock salt into a heated HLW-borehole, whereas temperature test 6 serves for the investigation of heat induced fracturing of the rock salt formation.

Progress and Results

- Temperature test field 4

This temperature test was started in January 1980 and shut down in November 1981. Measurements continued until January 1982. In this test a heater of 5.4 m length and 200 mm diameter was used in a 15 m deep vertical borehole. The initial heater power was 9000 Watts. Due to corrosion the heater power decreased in the following manner :

Heating day	Power
0 - 148	9000 Watts
149 - 315	5400 Watts
316 - 346	5130 Watts
347 - 688	3960 Watts

The following measuring results were obtained :

. Maximum salt temperature on heating day 137 = 280° C

. Average temperature gradient at the borehole wall on heating day 137 = 49° C/7.5 cm

. Accumulated water release on heating day 688 = 3386 g

. pH-value of the condensate in the cool trap = 3

. Analysis of the borehole atmosphere

- no Cl_2, SO_2, HCl, H_2S
- O_2 max. 4 %, CO max. 0.3 %, CO_2 max. 12 % and CH_4 max. 1.3 %.

- Temperature test field 5

Temperature test 5 was started in April 1982. This test was performed in the so-called "Rock Salt with Polyhalite Seams". Polyhalite ($K_2 Mg Ca_2 (SO_4)_4 \cdot 2H_2O$) contains crystalline water and is also contained in the older halite, which is considered to be a suitable disposal medium.

In order to investigate a significant beginning of heat induced release of crystalline water from polyhalite, the salt formation should be heated stepwise to 100° C, 150° C, 200° C and 250° C. The test was performed in a 7.0 m deep horizontal borehole with 280 mm diameter. The heater was 3.04 m long with a diameter of 200 mm.

Figure 52 shows the time- and temperature dependent water release which was measured during the heating period. Since a salt temperature of only 230° C was achieved in heating step 4 it is planned to continue to test in 1983, having a fifth heating step with a maximum salt temperature of about 260° C.

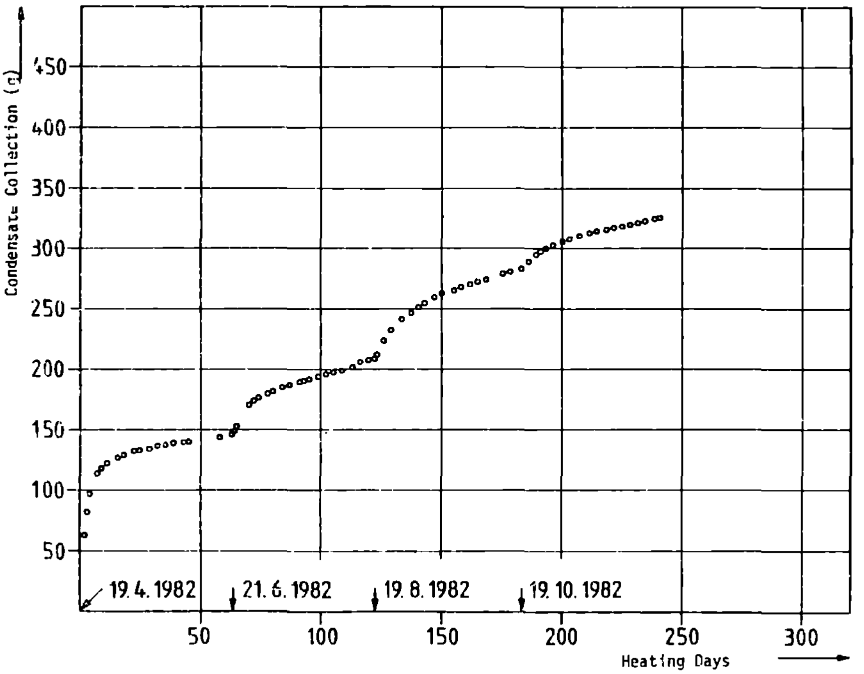


Fig. 52 : Temperature test 5 - Time and temperature dependent water release

A certain change in water release behaviour was only observed in heating step 3 (200° C). The amount of released water of 75 g in this heating phase was higher than that observed in the other heating steps, except heating step 1 (100° C), but the high amount of released water of approximately 146 g in heating step 1 is considered to be due to a release of adsorbed water only.

It seems that a release of crystalline water occurs in heating step 3, but is also finished already in this heating step because the part of the rock mass which achieved a temperature of 200° C or more in heating step 3 and 4 was comparatively small. This finally resulted in smaller release rates in heating step 4.

- Temperature test field 6

  In 1981 and 1982 the concept for temperature test 6 was developed. In this test seven boreholes in a hexagonal configurations with a spacing of 5.0 m will be heated with a total heat power of approximately 120 kW. Different geophysical measuring methods, as for example seismic monitoring, deformation measurements with extensometers, measurements of permeability and stress measurements will be applied in order to investigate heat induced fracturing of the rock salt formation. In 1982 the main instrumentation, as for example heaters, power control panels and measuring probes were procured. The heating period will be started in the third quarter of 1983.

Liberation and diffusion of water- and gas components within rock salt

Contract : 130-80-7 WASD, part 2, GSF.

Objective and Scope

The investigations in laboratories and the in-situ experiments have shown that besides water, rock salt also contains different gas components. As a result of disposed high level radioactive waste, further gases may be generated by radiolysis and thermal cracking of the main and minor minerals. All these volatile components may have an influence on the integrity of the host rock, the corrosion of the containment and the distribution of liberated radionuclides.

Progress and Results

- Investigation of natural gases included in rock salt

  In order to determine the gas liberation from the unheated rock salt some dry-drilled boreholes have been sealed and rinsed with very pure nitrogen. After 14 months, 22.4 wt% O_2, 210 vpm CO_2, 1 vpm H_2S, 100 vpm CH_4, 1 vpm C_2H_6 and 1 vpm further hydrocarbons were analyzed within the nitrogen. The origin of the oxygen and carbon dioxide is not defined. It is possible that these components have been liberated from the rock salt or may have diffused into the borehole. The

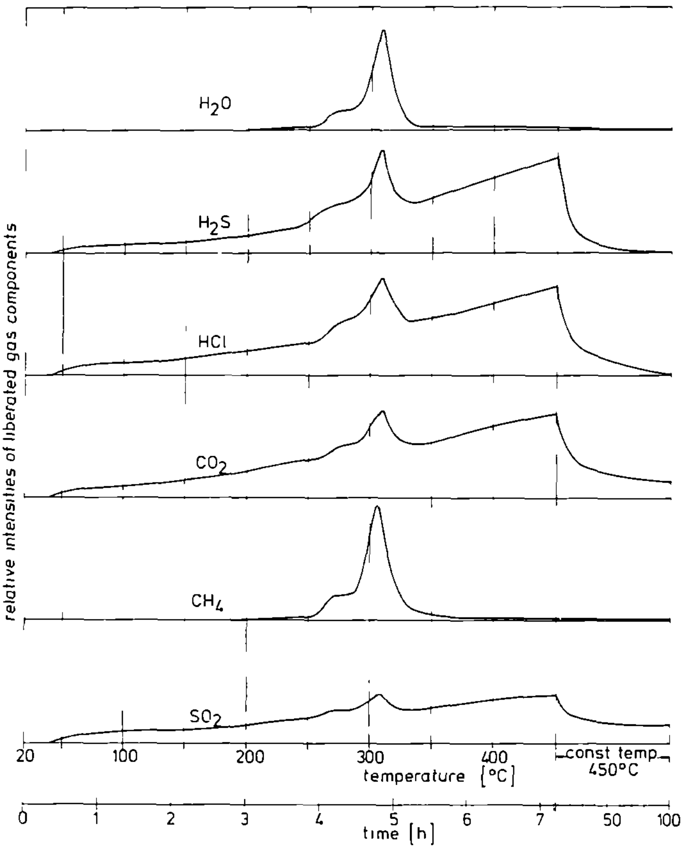


Fig. 53 : Liberation of the gas components H_2S, HCl, CO_2, CH_4, H_2O and SO_2 versus temperature and time. Mineralogical composisition : 73.4 wt% Halite, 20.5 % Polyhalite, 5.2 wt% Anhydrite. Total gas content : 4.3 ppm H_2S, 20 ppm HCl, 183 ppm CO_2, 35 ppm Hydrocarbons, 1.26 wt% H_2O, amount of SO_2 not measurable.

components H_2S and the hydrocarbons have been liberated from the rock, for they are not present in the air in such amounts.

Figure 53 shows the intensity of the liberated components H_2S, HCl, CO_2, CH_4, SO_2 and H_2O versus the time and temperature as measured with a mass spectrometer. It shows that gas liberation, especially of the components HCl, CO_2 and SO_2, begins above room temperature. At about 250° C the water of the hydrated minor minerals is released rapidly and the crystal lattice of the rock salt is destroyed, which leads to greater liberation peaks of all components.

- Radiolytical production of gases

  In order to determine gas production by radiolysis, rock salt samples of different mineralogical compositions have been irradiated with 10^7 rad in gastight glass phials. In the residual volume of these phials, hydrogen and methane were found, but comparatively less oxygen. By heating the irradiated salt, greater amounts of HCl and CO_2 were found as compared to not irradiated salt.

Investigation of the processes during flooding of a repository for high-level wastes with water and brine

Contract : 130-80-7 WASD, part 3, GSF.

Objective and Scope

These investigations are dealing with the effects of a water or brine intrusion into a high-level repository. In 1982 the activities concentrated on field measurements within flooded shafts, laboratory studies of the transition of ions from highly saturated solutions into less concentrated phases as well as model calculations.

Progress and Results

- Field measurements in flooded shafts

  These field measurements are being conducted so as to understand the naturally occurring processes in flooded mines. Temperature conductivity and flow logs were measured and water samples from four shafts, in which further investigations are planned or have already been performed, were taken. In one shaft a tracer experiment was begun to study the mechanism of transport of matter through areas with constant composition, temperature and turbulent flow as well as through liquid-liquid boundaries. The $ZnCl_2$ tracer was introduced in the NaCl solution, the homogenization velocity within this layer and the arrival of the tracer in the $MgCl_2$ solution and in the groundwater were measured. The $MgCl_2$ solution with the higher density is situated under the NaCl solution and the groundwater with the lowest density above the NaCl solution. All three solutions are characterized by homogeneous composition, temperature and turbulent flow. A very fast homogenization of the tracer within the NaCl solution was measured but until now no measurable transition across the two liquid-liquid boundaries was detected (the experiment started in August 1982).

Thus the results already obtained in laboratory experiments were confirmed in an in-situ experiment. The transport of matter within a homogeneous solution is controlled mainly by the flow, whereas the transport mechanism across liquid-liquid boundaries is the diffusion. This experiment proved that density boundaries are barriers which have to be taken into account in the mathematical transport modeling of nuclides along the water path.

- Laboratory experiments

  Experiments with glass tubes were set up and performed. These experiments tried to simulate certain aspects of transport phenomena within brines in shafts and drifts.

  In one experiment, a vertical glass tube was filled with a highly saturated $MgCl_2$ solution (68.3 mol $MgCl_2$/1000 mol H_2O) at the bottom and NaCl saturated solution at the top. Each solution was kept at a constant temperature by thermostats. It was found that a sharp temperature difference between the solutions is responsible for a sharp transition from one solution to the other. If there is a temperature gradient between the solutions, then intermediate layers will originate. In this experiment turbulent flow was observed in both solutions. The origination of a flow and the type of flow depends on the temperature-field and the concentration of the solutions. The transition of ions across the sharp liquid-liquid boundary was measured and a diffusion of Mg^{+} in the NaCl solution and Na^{+} in the $MgCl_2$ solution was observed. As a result of this diffusion both solutions became oversaturated in NaCl in a narrow zone below and above the density boundary and a thin crystalline NaCl layer soon covered the whole boundary. The crystallization of NaCl at this boundary is a natural effect in such solutions. This effect will be studied further as it may gain importance as a natural barrier.

- Model calculations

  Mathematical investigations on the stability behaviour of vertical and horizontal fluid columns with different arrangements of the temperature field have been performed. The stability boundaries for convection flows with a finite length of the cell structures have been determined. The modes considered hereby are of simple and higher types. Solutions for linearized equations have been given. These solutions are valid for small scale cells but not for shaft dimensions.

- In-situ tests in the Asse mine

  The test field for a flooded tunnel experiment has been equipped. The experiment will start in early 1983. The main aims of this test field will be the investigation of material release from a heated borehole, the development of suitable emplacement borehole seals and the comparison of predicted and measured flow and leach rates.

Measurements of deformations in underground openings in connection with in-situ experiments

Contract 130-80-7 WASD, part 4, GSF.

Objective and Scope

Already existing rooms or especially newly mined openings in the Asse salt mine are used for the performance of in-situ heating experiments with regard to a disposal of high-level radioactive waste. Parallel to these heating experiments, extensometer and convergence measurements are performed in order to investigate the deformation behaviour of the surrounding rock mass. The measuring data are used for comparison with calculated data in order to evaluate the validity of the theoretic models.

Progress and Results

- Deformation measurements

  In 1982 deformation measurements have been performed in three underground excavations :

  . Temperature test field 4, 750-m-level

  . Temperature test field 5, 775-m-level

  . Brine migration test field, 800-m-level

  The deformation measurements in temperature test field 4 were started in 1978 during excavation of the test room. From April 1978 until April 1982 a total closure of approximately 62 mm of the 6 m x 6 m wide room was observed.

  15 m below the measuring level a 9000 Watts heater gas was in operatio from January 1980 until November 1981. The influence of heating was measurable, but did not influence the stability of the surrounding rock mass.

  In January 1982 the deformation measurements concerning the temperature test 5 were initiated. Among others, a four-anchor-extensometer was installed perpendicular to the heater borehole axis at the heater midplane. The distance of the anchors to the heater were :

  anchor 4 = 6 m
  . anchor 3 = 12 m
  anchor 2 = 18 m
  anchor 1 = 21 m

  Figure 54 shows the deformation/time diagram of this extensometer. It can be seen that due to the heating of the rock salt with a maximum power of about 4500 Watts, a signigicant influence on the deformation was only observed at anchor 4 and 3.

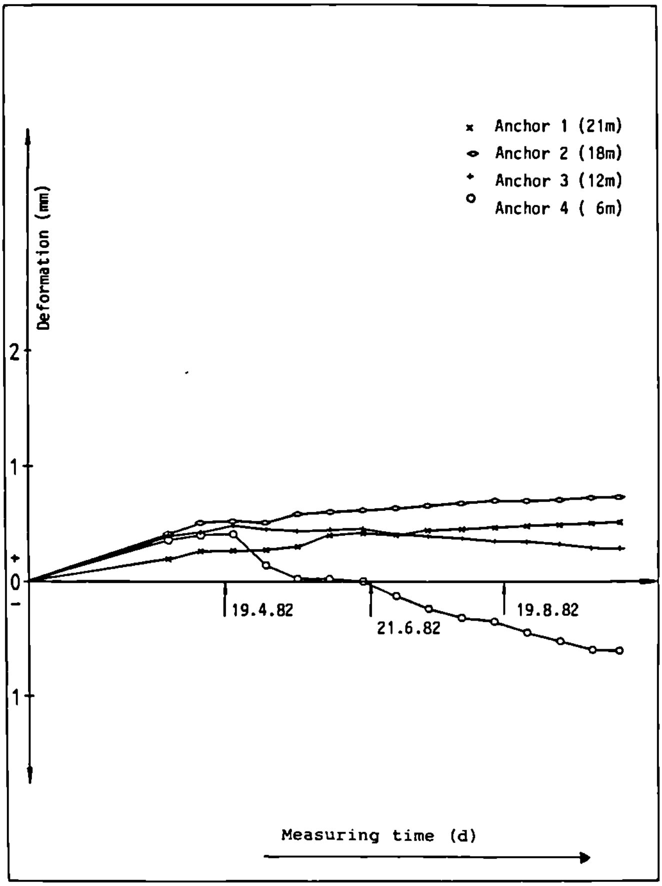


Fig. 54 : Temperature test 5; Deformation/Time diagram of extensometer SE3

In early 1982 the so-called Brine Migration Test Field was mined by using a continuous miner. This was the first time at the Asse salt mine that no explosives were used to excavate an underground opening. It is of high interest to obtain some deformation data as compared to such rooms which were excavated by blasting (e.g. Temperature Test Field 4). For this reason two convergence measuring levels were installed parallel to the excavation works. The total closure of the 10 m to 7,5 m wide room from January 1982 until October 1982 was approximately 20 mm. This is in good agreement with the closure rate of Temperature Test Field 4. In order to evaluate possible long time differences, the measurements are to be continued.

In addition to the planned so-called "Hexagon Heating Test" in Temperature Test Field 4, which will be initiated by mid 1983, all equiment, such as rod extensometers and displacement gages, were procured in 1982.

Determination of absolute stress in rocks under ambient and higher temperature conditions

Contract : 130-80-7 WASD, part 5, GSF.

Objective and Scope

Stress measurements are being carried out in order to obtain design parameters for underground constructions. The methods for measuring stresses, however, are mostly developed for an elastic material (e.g. overcoring techniques). If these methods are applied to rock salt - which behaves like an elastic-visco-plastic body - for the dimensioning of a radioactive waste disposal, then an examination of their applicability is required. Possibly an adaptation, by calibrating the devices, must be carried out previously.

Progress and Results

- Measurements of stress components

In 1982 the measurements to obtain components of the stress tensor in the secondary stress-field of the Asse salt mine have been continued. For in-situ tests the methods of "hard inclusion" and "hydraulic fracturing" were used. The results of these tests showed that :

a) the state of stress in the vicinity of the mining excavations does not seem to be lithostatic

b) there might be a greater horizontal than vertical stress component

c) a diminution of stresses is indicated if the results of the measurements are compared with the calculated vertical stress.

The stress monitoring station ("hard inclusion") was installed in the vicinity of the temperature test field 5 on the 775-m-level. No variation of stresses, however, was registered during all heating steps of temperature test 5 (see fig. 55). It is assumed that the thermally-induced stresses are either not great enough to show an effect on the monitoring station which is about 30 m away, or they are reduced due to mining excavations.

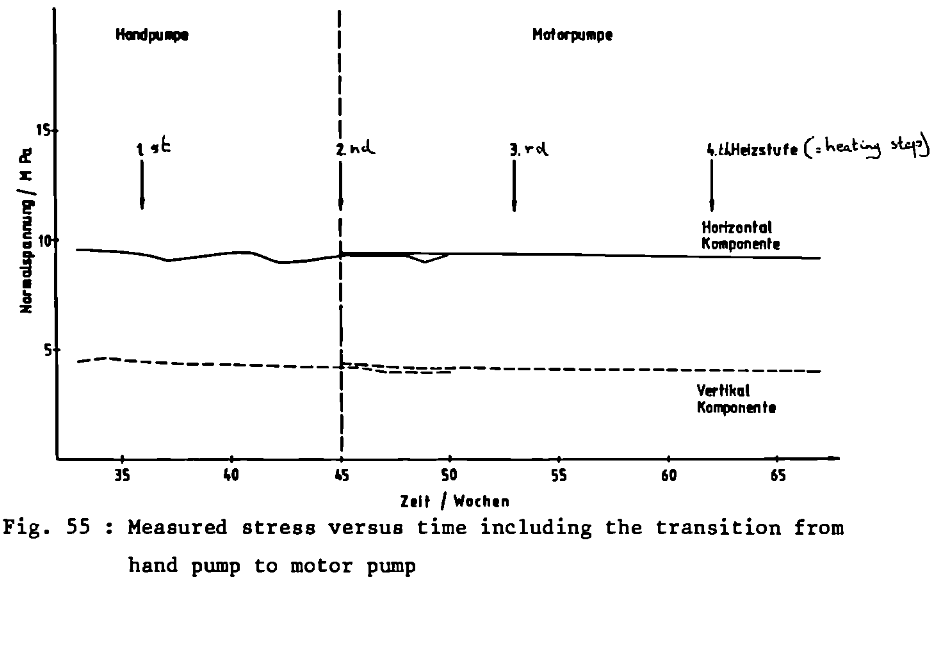


Fig. 55 : Measured stress versus time including the transition from hand pump to motor pump

Stress measurements, using the hydraulic fracturing method were made in a vertical borehole on the 775-m-level. Each of eight frac-sub-tests were used to determine the frac-pressure, the refrac-pressure and the shut-in pressure.

Assuming the elastic frac-theory the stress components were calculated.

A result in addition to the items a) - c) is that the refrac-pressure and the shut-in pressure increase with the distance to the wall. They remain constant, however, at a distance greater than 10 m.

The theory of pressure increase is based upon the decrease of radial stress due to salt creep.

Laboratory investigations of rheological salt rock properties under various conditions, including elevated temperatures and radiation

Contract 130-80-7 WASD, part 6, GSF.

Objective and Scope

The geomechanical experiments to determine the required mechanical short-term and creep properties of Asse salt rocks are carried out in the Institute Laboratory as well as within a subcontract in the experimental facilities of the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Hannover.

The test program performed in both test facilities contains a series of uniaxial and triaxial experiments in order to provide mechanical data of salt rocks with regard to stress-strain behaviour, failure and creep response under various test conditions as varying strain and stress rates, different constant stress levels and stress paths, elevated temperatures and radiation effects.

Progress and Results

- Uniaxial experiments

Experiments conducted at temperatures between 23° C and 200° C resulted in a decrease of the uniaxial strength in the order of approximately 30 %. The corresponding axial failure strain increased by a factor of about six. The Young's modulus was found to be nearly uninfluenced by increasing temperatures; however, the portion and magnitude of the elastic part of the deformation decreases.

Similar experiments as well as torsional tests and true uniaxial tensile tests were performed with samples of Older Halite from another salt dome in Northern Germany. Only minor differences in the mechanical behaviour were found as compared with the results of samples from the Asse mine.

Preliminary tests to determine the coefficient of static friction between the surfaces of steel canisters and adjacent rock salt were carried out. This coefficient was found to be approximately 0.35 at room temperature and very low connection pressure. An apparatus to determine the coefficient of static friction at expected repository conditions, i.e. elevated temperatures up to 200° C and normal stresses up to 20 MPa, is projected in detail.

- Triaxial experiments

Corresponding to the uniaxial mode, triaxial experiments started with right circular cylinders of Older Halite from another salt dome of the northern part of Germany. The overall test matrix covers strain controlled tests at a confining pressure of 10 MPa, different temperature levels between 25 and 150° C and axial strain rates ranging from 10^{-4} to 10^{-2} min^{-1}. Scope of this test series is the evaluation of the rate- and temperature- dependent stress/strain-behaviour of the salt up to the post-failure region; this in comparison to corresponding Asse rock salt samples. Within this matrix the room temperature experiments with samples from different depths could be completed.

Within the test program 1982 additional triaxial tests were carried out to define more precisely creep against fracture or creep failure respectively. Furthermore, these experiments reconfirmed that the failure strength depends on the strain rate. It can be seen from fig. 56 that - additionally dependent on the confining pressure σ_3 - the maximum deviatoric stress is influenced by the strain rate and that failure processes additionally are activated above critical values of the individual strain rate.

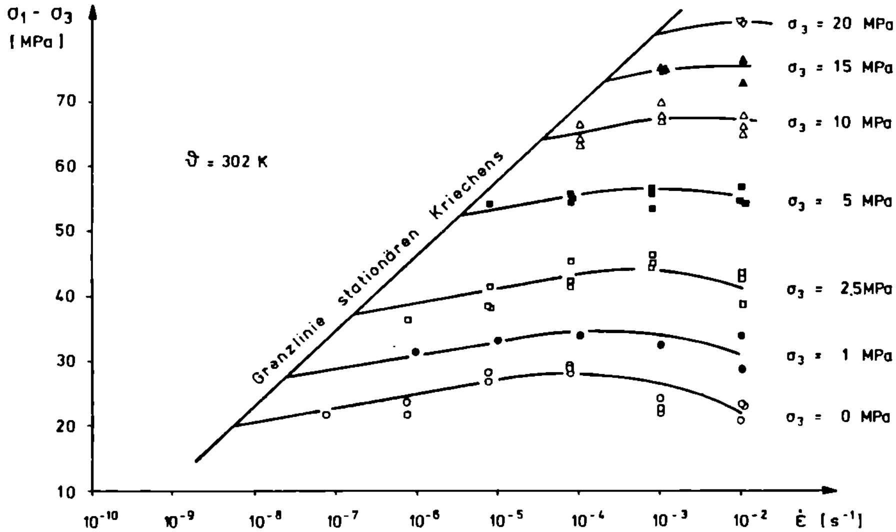


Fig. 56 : Maximum differential stress at failure as a function of axial strain rate, younger halite Na3β, Asse salt mine

For triaxial automated data acquisition, their reduction and evaluation, a modular software program was developed, tested and implemented. This implemented software package, together with the existing hardware structure results in a precise and powerful capability and a more time- and manpower saving performance of exprimental work as well as of data evaluation.

For further homogenization of the temperature field in a salt sample during triaxial testing, a 3-zone heater control unit for the triaxial test vessel was developed. First tests were run.

After a first literature survey with regard to radiation effects on the mechanical salt rock properties, preparatory work for radiation tests in a research reactor and laboratory experiments following in 1983 were performed.

Geophysical investigation and monitoring of rock behaviour in the vicinity of underground heating experiments

Contract : 130-80-7 WASD, part 7, GSF.

Objective and Scope

Due to the local heating of rock, changes in the distribution of stresses and possibly fracture may occur. Concommittant sudden stress releases will be detected and located by means of a seismic monitoring system.

Furthermore, active seismic transmission measurements (hammer blow) shall be applied as a non-destructive tool for detecting changes of rock properties such as microcrack density.

Progress and Results

- Microseismic activity

  Microseismic events were recorded for 2 1/2 years now, so an empirical classification of types of events has become possible. Some examples are shown in figure 57. No such events have been located closer than 100 m to a present or future heating experiment.

  Formerly developed computer programmes for the location of seismic events have been supplemented by least squares versions. Further tests proved quite satisfactory.

  As a still remaining source of location errors, the determination of arrival times could be improved by applying the prediction error filter method.

- Seismic transmission measurements

  The measurements about the test site IV/Hexagon have been repeated, so that seismic velocity data exist from October 1981, May 1982

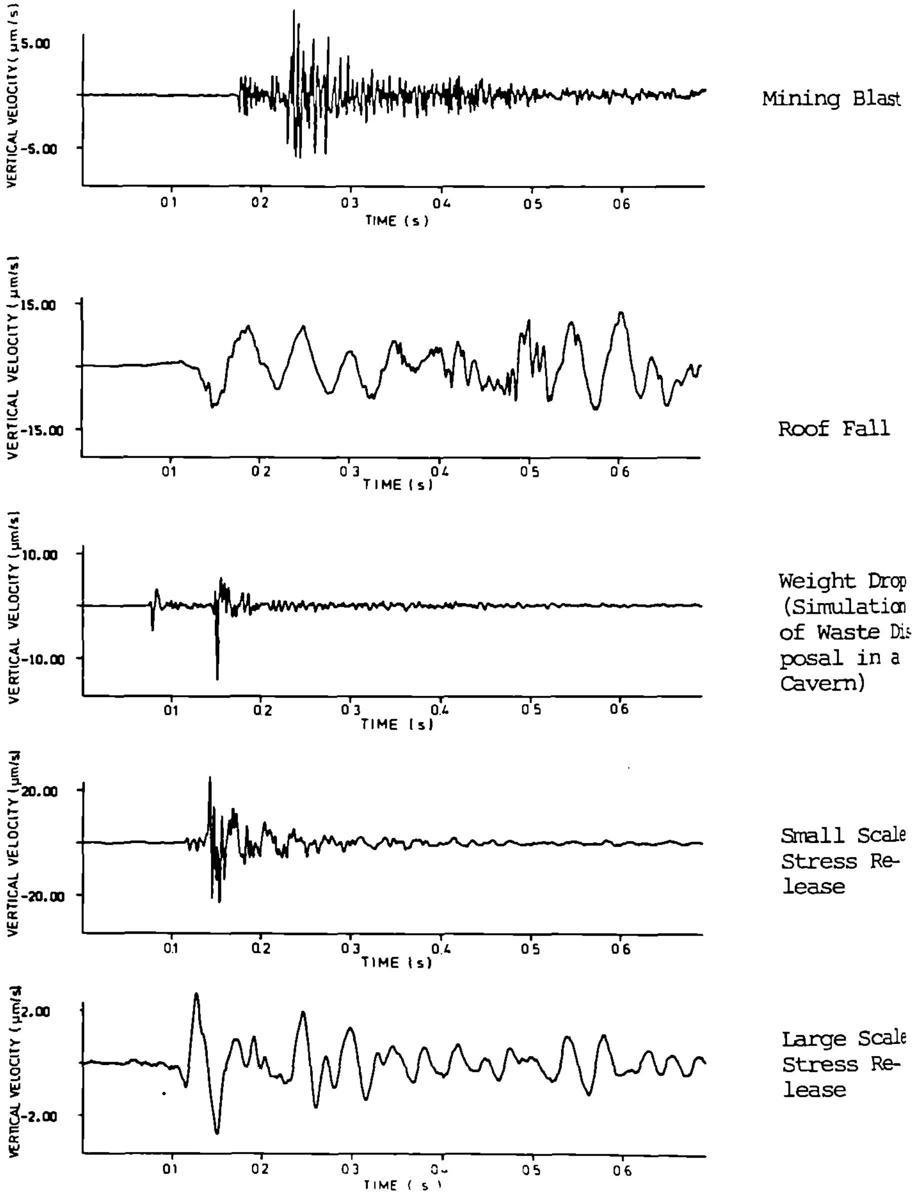


Fig. 57 : Examples of different types of seismic events

and November 1982. One measuring line shows a steep decrease of both seismic velocities between October 1981 and May 1982. Although the dimension of this effect is unlikely, it must be mentioned that the heater of experiment IV has been turned off in November 1981.

Another system of measuring lines has been installed in the vicinity of test site V. Measurements have been taken in November 1981, March 1982 and May 1982. Except close to the heater, temporal changes are not very pronounced. Measuring lines close to the wall clearly yield slower velocities.

Mineralogical investigation of thermometamorphic processes and coordination of the programme

Contract : 130-80-7 WASD, part 8, GSF.

Objective and Scope

Thermometamorphic processes in salt rocks can be expressed both in changes of the mineralogical composition and of texture. As it is known that both can influence the petromechanical behaviour of the rocks, the effects of such changes have to be investigated.

The mineralogical studies are concentrating, by means of microscopic and X-ray methods, on phase changes in heated rock samples.

Textural changes have to consider morphology (size and shape of grains) as well as physical properties and orientation of the crystal lattice.

Progress and Results

- Performance of thermally altered rock salt samples

  In 1982 works in this field were concentrated on the first run of a laboratory furnace, which was especially developed for this aim, for the heating of core samples.

  The central unit is a stainless steel pressure container with an inner diameter of 245 mm and a height of 400 mm, layed out for a pressure of

10 bars. The diameter of the central heater borehole is 30 mm, the electrical capacity 750 W. The outer container wall is surrounded by a second heater tube (oil) for a well defined variation of the temperature gradient. Temperatures are being measured by six CrNi-thermocouples in a defined (r, φ, z)-coordinate system.

From June '82 onwards this heating device was tested in a first three months test run with a maximum temperature in the rock salt of 200° C. The heated rock salt core is now being cut and prepared for microscopical investigation.

- Physical investigation of mechanical properties of rock salt and rock salt textures

Basic investigations of the mechanical properties of polycrystalline salt have been carried out in order to study the brittle-to-ductile transition and the textural development. It could be shown that the ductility is correlated with the change of the slip mode on {110} planes from planar to wavy. Waviness is generated by cross slip of dissociated screw dislocations and leads to the dispersion of dislocation pile-ups, thus preventing crack nucleation. Application of cross slip theory allows for a quantitative estimate of the brittle-to-ductile transition temperature.

Extrusion of salt leads to a (100) (111) double fibre texture. In natural rock salt the (100) fibre is replaced by (115) around room temperature. The temperature dependence of the pole intensities together with microstructural investigations suggest the (100) and (115) components to be primarily due to dynamic recrystallization. The (111) deformation texture agrees with model calculations based on both the {110} (110) and {100} (110) slip systems, generally observed as primary and secondary slip systems, respectively. As diapirism resembles an extrusion process, the results suggest a double fibre texture near (100) and (111) in salt domes in the direction of flow, the (100) component being dominant.

In-situ investigation in the Asse salt mine of the stability of borehole casings and development and test of a standard convergence probe

Contract : 266-80-7 WASD, part 1, KfK, Karlsruhe.

Objective and Scope

This work aims at determining the pressure load on a borehole casing by heat induced convergence. To permit in-situ measurement of borehole convergence a standard probe was developped and tested.

The final stage of this contract is concerned with the evaluation of the measurements and their modelling.

Progress and Results

The heater experiments were performed in Asse at 775 m depth, using a mobile convergence measuring probe ("standard probe"), developed by INE/KfK.

The applied heater powers of 1.2 - 1.4 kW produced maximum salt temperatures of about 180° C at the borehole wall; the test periods were about three months each.

For the computational investigation of the thermomechanical effects occurring in these experiments an extended version of the commercial finite-element program ADINA was used.

The complex behaviour of the rock salt was described with the aid of a thermoelastic-plastic material model with secondary creep, which was adapted to available laboratory data.

The numerical analysis was performed using a two-dimensional model with the following boundary loading condition :

σ vertical = 16 MPa, σ horizontal = 13 MPa.

The overall results of the finite-element calculations agree satisfactorily with the measured results so that a favourable valuation of the computer models and material laws used can be derived.

Figure 58 shows the result of borehole closure obtained in the heater test 2 (1.3 kW). The influence of the stress boundary conditions and of the horizontal stress anisotropy in the rock at the place of experiments were analysed by additional calculations. The first effect is demonstrated in fig. 59.

Assuming a horizontal stress, an anisotropy of 20 % produced a negligible excentricity of the borehole closure in the heating phase of the experiment (fig. 60).

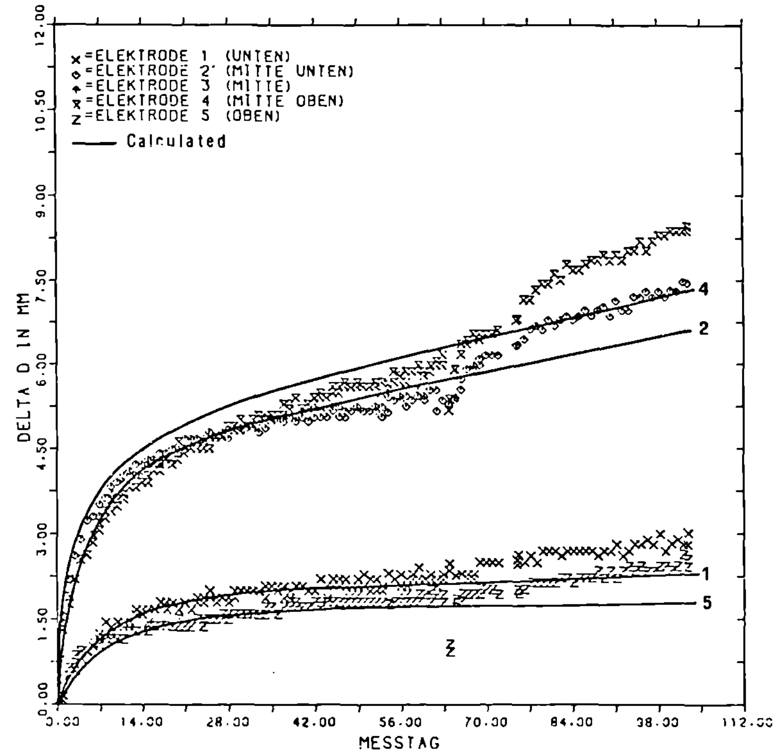


Fig. 58 : Comparison of measured and computed borehole closure for experiment II

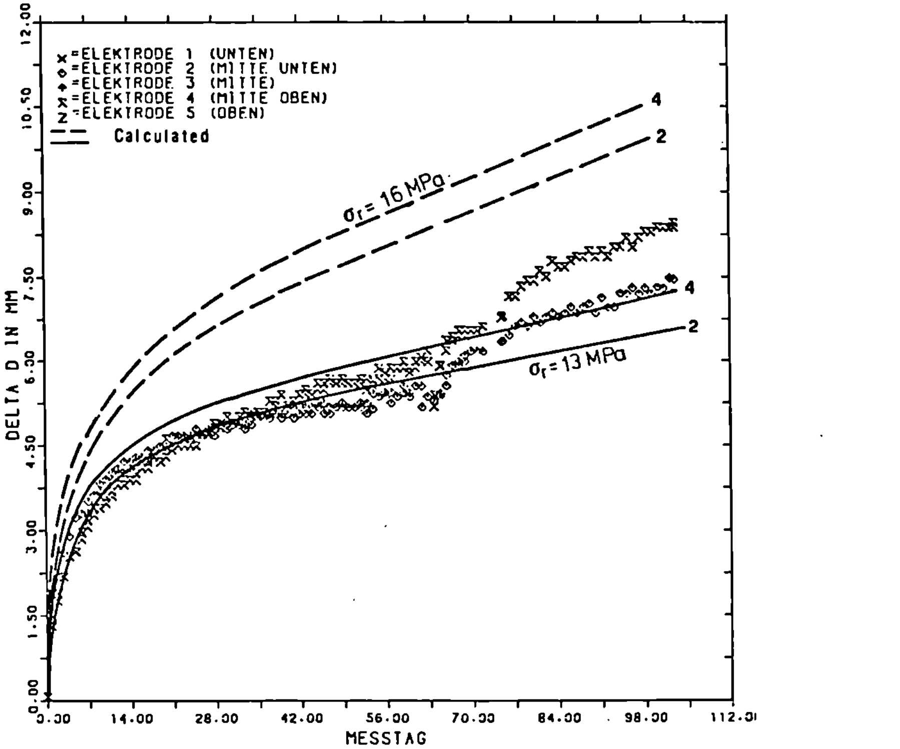


Fig. 59 : Effect of different boundary conditions on borehole closure (experiment II)

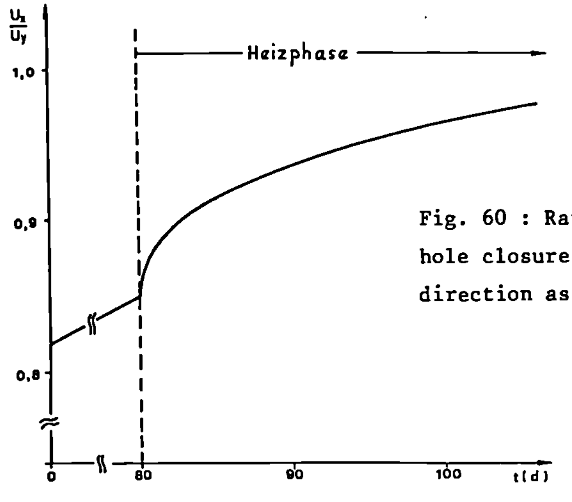


Fig. 60 : Ratio between borehole closure in X- and Y-direction as a function of time

Measurement of convergence and pressure in the dry-drilled borehole in the Asse salt mine

Contract : 142-80-7 WASN, part 1, ECN, Petten.

Scope and Objective

Determination of convergence phenomena under isothermal and heated conditions in salt rock.

These convergences are measured in a 300 m deep, dry-drilled borehole, from the floor of level - 775 m in the Asse-II salt mine. The initial diameter of the borehole was about 310 mm.

Progress and Results

- Isothermal convergence measurements in the dry-drilled 300 m borehole

  In order to investigate the change in diameter in the time over the whole length of the hole, an auxiliary probe has been constructed.

  The results of the measurements are given in fig. 61 and 62. These results should be handled with care as there is a discrepancy at 292 m with the static measurements performed earlier, which are far more accurate. The results of the first 100 m are influenced by the small bulges of salt growing on the wall surface and probably also due to the adjacent room and galleries.

- Convergence and pressure measurements in heated areas in the dry-drilled 300 m deep borehole

  After assembling and testing of the probe at ECN the equipment was transported to the ASSE-mine. There the system was assembled again and after a final check of the instrumentation the probe was lowered in the hole and got stuck at about a depth of 260 m.

  The diameter of the probe had to be fixed at an early stage of the design based on a certain assumed date of lowering the probe in the hole. And as the lowering of the probe was done later than planned, it could not reach the desired depth of 292 m anymore. The experiment was started mid 1982 and was terminated two months later due

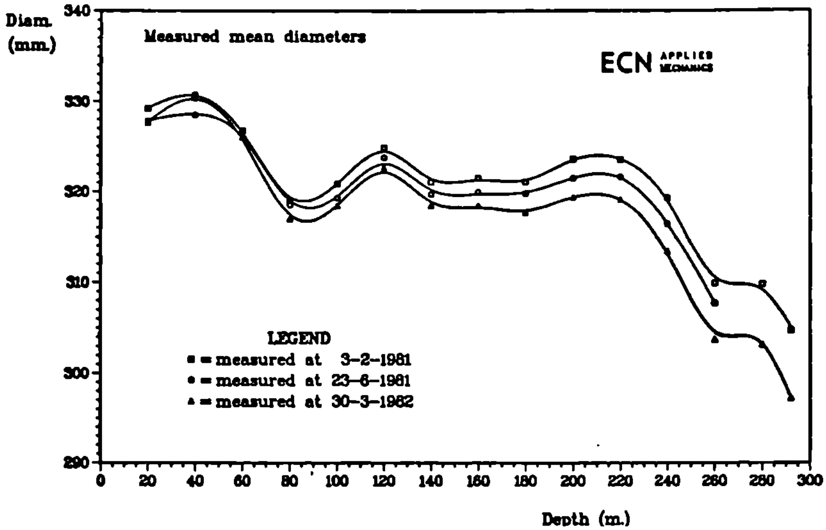


Fig. 61 : Borehole diameter as function of depth

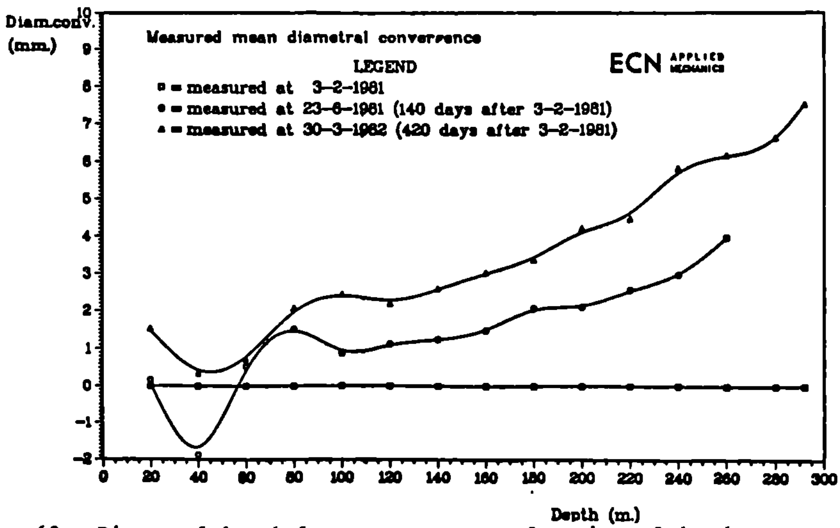


Fig. 62 : Diametral borehole convergence as function of depth

to a fatal breakdown in the data transport system. The aim, however, to establish the maximum pressure on the canister at elevated temperature was reached. The maximum pressure measured on the probe was about 350 bars at 175° C max. salt temperature, this value corresponds with previous executed analytical simulation.

In fig. 63 the temperature behaviour of the probe as function of time is given for the first 10 days. The first part of the curve shows the temperature rise due to bad conductivity between probe and salt. After closing the gap between probe and salt, the temperature drops and rises slowly again. The effect of a short power breakdown after 4 days is also visible.

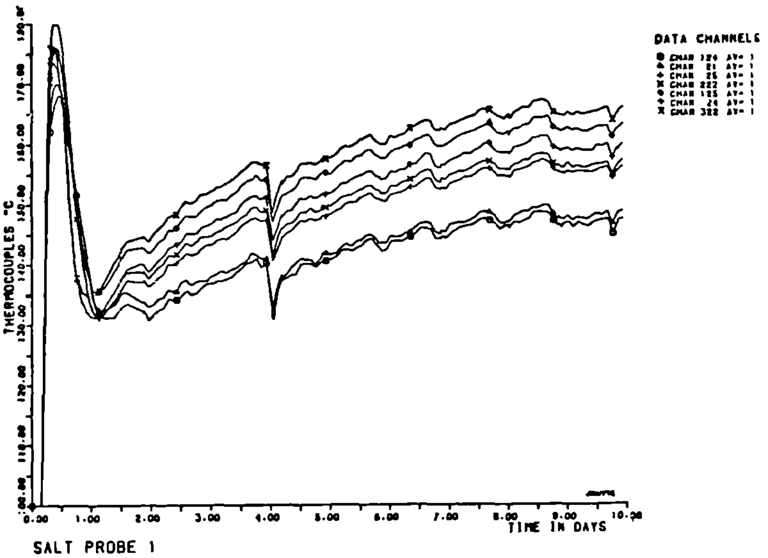


Fig. 63 : Temperatures recorded on the probe after its heating

Laboratory and in-situ measurements of cataclastic effects in rock salt

Contract : 142-80-7 WASNL, part 2, ECN, Petten.

Objective and Scope

The aim of the work is the detection of structural changes in rock salt, surrounding a vertical deep borehole with a diameter of 300 mm provided with a heater, by the measurement of the acoustic travel times in the rock salt within the direct surroundings of the heated part of the borehole.

Progress and Results

- Preparation of in-situ experiments

  "Acoustic measuring tubes" will be inserted into two parallel horizontal measuring boreholes with 66 mm diameter. The two measuring boreholes with a length of 20 m to 25 m will be drilled in parallel, horizontally about 1.3 m apart, towards the heated zone of the vertical 300 mm Ø borehole. They will penetrate the heated zone, passing the vertical borehole at a short distance.

- Preparatory activities

  Construction of the prototype of two rubber acoustic measuring tubes with a length of about 2100 mm and a diameter of 65 mm, each containing seven seismic elements and the accompanying electronic devices. This has been carried out and tested in the laboratory making use of a concrete model, scale 1:1.

  The testing of the measuring tubes and the electronics underground in the ASSE rock salt mine in Germany. These tests have been carried out successfully in two separate phases

  First phase :

  Using four horizontal parallel 66 mm Ø boreholes at different distances from one another, depth 2100 mm each. The aim was to check the construction of the tubes and the seismic and electronic devices as well as the suitability of the transmitter-receiver design at underground conditions. The results were positive.

Second phase

The simulation of the future measuring tubes into two parallel horizontal 66 mm ∅ boreholes of 4200 m length; the tubes being placed in four different positions. The boreholes were drilled in the wall of a 6 m wide part of a gallery at 850 m depth. The results were completely satisfactory. With a borehole periscope (endoscope) only slight structural changes along the walls of the 66 mm ∅ boreholes were observed. For sure no visible fractures or cracks of the type that would certainly occur in other types of rock at this depth of 850 m were present in this rock salt. The visible slight structural change consisted of differences in crystal size. The crystals in the farther part of the borehole seemed larger than those nearer to the gallery. The obtained seismic data showed also only slight differences : the acoustic wave velocity at a distance of three to four meters from the gallery wall was not more than about 6 % higher than the velocity near the gallery wall. This may lead to the conclusion that under natural circumstances relatively slight structural differences in rock salt can be detected by means of acoustic velocity measurements.

As a result of the latter test the design of the rubber measuring tube has been adapted to long measuring holes.

- Laboratory experiments

In order to get a better insight into the acoustic behaviour of rock salt,tests have been carried out with rock salt blocks from the ASSE-II mine. These blocks of about 120 x 120 x 120 mm size were loaded compressively in the 3 x 3.5 MN triaxial compressive machine.

At triaxially different loadings it appeared that the acoustic velocity will decrease considerably (15 % to 20 % has been measured) in the direction perpendicular to the axial microcataclasis; this cataclasis was after unloading clearly visible. In the direction parallel to the axial cataclasis, however, the velocity decreased only several percents.

At triaxial hydraulic type loadings it appeared that the acoustic velocity at pressures equivalent to the range of about 300 m depth to 1250 m depth will vary only about 1.5 %.

Thereby it has to be taken into consideration that the accuracy at this short a distance of 120 mm will be not more than about 1 % to 1.5 %. The velocities varied between 4560 m/s and 4620 m/s.

The acoustic velocities were measured in a 190 mm Ø and 300 mm long core of rock salt from the ASSE-II mine at a relatively low pressure in the uniaxial compressive machine. A maximum velocity of 4480 m/s was recorded.

In order to carry out experiments with larger sized blocks of about 300 x 300 x 300 mm in the 3 x 3.5 MN triaxial compressive machine a number of such blocks were cut from crude blocks rock salt from the ASSE-II mine in the workshop of ECN at Petten.

2.2.3. (first part) ENGINEERED BARRIERS : WASTE CANISTER AND STRUCTURAL MATERIALS

The objective of this project is to identify suitable container materials with sufficient resistance to general and localised corrosion to isolate high level nuclear waste from the disposal environment for 500 - 1000 yrs. For producing high endurance waste containers, two approaches are applied. Firstly, they could be fabricated from a metal possessing a high resistance to general and localised corrosion so that rather thin overpacks can be used (e.g. Ni and Ti-based alloys). The alternative approach is to use a metal of comparatively low corrosion resistance, but in a much greater thickness to make allowance for corrosion losses (e.g. cast and forged carbon steels).

The corrosion behaviour of both kinds of materials are being examined under various conditions in the three host rocks considered, both at laboratory scale and "in situ". A co-ordinated testing programme on samples for the three reference materials respectively Hastelloy C4, Ti- 0,2 % Pd and Mild Steel, originating from one melt, will start in 1983. Participating laboratories are SCK/CEN, KfK, CEA, CNRS, UKAEA and JRC-Ispra.

Future work will also include study on design of HLW containers and development of mathematical models to predict the long term behaviour of waste containers under disposal conditions.

With regard to repository structures SCK/CEN is examining different galvanization treatments and anti-corrosion coating systems, to be used for the lining material (e.g. ductile iron) of the underground experimental laboratory in the clay formation.

Reported contracts :

Corrosion studies on candidate container and gallery lining materials in a clay environment

Contract : 144-80-7 WASB, part 2, SCK/CEN, Mol.

Objectives and Scope

The corrosion behaviour of candidate container materials is being evaluated under various conditions representative for a clay formation. Furthermore different galvanisation treatments and anti-corrosion coating systems are examined for the protection of lining materials in underground galleries.

Progress and Results

The corrosion behaviour of candidate container materials are evaluated with samples in direct contact with the Boom clay, in humid clay atmospheres, in interstitial clay water and Antwerpian groundwater. Tests are carried out both in the laboratory at Mol and "in-situ" at Terhaegen, with a large number of candidate materials (stainless steel alloys, Ni-based alloys, Titanium, etc.) in the as-received and heat treated condition.

A large number of measured data is now available, obtained under different test conditions and after various exposure times. Although a synthetic analysis of these data is still lacking, it can generally be concluded that most of the materials show a satisfactory behaviour.

The tests with stressed specimens (bend beams, U bends, small size containers) to examine the susceptibility to stress corrosion have been continued and exposure times of 28.000 hours have been reached. From the tested materials (AISI 304, 304L, 316, UHB 904L, 1803 MoT, Inconel 625, Hastelloy C and commercial pure titanium) crack initiation appeared only with AISI 304 and AISI 316 samples.

The "in situ" corrosion tests carried out in an open system, in inert furnaces placed in boreholes in a clay quarry at Terhaegen and the characterization of the environment at three temperatures (13° C, 50° C, 150° C) are continuing. Post-corrosion analysis of candidate canister materials after exposure of 9 months at 13° C and 50° C revealed the fact that corrosion starts underneath Cl^- and S rich deposition and corrosion products. A limited number of candidate canister materials suffers at 50° C from a kind of bulging attack.

Besides the corrosion testing the experimental conditions for applying a Zn coating on linings of ductile iron for the underground experimental room have been determined.

The best galvanization treatment has been achieved following a procedure based on : degreasing in trichloretyhlene, rinsing, blasting with a surface finish of SA3, flushing during 5 min. in an aqueous solution of 200 g $ZnCl_2$ and 200 g NH_4Cl and a galvanization treatment during 5 to 10 min. at 460° C. This galvanization treatment results in a coating thickness between 100 and 150.10^{-6} m and a good adherance.

The galvanization treatment results in a change of rugosity of the surface and, independent of the rugosity of the surface to galvanization results, a galvanization on a surface with a rugosity of $3.6\ 10^{-6}$ m. The mechanical properties of ductile iron (grade 60) are practically not influenced by the galvanization treatment.

An additional protection layer has been applied using two painting layers composed of a primer SAPTOPOX layer (based on a mixture of epoxy and coaltar) and a finish layer of SAPTOPOX SVL (a coaltar epoxy paint). The 200.10^{-6} m painting layer has been qualified by thickness, porosity and adhesion measurements using ASTM norms.

The corrosion phenomena of ductile iron (grade 60), protected with different anti-corrosion coatings tested in direct contact with clay at 13° C, have been elucidated. All corrosion phenomena are governed by the dominating effect of sulphur.

A galvanization treatment or alloying ductile iron grade 60 either with 6 % Si or 19.5 % Ni reduces considerably the metal loss, either due to anodic protection of the underlying bulk ductile iron or the formation of adherant protective corrosion layers. No pronounced difference of the weight gain as a function of the substrate material (grade, galvanization treatment) has been measured. Post corrosion analysis of ductile iron grade 60 protected with the same anti-corrosion coatings and tested up to 16 months in the humid clay atmosphere at 49° C resulted in similar conclusions.

The anti-corrosion coating systems based on paintings and plastics give for exposure times up to 16 months more promising results than the galvanization treatment.

The construction of a dynamic high-pressure high temperature system for carrying out corrosion tests in aqueous environments at maximum temperatures of 300° C and 150 $kg.cm^{-2}$, has been finished. A prototype corrosion loop to carry out corrosion experiments in direct contact with clay in the underground experimental room with a retractable furnace has been constructed and tested (see fig. 66).

Equipment for corrosion monitoring during very long exposure times of structural material of galleries and candidate canister materials in direct contact with clay and a humid clay atmosphere has been tested prior to use in the underground experimental room. The methods are based on linear polarization measurements or measurement of the varia-

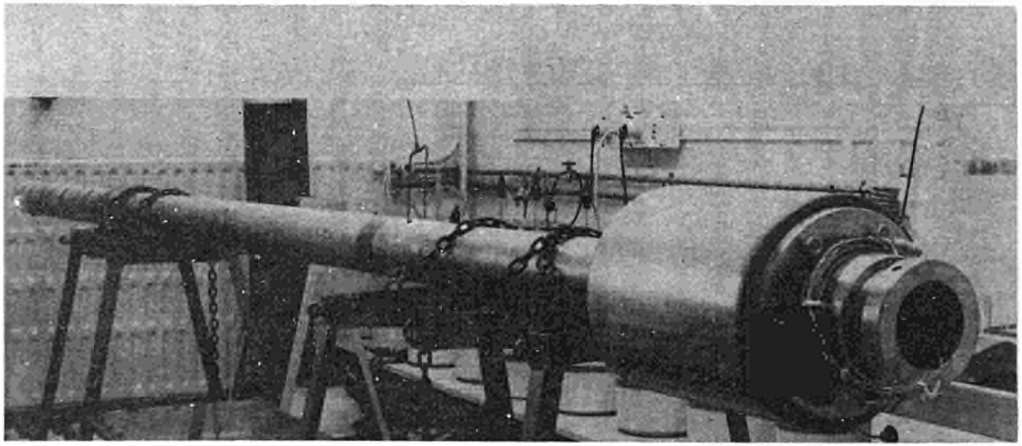


Fig. 66 : Photography of prototype loop system for "in situ" testing of candidate canister materials in direct contact with clay

tion of the electrical resistivity of wires, tubes or plate material caused by corrosion attack.

A device for redox potential measurements in direct contact with clay is in operation in the open clay pit at Terhaegen. The redox potential decreases with increasing distance to the oxidized clay surface and exposure time. The device is being adapted for use in the underground experimental room.

For the assessment of the influence of gamma-radiation a test facility has been set up, using a cobalt source, in the RITA loop at the BR-2 reactor. The first results are expected for september 1983.

Corrosion studies on packaging materials for HLW in a saliferous environment

Contract : 250-80-7 WASD, KfK, Karlsruhe.

Objective and Scope

To identify materials suitable for the manufacture of HLW containers serving as a barrier in a repository installed in a salt formation.

Progress and Results

Detailed corrosion studies were performed during the period of reporting on some selected metallic materials. The materials, subjected to immersion tests (aging experiments) were Ti 99.8-Pd, Hastelloy C4 and mild steel as well as the casting materials spheroidal graphite cast iron (GGG 40.3), Ni-Resist D2 (GGG-NiCr 20.2) and Ni-Resist D4 (GGG-NiSiCr 30.5.5.). To record the influence of manufacturing and process parameters on the corrosion behaviour of the materials welded specimens (Ti-Pd, Hastelloy C4, mild steel) and annealed specimens (Hastelloy C4) were investigated in addition to specimens (sheet metals) in the as-delivered condition. The materials were tested under defined hypothetical accident conditions in the repository.

The corrosion medium used was quinary salt brine (Q-brine) with the following composition (wt.% at 55° C) : 26.8 % $MgCl_2$; 4.7 % KCl; 1.4 % $MgSO_4$; 1.4 % NaCl and 65.7 % H_2O.

The major results obtained after the last sampling (maximum test duration) with and without gamma irradiation of the corrosion medium have been compilet in tables 46 and 47. The completed studies allow the following statements to be made :

Without Gamma irradiation

- The materials Ti-Pd, Hastelloy C4, Ni-Resist D2 and Ni-Resist D4 showed a high corrosion resistance at the end of the test duration choosen in the previous tests (146 to 280 days depending on the material). All the materials were subjected to uniform corrosion with only a minor corrosion rate. The lowest corrosion rates were exhibited by Ti-Pd, namely 0.3 μm/a and by Hastelloy C4, namely 0.05 μm/a - 1.2 μm/a (depending on the temperature and the material condition). The corresponding corrosion rates for both Ni-Resists at the test temperature of 90° C were approximately 2 μm/a which means that they were also low. All the materials indicated above have so far been free from local corrosion attacks.
- Much higher than in the other materials investigated were the corrosion rates of spheroidal graphite cast iron, namely 40 μm/a at 90° C, and of mild steel, namely 55 μm/a at 90° C and 230 μm/a at 170° C. respectively. The corrosion rate of spheroidal graphite cast iron was irregular, but no local corrosion attacks have so far occurred in this material. In case of mild steel minor attacks by pitting corrosion (maximum depth of pit approximately 50 μm) have been observed at 90° C and strongly uneven corrosion at 170° C. Since mild steel, if applied, must be designed anyway as a thick-walled container on account of its high corrosion rate, the minor local corrosion attacks found in this materials are acceptable.

With Gamma irradiation (cobalt-60 source, dose rate 10^5 rad. hr^{-1})

- Except for Ti-Pd (0.2 μm/a), the corrosion rates of all materials examined increased considerably under irradiation as compared with the corrosion rates in the absence of irradiation.

Material	Condition	Temperature °C	Maximum Test Duration (d)	Corrosion Rate (µm/a)	Pitting Corrosion	Crevice Corrosion	Stress Corrosion Cracking
Ti 99.8-Pd	A	90	280	0.31	-	-	-2)
	A	170	212	0.33	-	-	-2)
Hastelloy C4	A	90	280	0.05	-	-	-2)
	A	170	212	0.15	-	-	-2)
	W	170	212	1.20	-	-	0
Mild steel	A	90	146	55.0	x1)	-	-
	A	170	146	230.0	-	-	-
Spheroidal+) Cast Iron	A	90	247	40.0	-	-	0
Ni-Resist D2+)	A	90	165	1.9	-	-	0
Ni-Resist D4+)	A	90	165	2.0	-	-	0

A = as delivered condition; W = annealed specimens;
- = no corrosion attack; x1) = minor corrosion attack (maximum depth of pit about 50 µm);
2) = test period 113 days; 0 = no study performed;
+) = tested without casting skin.

Table 46 : Results of corrosion in Q-brine, without Gamma-irradiation, after the latest sampling

Material	Condition	Test Duration (d)	Corrosion Rate (µm/a)	Pitting Corrosion	Crecive Corrosion
Ti 99.8-Pd	A	280	0.2	-	-
Hastelloy C4	A	280	3.8	x	x
Mild Steel	A	71	215.0	x	-
Spheroidal1) Cast Iron	A	78	260.0	x	-
Ni-Resist D21)	A	160	156.0	x	-
Ni-Resist D41)	A	160	78.5	x	-

A = as delivered condition, 1) = tested without casting skin;
x = corrosion attack; - = no corrosion attack.

Table 47 : Results of corrosion on plane specimens in Q-brine at 90° C, under Gamma-irradiation (10^5 rad/h), after the latest sampling

- At the end of a testing period of 280 days only Ti-Pd, among all materials examined, has been free from pitting and crevice corrosion, even under irradiation. In all the other materials pitting corrosion was considerable when exposed to irradiation.

It can be concluded from the previous results that it seems possible to design HLW containers as a barrier in the repository, if one chooses material pairs containing Ti-Pd or Hastelloy C4. Final statements cannot be made before the long-term experiments are completed. It is necessary above all to study the influence of the impurities, present in the salt brines, on the long-term corrosion behaviour of the materials and to determine the corrosion mechanism. This type of investigations, involving immersion tests and electro-chemical methods of measurement, are under way.

As a supplement to corrosion tests in the laboratory, a detailed experimental program was worked out for testing the corrosion behaviour of selected materials under in situ conditions of the Asse salt mine.

Corrosion studies on candidate materials for waste containment in crystalline rock

Contract : 248-81-7 WASUK, UKAEA, Harwell.

Scope and Objectives

Under this contract the corrosion behaviour of candidate containment materials in a granite environment is evaluated. Most effort has been devoted to the corrosion allowance materials like cast and forged carbon steels.

Progress and Results

- Laboratory test programme

Discussions with fabrication specialists indicated that either casting or forging techniques could be used for producing thick steel overpacks. Cast steel was favoured to cast iron because of its better weldability. Accordingly the programme has concentrated on standard cast (ie BS 3100 Grade A1 1976) and forged (ie BS 4360 Grade 42A) steels and on a low carbon forged steel (ie 0.045 % C, 0.06 % Si, 0.15 % Mn).

. General corrosion and pitting

One important precept of the corrosion allowance approach to waste containment is that the dominant factor controlling the rate of general dissolution is the rate of oxygen transport. Thermodynamycally, however, carbon steels may also corrode in the absence of oxygen. Consequently, it is important to determine the rate of dissolution under anaerobic conditions. This argument applies equally to geologic and marine disposal. In the last case the investigation was undertaken in seawater. Current results indicate that the rate of corrosion declines with time (figure 67). However, even the rate determined after 500 h is only equivalent to a general metal loss of - 20 mm in 1000 years. Parallel experiments with a gamma-radiation flux of 1.5×10^{5} R h^{-1} have shown that this increases the dissolution rate by roughly a factor of three (figure 67), but once again the rate declines with time. Localised attack such a pitting or crevice corrosion has not been observed in any of these tests.

An extensive programme with coupon specimens buried in powdered granite is now being initiated to investigate corrosion behaviour under conditions involving restricted oxygen transport. Results from a preliminary test, which lasted 9260 h and involved a 12 cm deep granite bed saturated with 10 ppm chloride solution and heated to 100° C, indicate a general dissolution rate equivalent to a metal loss of 70 mm in 1000 years. This is probably a pessimistic result because the rate of transport of oxygen through the shallow granite bed would be higher than that likely to be achieved in a waste repository. The specimens were covered by a black magnetite surface film, and contained areas of localised attack either in the form of pits or broader irregular patches. The maximum depth of local penetration was approximately 0.8 mm. This is comparable with predictions based on the empirical pit growth relationship established by Romanoff from long term "field" experiments in soils, i.e.

$$P = 0.746\ T^{0.37}$$

where P is pit depth in mm and T is time in years. The Romanoff rate equation predicts that the maximum pit depth to develop in wrought steel over 1000 years should be ∿ 9.6 mm.

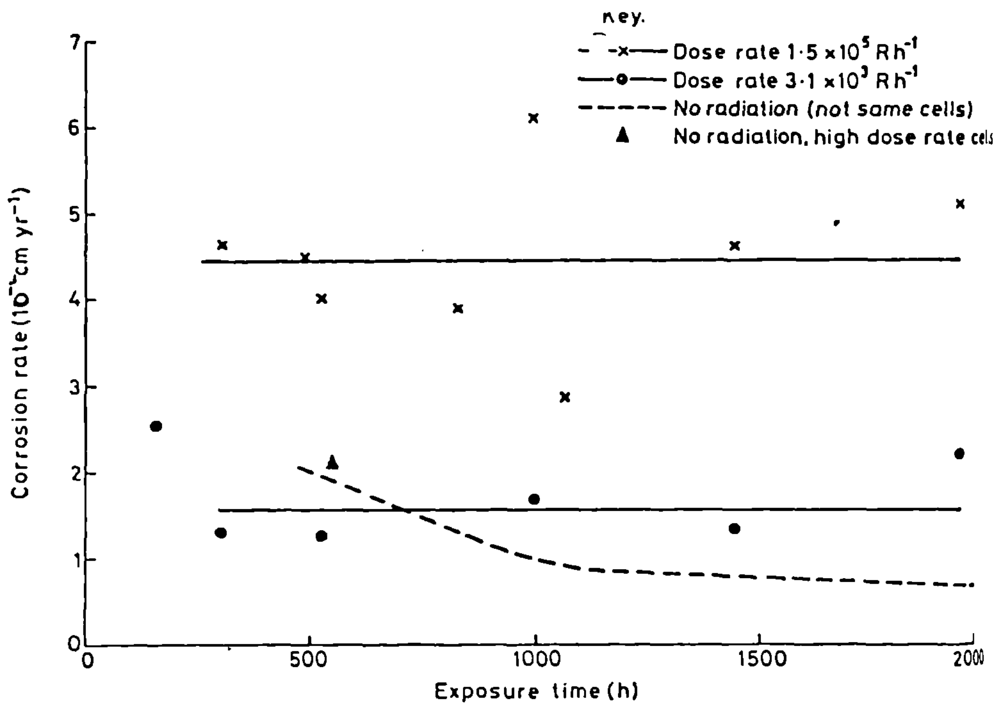


Fig. 67 : Corrosion rate vs exposure time. Influence of radiolysis. Forged steel specimens immersed in de-aerated substitute sea water at 90° C under an argon blanket

. Environmental cracking

Environmental cracking (i.e. stress corrosion and hydrogen embrittlement) is one possible degradation process to which the corrosion allowance concept does not fully apply. Reported cracking rates vary between 10^{-7} and 10^{-4} mm sec^{-1}; therefore, even at the slowest rate an overpack thickness of > 3 m woulb be needed to prevent penetration in 1000 years. Consequently work on this topic is aimed at assessing the possibility of avoiding the problem,either by identifying resistant steels or by stress relieving the overpacks prior to disposal.

This work is being undertaken in $NaCO_3$ solutions, because HCO_3^- and CO_3^- ions can be major constituents of granitic groundwaters and because these solutions are known to cause stress corrosion cracking of structural steels. Current results indicate that both cast and forged carbon steels are susceptible to cracking, but only at stresses exceeding approximately 500 N mm^{-2}. This is roughly 50 % of the yield strenghts of the steels. Additional tests with water quenched specimens, simulating weld heat affected zones, have indicated a treshold stress of $\sim$200 N mm^{-3}. This indicates that sealing welds are likely to be regions of high cracking susceptibility.

Field Experiment

This experiment in the UKAEA's test site at Troon, Cornwall, has been underway for $\sim$ 25 000 h. A recent inspection indicated that none of the corrosion resistant metals, which include stainless steels, Ni-Cr alloys and titanium alloys, had suffured localised attack; their rates of general corrosion were negligible. Two additional racks containing cast and forged carbon steel coupons have now been added to the test assembly.

- Conclusion and future work

The results from the current year's work suggest that a carbon steel overpack thickness of 50-70 mm should be sufficient to make allowance for general corrosion losses over a 500-1000 year's containment period. Localised corrosion may occur under conditions involving restricted oxygen transport, and therefore further work is planned to estimate the additional metal thickness required to make allowance for this mode of attack. The risk of stress corrosion cracking is greatest in the hard metallurgical structures produced in weld heat-affected zones. The possibility of minimising this risk by using ultra-low carbon steels, which produce comparatively low hardness welds, will be investigated.

In addition to the above on-going projects, work will be initiated to investigate the possible effects of bacteria on the corrosion of carbon steels. Work will also be initiated on the development of a mathematicai model to predict the long term corrosion of carbon steels under disposal conditions.

Evaluation of corrosion behaviour of candidate materials for HLW containers in granitic environments

Contract : 252-81-7 WASF, CEA, Fontenay-aux-Roses.

Scope and Objectives

Under this contract the corrosion behaviour, in particular stress corrosion, is analysed of corrosion-resistant materials in a granitic environment.

Progress and Results

Tests performed during 1982, were done to complete data on the following commercial materials : Ni-alloys 625 and 825, Hastelloys C276 and C4. The tests were done at 80° C in a synthetic medium, simulating granitic water with higher concentration for some ions (Cl^- and H_3O^+).

Stress corrosion cracking was studied on the Nickel alloys 625 and 825 at 80° C using a slow strain rate tensile testing machine. The results show cracking susceptibility of 625 alloy for several values of pH and electrode potential (fig. 70) whereas no cracking susceptibility was identified for 825 alloy. Scanning electron micrographs have confirmed these results.

In order to perform electrochemical measurements and straining tests at 170° C, a special autoclave was designed and built. It is made of Ti-Pd alloy with an internal PTFE cell. Preliminary tests indicated satisfactory performances of this new device.

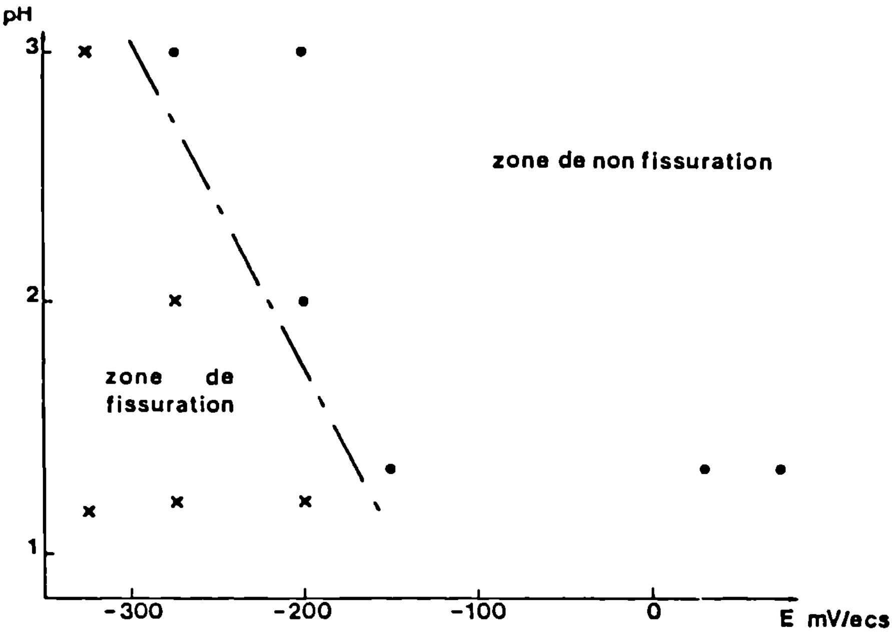


Fig. 70 : Alloy 625, corrosion susceptibility under stress as a function of stress and electrode potential in granitic water nr 1.

Crevice corrosion

The crevice corrosion resistance is about the same for both Hastelloy C4 and C276 (fig. 71). Only for values of the ph below 2, Hastelloy C4 gives higher values for the peak-activity (measured in micro-amperes per square centimeter).
Thermal treatments occurring during container manufacturing (e.g. welding) may influence the corrosion behaviour. Tests carried out on Hastelloy C276 showed a significant increase in crevice corrosion susceptibility on samples heated at 835° C during 10 minutes.

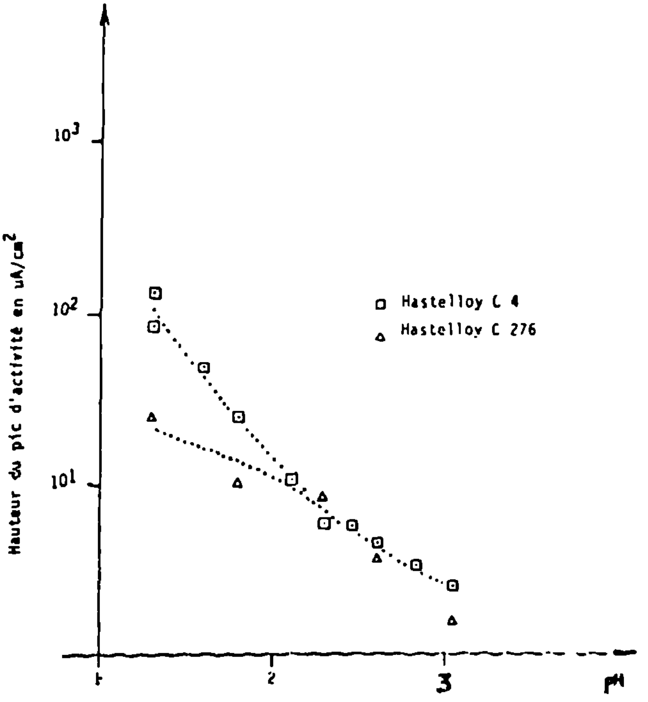


Fig. 71 : Comparison of peak-activity versus pH curves for Hastelloy C4 and C276 (sensitivity to corrosion by crevices)

Study of corrosion phenomena, study of particular surface films

Contract 249-81-7 WASF, CNRS, Vitry-sur-Seine.

Scope and Objective

This work consists of an investigation of surface film characteristics and of corrosion behaviour of some high performance nickel base and titanium base alloys in three synthetic geologic environments : granitic water, clay water and salt brine.

Progress and Results

- Nickel base alloys*

  . Surface film analysis

  Relative concentration depth profiles of elements in surface films were determined using glow discharge spectrometry. For films formed on HC4 alloy after 70 hr immersion in aerated 3 % NaCl solution at 90° C, the film thickness is larger and the enrichment of elements like O, H is more important near the external surface, than for films created in a deaerated solution. In deaerated conditions, the concentrations of the major elements like Cr, Ni, Mo in the film increase sharply from the external surface to the alloy matrix.

  In the film formed in deaerated salt brine at 90° C, the corresponding depth profiles are similar. Furthermore, an enrichment of Mg appears, which is likely due to the presence of this element in the brine.

  The films created in granitic water at 90°C are about twice as thick than in salt brine. The concentrations of Cr, Ni, Mo increase smoothly, while those of O and H decrease from the external surface to the alloy matrix. Mg and Si are also present.

* The alloy designations HC4, 625 and UB6 correspond respectively to Hastelloy C4, Inconel 625 and Uranus B6.

The surface films on HC4 and 625 alloys were stripped off by selective dissolution of the alloy matrix. Transmission electron diffraction would show that they have a cristalline structure. However under the electron beam, the films have been distorted, being probably too thin.

. Electrochemical study

Voltametric curves were recorded for alloys in the above environments. In deaerated brine, when the temperature increases from 20° C to 90° C, the corrosion potential E_{cor} becomes nobler by about 100 to 300 mV, depending on the alloy. The corrosion current density i_{cor} increases from ≃ 10 to 200 A/cm^2. At 20° C the passive range is very broad, ≃ 500 mV, whereas at 90° C it becomes nearly non-existent. After an anodic voltametric direct and reverse sweep (1000 mV/hr, i max = 100 μA) 625 and UB6 alloys are pitted at 20° C. At 90° C all the alloys including HC4 are pitted. Hysteresis found on the reverse voltametric curves is indicative of the alloy susceptibility to pitting corrosion. In oxidized clay water at 90° C, E_{cor} potential of the alloys is more positive in aerated solution (- 560 mV/SCE) than in deaerated solution (- 870 mV/SCE). The broad passive potential ranges and the weak values of critical current density i_{crit} show the high passivation aptitude of the alloys in this environment. Because of the inhibiting effect of sulfate and carbonate in solution, the pitting potential is nearly unchanged when 0,1 M/l of chloride is added. In reducing clay water, an addition of small amount of fluoride shifts the potential E_{cor} to the noble values. It increases the corrosion current density i_{cor}, the critical current i_{crit} and the passivation current i_p.

A similar effect is found for H_2SO_3 addition which also give rise to an intensity maximum on the anodic curve at about - 200 mV/SCE. For granitic water, a carbonate addition provokes a contrary effect and improves the corrosion resistance of the alloys.

In aqueous solution at 90° C, 304 steel is susceptible to pitting if the activity of Cl^- ions (Cl^-) is higher than a value which depends on the activity of the inhibiting ions (CO_3^{--}), according to the relation :

$$\log(Cl^-) = 1.7 + 1.7 \log(CO_3^{--})$$

Complex impedance measurements were carried out. High frequency impedances provide the following solution resistance, in ohm.cm^2 $\pm$ 10 % :

T (°C)	Granitic w.	Ox. clay w.	Salt brine	NaCl 3 %
20	300	150	1.5	3
90	160	70	0.8	3

These data are used in the correction of the voltametric curves. Nyquist diagrammes were obtained, which pointed out the importance of the diffusion process or the charge transfer process, depending on the test conditions.

- Titanium alloys

. Surface film analysis

Crystal structure of the passive film on Ti and Ti-0 2 % Pd alloy was determined using electron transmission diffraction. The film was stripped off by selective dissolution of the metal matrix in the mixture ethanol-10 % bromine. Electron diffraction patterns show that films formed in clay water at 90° C are amorphous.

. Electrochemical study

The electrochemical data point out the excellent passivation aptitude of Ti and Ti-Pd alloy in clay water at 20° C and 90° C, where both materials passivate spontaneously. The passive ranges are very broad (2-3 V). The effet of alloying Pd appears : (i) on the cathodic overpotential, markedly higher in the case of Ti-Pd alloy than in Ti, (ii) on the transpassive potential, which is less dependent on the temperature in the case of Ti-Pd alloy. The deaeration of the environment shifts also the corrosion potential of both materials towards the active direction. For both materials, it also appears that the stability of the passive film increases with chloride concentration. Thus, whilst the increase in Cl^- concentration would raise the probability of pitting, it also increases the passive potential domain and decreases the passive current.

2.2.3. (second part) ENGINEERING BARRIERS : BACKFILLING AND SEALING

The aim of the works reported below is to select and test a limited number of materials suitable for backfilling and sealing of radioactive waste repositories and related perforations such as exploratory boreholes drilled from ground surface.

Particular attention is paid to the engineering aspects of the backfilling operations, together with a preliminary effort regarding the behaviour of the materials vis-à-vis radionuclide transfer.

Reported contracts

Review study on backfilling and sealing of radioactive waste repositories

Contract : 204-81-7 WASUK, Mott, Hay & Anderson, Croydon.

Scope and Objectives

The principal objectives of this research programme are :

- To identify the operational and placement properties required for backfilling and sealing materials and identify any analytical methods required for design.

- To identify the engineering procedures required for backfilling placement holes/sites, shafts, galleries and tunnels in high and medium level waste repositories in crystalline, argillaceous (strong and weak) and saliferous host grounds.
- To identify the research and/or development requirements, considering if appropriate, the form a demonstration facility might take.

Progress and Results

The research was undertaken in two phases. Phase I comprised primarily fact finding, establishing the roles of the backfill and sealing materials as a geochemical barrier/stabiliser, to control corrosion, to inhibit groundwater flow, to provide ground support, etc. The desirable properties of the backfill in the operational mode and from the installation view point were investigated simultaneously, an inventory of potentially suitable materials was drawn up and enquiries were made as to availability, production rates, costs, etc.

In Phase II the potential backfilling and sealing materials were classified according to their ability to meet operational and installation requirements. The study also examined availability, existing knowledge about the materials and costs. This information was then critically reviewed in relation to design and performance requirements in repository situations in the various potential host grounds covered by the study.

The final section of the report will present the conclusions reached from the overall study will identify those areas about which significant uncertainty exists and make proposals for ongoing research.

During 1982 the extensive inventory and review of potential backfilling and sealing materials was substantially completed. To render the data manageable it was decided to develop a standardised proforma presentation and to incorporate this into an Appendix to the report; only a summary will be given in the main text. Thus, greater attention is focussed upon those materials of greatest potential application.

The study has shown the importance of an integrated approach to construction method and programme, waste unit form and hcst ground and the type and properties of the backfill materials. Various parametric studies have shown the sensitivity to known areas of practical difficulty in effecting intimate contact between backfill, lining and/or hostrock in underground situations. Geochemical assessment has proved to be very difficult, not only because of the inherent complexity and dynamic nature of the environment that will arise in a repository situation, but also due to the unsystematic nature of much of the existing research.

In is anticipated that a final draft of the report will be completed by the end of March 1983.

Studies on backfilling and sealing materials in clay

Contract : 144-80-7 WASB, part 3, SCK/CEN, Mol.

Scope and Objective

Selection of borehole plugging and backfilling materials for a repository in plastic clay.

Progress and Results

A first part of the study was devoted to a mixture of crushed Boom clay, cement, bentonite and crushed limes, mixed in various proportions, with the objective of selecting those which present the most favorable characteristics in order to form a valuable plugging or backfilling material.

The leading properties of such mixtures were low permeability, porosity, shrinkage and settling associated with good resistance characteristics. A complementary study was done in order to test the setting and injection possibilities for such a mixture with some types of pumps existing on the market.

A minimum quantity of water should be added to the mixture so that it remains still pumpable.

A second part consisted of researches in the field of mixtures made of Boom clay and organic resins (two components polyurethane or epoxy). Several parameters have been tested as clay load, casting temperature, mechanical characteristics for each composition, etc. In this case the best mixture was made of supple epoxy resin, which presented the best permeability, shrinkage and mechanical resistance characteristics.

All the mixtures made of clay with a large proportion of organic resins remain very expensive and must be reserved for very special uses.

Studies and research relating to borehole plugging in clay

Contract : 199-81-7 WASI, ENEA, Casaccia.

Scope and Objective

The main goals of the project are the following :

- selection and evaluation of the borehole filling materials from the point of view of sealing;
- laboratory and in situ check of the sealing properties of selected materials.

Progress and Results

This contract only started in July 1982.

While the CEN in Mol is studying different plugging mixtures, on the italian side the emphasis is on development of suitable testing instrumentation and techniques. It has been decided that the important parameter is the permeability through the plugged sections of the clay formation. The present plans are to develop a remotely controlled device, capable of pressurizing the water present in the borehole under the plug, and a wireless data transmission system capable of transmitting the pressure decay value to a receiver located near the test borehole. It is planned to perform such a test in the vicinity of the underground laboratory at MOL, the receiver being located in the access shaft.

Emplacement techniques and characteristics of back-filling and sealing materials for repositories in granite

Contract : 202-81-7 WASF, CEA, Fontenay.

Scope and Objective

Critical review of existing knowledge and of the properties to be considered, and second, a limited test programme carried out on certain materials or components chosen from the first step. The experimental phase is focussing on the emplacement techniques and the geotechnical and physico-chemical properties of the material in place.

2.2.4. CHARACTERIZATION OF INTERNAL EQUILIBRIA IN GEOLOGICAL FORMATIONS

The bulk of this chapter deals with experiments performed either in the laboratory or in-situ, with a view to determine geochemical, mechanical and hydroleological properties of rock formations at ambient and/or elevated temperatures.

The three types of potentially suitable host formations are covered to a larger or smaller extent. As regards clay, attention is focused towards geochemical and geomechanical properties, the characterization of pore water chemistry, the measurement of heat transfer properties, and modifications brought about by intense heating.

Another part of the research is devoted to the potential for fault propagation (from tectonic origin) in plastic clays.

For granite, research has concerned geochemical, heat-induced interactions between rock, water and waste glass. The measurement of geomechanical properties and the determination of fracture porosity and permeability is another topic of interest. A link between these two aspects is formed by a study of silica precipitation in fractures under the effect of a thermal gradient.

Finally, specific attention is directed towards the influence of brine-salt interaction on the rheological behaviour (creep rate) of stressed salt, and its consequence on solute transport through salt.

A somewhat adjacent field of research is the programme of investigations for assessing the suitability of the disused KONRAD iron mine for deep disposal of low and intermediate level waste.

All the above information must be considered as input data for the eventual safety assessment of a given disposal site. The general framework of this assessment is given by the so-called "geoprospective" approach. An attempt is made with a view to establishing a general predictive simulation model in which "geodynamic" factors, quantified by geological evidence, can be introduced to forecast the future natural geological evolution of a potential repository site.

The following contracts are reported :

Characterization of Boomclay

Contract : 144-80-7 WASB, part 4, SCK/CEN, Mol.

Scope and Objective

The aim of the physico-chemical characterization tests was the study of the influence of air oxydation on Boomclay, the evaluation of its redox potential (Eh) and the effects of gamma-radiolysis.

The aim of the geotechnical tests was the study of two basic aspects of the geomechanical behaviour of the argilaceous material :

- the influence of freezing, heating and thermal cycling on the geomechanical properties of the clay without considering the time factor, i.e. "instantaneous" tests
- the creep behaviour of clay samples under stress, which is a time-dependant phenomenon.

Progress and Results

- Physico-chemical characterization

  The correct application of the influence of air oxidation on Boom clay has led to a general revision of the experimental methods contributing to the study of radionuclide migration. Two glove-boxes with controlled atmosphere have been equipped for sample preparations. Eh, pH combined cells have been designed to prevent air contamination during measurement or sample transfer. A working formula for an interstitial solution has been established on the basis of successive dilutions. Final adjustment of the synthetic solution formula has been performed by means of exchange tests between clay and solutions. Table 52 gives the composition of interstitial clay water under reducing conditions. The solution composition, not altered by the addition of clay, was regarded as adequate.

39.8 Na_2SO_4	44.5 $NaHCO_3$
15.0 $MgSO_4$	39.4 KCl
10.1 NaF	19.9 NaCl
74.2 Na_2CO_3	saturated with $CaCO_3$

Table 52 : Composition in mg ℓ^{-1} of interstitial clay water (clay under reducing conditions)

Thermodynamics indicates that pyrite should confer very reducing properties (- 0.3 Volt (SHE)) to the clay medium. However various experiments bring up consistent Eh values in the range - 0.07 - 0.1 V. Careful oxidation tests supported by electron micrographs have shown that the reducing capacity of FeS_2 is quickly inhibited by oxidation products and that most of the reducing capacity of Boom clay is due to sites on the clay minerals other than FeS_2. In view of the collaboration with other laboratories the dilution technique has been applied to clay of different origins (Terhagen, Gorleben) in order to define the aqueous medium appropriate to migration studies in such materials.

Gamma-radiolysis in Boom clay was shown to produce only H_2 and CO_2. Radiolytic oxygen is entirely consumed by the reducing components in clay. The ratio CO_2/H_2 increases between 0.07 and 0.16 as the gamma-dose increases from 5.10^8 to 2.10^9 rad. In the last case hydrogen production amounts to 2.9 mmole/g clay as in situ. However, sufficient cooling time and adequate repository configuration may well make gamma-radiolysis negligible. Actually the interest is being shifted towards the persistent alpha-radiolysis in the hypothesis of radionuclide dispersion in the formation.

- Geomechanical characterization

The geotechnical tests in laboratory have been carried out on clay samples coming from both outcropping zones and "in situ" during the digging of the underground experimental facilities at - 220 m under the Mol Site.

- Geomechanical test on the influence of freezing, heating and thermal cycling

  This test programme, which has started early 1980, has been finalized at the end of this year.

  Numerous results on temperature-dependant compressibility, permeability and shearing characteristics habe been gathered.

  Other data about dynamic modulus, orthotropic characteristics of the material and Poisson's coefficients are now available.

  The tests have been carried out on clay samples coming from a quarry in the outcropping zone of the Boom clay formation near Boom.

- Geotechnical tests on creep properties at low and ambiant temperature

  The tested samples were taken both in the outcropping zone and at depth under the Mol-site. These tests, done in triaxial cells, aimed to obtaining the creep curve of the clay samples at different temperatures at a constant stress, representing a percentage of the failure stress at the same temperature. The stress at failure was, for each temperature, previously determined by a triaxial test, where the shear failure was obtained at constant deformation rate.

Thermal studies and research relating to clays

Contract : 206-81-7 WASI, ENEA, Casaccia.

Scope and Objective

The main goals of this research are the following :

- to obtain the in situ thermal conductivity of the clay;
- to obtain a correlation between the variation of thermal conductivity and the increase of temperature;
- to determine the pressure increase of interstitial water in clay in the presence of a thermal gradient;

- to develop a mathematical model taking into account the variation of thermal properties and the mass transport, associated with a thermal gradient.

Progress and Results

- Laboratory experiments

  - Measurement of clay thermal conductivity

    An automated system, based on the use of Von Hertzen Maxwell needle calibrated probes, has been designed and built to perform determinations of thermal conductivity in clay samples. The software for data acquisition, based on a HP-85 digital computer, computes the specific linear power of the needle probe, displays the trend of temperature versus time and computes and prints the thermal conductivity value.

  - Measurement of clay interstitial pressure

    Two heating experiments were carried out using a clay cylindrical sample to measure the pressure of interstitial water. The clay sample has been compressed with an oedometer before heating at a pressure of 160 KPa in the first test and 320 KPa in the second one. The heater was a plane thermal source with a thermal power of 7.1×10^3 Watt/m^2. The maximum interstitial pressure values reached were 87 KPa in the first test and 168 KPa in the second one. These values are higher than those that can be obtained with a simple diffusion model, using literature values for the thermal dilatation coefficient of clay. It seems that the micropiezometers have measured the overpressures caused by the change in state of the interstitial water, because the temperature increase in the clay was over 80° C.

- In situ experiment

The in situ experiment in an open clay quarry in the area of Monterotondo, Roma, started on March, the 3rd. The electric heater was connected to an alternating-current power supply at a constant power of 250 Watts. After 1200 hours the power was increased to 500 Watts.

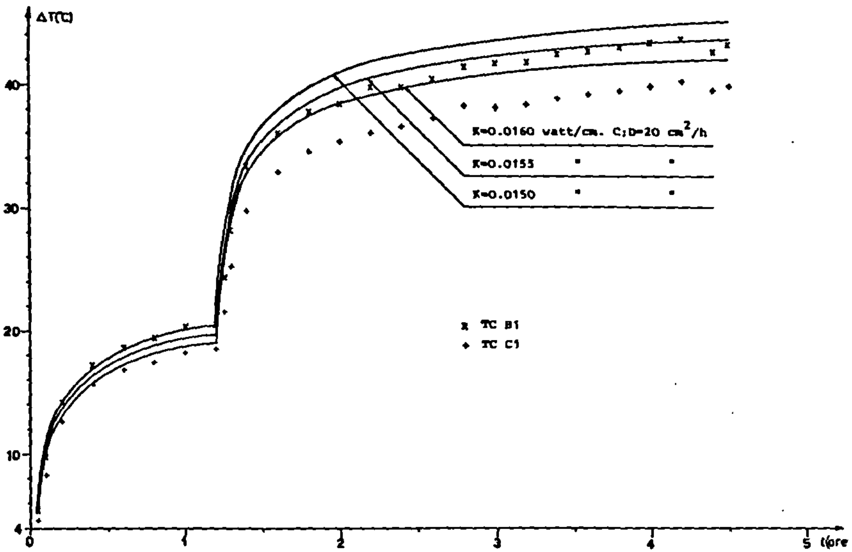


Fig. 76 : Theoretical and experimental temperature increases 50 cm fareway from the heater axis against time. Thermocouple B1 has recorded the maximum temperature increase, while thermocouple C1 has recorded the minimum one.

The instrumentation has regularly operated during the experiment. The temperatures measured in the clay have fitted well the theoretical values obtained with the MPGST code. Figure 76 shows theoretical and experimental temperature increase versus time in the hole nr 2, which was drilled at a distance of 50 cm from the heater axis.

As preliminary conclusion of this study the theoretical average value of clay thermal conductivity is 0.0160 Watt /cm.°C. A piezometer has been also installed at a depth of 8.50 m in the clay quarry to study the possibility of measuring the interstitial overpressures caused by the thermal gradient around the heater.

- Theoretical studies

The equations that describe the transport of heat in a saturated clay medium by conduction and convection have been written. These equations take into account the coupling of thermal, hydraulic and mechanical phenomena. The resulting model is strongly non linear and can best be handled by finite element numerical procedures. The ranges of numerical values for the important parameters and how they can be dependent on mechanical and thermal variables have been discussed. In addition an interpretation technique for experimental data has been described and a sensitivity analysis of the dependence of relevant parameters from experimental data has been included. The theoretical work has again pointed out the lack of experimental data on clay behaviour in particular in the field of the interstitial overpressure measurements.

Evaluation of modifications induced in clays by intrusive subvolcanic bodies

Contract : 152-80-7 WASI, ENAE, Casaccia.

Scope and Objective

This contract aims at obtaining direct information on the modifications produced in clay by a very hot subvolcanic body, intruded in it and subjected to a very slow cooling, individuating mineralizing fluxes activated by heating, evaluating thermal levels and extension and intensity of thermal halos originated in clay.

Progress and Results

23 samples have been collected by means of 12 boreholes. 124 m of continuous coring has been obtained. The selected samples from thermometamorphosed clay correspond both to the peripheral zone and central one with regard to the intrusive body. Unaltered more external clay samples were collected as a term of comparison. Granulometric, petrographic, mineralogical and chemical analysis were done both on the total sample and on the fraction smaller than 2 µm.

The proposed objectives have been obtained. They are here reported :

a) Thermal influence, including simple dehydration, did not extend beyond 6 m from the subvolcanic body in its peripheral zone. Mineralogical modifications and chemical mobilization is not more extended than 2 m. The metamorphosed clay shows important modifications in mineralogic paragenesis as well as in physical characteristics of some components.

   Neoformation of K-feldspar and Na-Ca feldspare is particularly evident. As far as occurrence of phyllosilicates is concerned only smectite and minor amounts of illite have been observed. These minerals show a better cristallinity with regard to their homologues in unaltered clay. The temperature level reached in the peripheral zone is thought to have been 400° C, against 800° C in the intrusive body.

b) Clay overlying the central part of the intrusive body shows thermal influence for a total thickness of 12-14 m. Mineralogical modifications and chemical mobilization does not exceed 4 m from subvolcanite. Temperature in the first 2 m thick layer is evaluated 400-600° C, according to a pyroxene-K feldspar-Na-Ca feldspar paragenesis. In the overlying 2 m layer pyroxene and Na-Ca feldspar disappears, while the amount of K-feldspar and smectite increases. The original temperature is thought to have reached 100-400° C. Dehydration phenomena are observable only between 4 and 14 m from the intrusive body. Dehydration strongly influence physical and geomechanical characteristics.

It most be pointed out however that exchange capacity of thermometamorphosed clay is quite similar to that shown by normal clay.

Propagation of seismo-tectonic displacements through clay deposits

Contract : 238-81-7 WASI, ENAE, Casaccia.

Scope and Objective

The main aim of this programme is to model the behaviour of a clay formation, affected by seismo-tectonic displacements and consequently its constitutive law, i.e. the mathematical equation describing the physical behaviour of the material.

Progress and Results

A literature study on the constitutive laws of argillaceous materials and on the modeling of their deformation behaviour has been carried out.

Some numerical simulations of the effects in a clay layer of a displacement in the basement have been performed. However a conventional constitutive law of the material has been used and its applicability to deep clays is doubtful. These first results can be useful for a rational planning of future work. Two particular problems presently being addressed are :

- how to model the generation and propagation of fractures in a plastic medium such as clay;
- the possibility of simulating fracture phenomena through the development of shear bands.

An obvious conclusion of the modeling work is that more experimental and observational data are needed.

Laboratory experiments addressed to the need of obtaining empirical data are designed. In the first phase the experiments are aimed at the verification of constitutive laws. For this purpose triaxial cells and oedometers will be used. The first series of experiments has been planned and work is expected to start as soon as the triaxial cell becomes available. This is a cell that has been designed especially for this work and that allows tests with both controlled stress and deformation rate. The experimental system can reach pressures representative of the expected disposal depth. The actual modelling of fractures in clay will be carried out in a second phase with data from centrifuge experiments.

Experimental studies on pore-water composition in clay formation

Contract : 151-80-7 WASI, ENEA, Casaccia.

Scope and Objective

This work aims at studying the geochemical characteristics of pore water in clay deposits, being of paramount importance for the mobility of radio-nuclides as for the corrosion processes on container and structural materials in repositories.

Progress and Results

A first part of the work is the development of an analytical methodology, at micro-scale, for the determination of dissolved constituents in pore water. In the course of 1982, application work has been initiated.

Preliminary investigations on the chemical composition of the pore water of some clay formations have been developed. Three samples showing different mineralogic and granulometric characteristics, have been selected. These samples also correspond to different paleosedimentary environments.

Pore water has been obtained employing a squeezer system that can reach a pressure of about 750 kg/sq.cm. About 70 % of pore water content has been extracted.

Checks on the possible chemical variations of pore water obtained by progressive squeezing and between different specimens, have been performed. Significative variations have not been detected in progressive squeezing, whereas the results related to the different specimens appear more scattered.

The salinity in the different clay types ranges from 4 g/l to 9 g/l.

The data related to the chemistry are compared in figure 77.

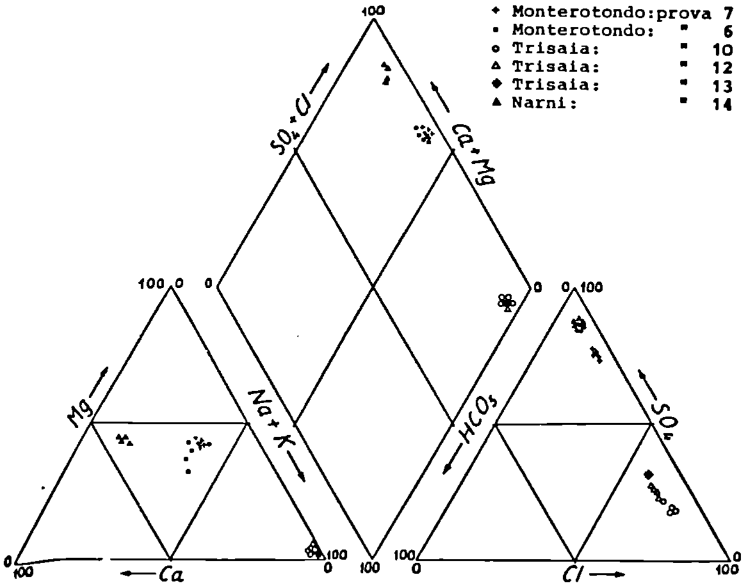


Fig. 77 : Geochemical classification of pore water

Pore water shows a calcium-magnesium-sulfate chemistry in the case of Narni clay, a chemistry ranging from calcium-magnesium-sulphate to sodium-chloride in the case of Monterotondo clay and a sodium-chloride chemistry in the case of Trisaia clay.

Due to the fact that the chemistry of pore water is a factor of major concern with regard to the processes of the possible radio-nuclides migration, the obtained data stress the need for extending this kind of analysis to a much larger amount of the clay types occurring in Italy.

Interaction of fluids, rocks, grouts and waste under repository conditions

Contract : 128-80-7 WASUK, part 2, NERC/IGS, Harwell.

Scope and Objective

Generic studies on the characterization of the physical and chemical properties of alteration products from granitic rock and groundwaters during the reaction of borosilicate waste forms with water and rocks. This experimental work is completed by some modelling work on solute transport in fissured rocks.

Progress and Results

A suite of experiments, reacting a simulated borosilicate waste glass, a monzogranite and deionised water in the temperature range 100° - 350° C, were commenced. Th experiments at 100°, 150° and 350° C have now been completed and the remaining experiment at 200° C will be completed shortly. Experiment durations were 200 days and the reactant fluids were sampled and chemically analysed for 40 components in solution at 8 discrete time intervals. X-ray diffraction analysis and scanning electron microscopy examination have been carried out on solid products where appropriate.

An experiment, reacting monzogranite and deionised water at 100° C for 200 days, has been completed. Eight fluid samples were extracted during the course of the run, each being chemically analysed for 30 components in solution. Fluid data have been processed using a distribution of species-type computer program, "EQ3/EQ6". The results of this experiment are presently being written up for publication.

A suite of repeated leaching experiments on a simulated borosilicate waste glass at 100° C have been completed. A long-term (18 months) experiment, investigating the solid products of the interaction of simulated borosilicate waste glass and deionised water at 100° C, is nearing completion.

A solid alteration phase synthesis experiment, using a rhenium (as an analogue for technetium)-doped simulated borosilicate waste glass, has been completed at 350° C. Preliminary scanning electron microscopy has been carried out on the products of the experiment.

Work has continued on the development of a one-dimensional analytical solution for solute transport in fissured rocks. It includes the effects arising from diffusion into the matrix pores and sets them against the type of source term, the fracture frequency and the groundwater velocity. In addition a two-dimensional porous-medium model of water-flows along particular sections within the Altnabreac research site has been constructed to derive path-lengths and hydraulic gradients. Results from the two models have been combined to assess whether the use of a porous medium model at Altnabreac is justified and to perform a basic sensitivity analysis.

Thermal phenomena in crystalline rocks

Contract : 154-80-7 WASUK, UKAEA, Harwell.

Scope and Objective

Thermal phenomena are being studied in the two experimental programmes, Heat Transfer and Hydraulic Conductivity, at the AERE field research site in granite in Cornwall.

Progress and Results

- Heat transfer

  The heat transfer experiment was started in 1979 when an electrical heater was positioned in a hole at 45 m depth into the granite. About 72 resistance thermometers were placed in 24 adjacent holes at distances up to 25 m from the heater. The heater was operated at about 3 and 9 kW for periods of 1 and 2 years respectively and showed that the heat transfer through the rock was mainly by conduction. During 1982 the heater power was increased, for a final run, to about 15 kW and data at this increased power are still being obtained. The experiment is still continuing and enables corrosion specimens to be kept at about 100° C in one of the holes.

- Hydraulic conductivity

  The programme to study water flow through the fractures in the rock has continued. The object of this programme is to obtain experimental data for percolation theory of fracture flow being derived in the Theoretical Physics Division at Harwell.

  The experimental methods being used involve single hole flow measurements of fracture occurrence and interhole pressure drop and tracer measurements of fracture characteristics. These methods were developed and proven during 1981 in two vertical holes to 200 m depth. Both ^{82}Br and ^{131}I were used as tracers to identify the flow routes between the boreholes. About 30 hydraulic connections have been located.

During 1982 measurements were made in three other 200 m deep vertical holes. In addition two new holes were drilled and used. One, which is vertical and 700 m deep, was used to investigate the effect of increasing depth to likely depository depths. The other hole, which is inclined at 45° C to the vertical and is 200 m long, was used to determine the occurrence of near vertical fractures, which would be missed by vertical holes.

To date the statistics on the occurrence and characteristics of about 100 water bearing fractures have been obtained using the single hole methods. About 30 inter-hole connections have been mapped using tracers. This programme is continuing.

Mechanical behaviour of granite under pressure and high temperature

Contract : 146-80-7 WASF, CEA, Fontenay-aux-Roses.

Scope and Objective

This research aims at determining the mechanical properties of granite-samples from the Auriat site under normal and elevated temperatures.

Progress and Results

- Determination of the coefficients of expansion

  The measurements are carried out on cylindrical specimens (diameter 36 mm, length 80 mm) equipped with special extensometric gauges for temperature testing (longitudinal and transverse).

  The samples, which can be freely deformed, are placed inside a heating chamber and brought up to different temperatures in succession. The expansions E_1 and E_2 as a function of time are recorded and these enable an assessment to be made of the thermal equilibrium of the sample.

  Figure 78 for $\alpha_v = f$ (T), shows that the volumetric coefficient of expansion varies between 20.5 to 22 x 10^{-6}° C^{-1} in the range examined, which values compare with those found by direct measurement in granite. Longitudinal linear expansion E_1 is greater than transverse expansion E_2, E_1/E_2 lying between 1.1. and 1.5. These measurements thus show, as do the compressibility tests, that the Auriat granite is anisotropic; natural cracking is more developed along the planes perpendicular to the axis of the samples.

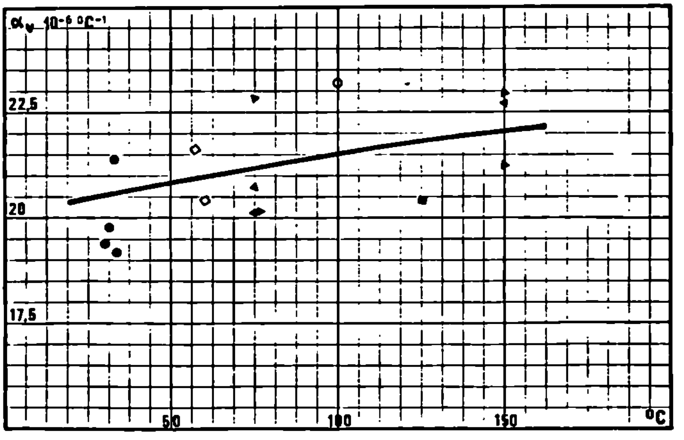


Fig. 78 : Expansion coefficient α_v as a function of temperature

- Effect of temperature under uniaxial compression

The samples previously used to determine the physical characteristics are subsequently tested under uniaxial compression at three temperature levels, 100, 150 and 200° C.

The results are summarized in table 53 in which the average characteristics at ambient temperature are given as an example, together with the values at higher temperatures. These characteristics are : compressive strength σ_c, Young's modulus E, Poisson's ratio ν, and the maximum variation of volume recorded during the test $\Delta V/V$ max.

If account is taken of experimental scatter, the results show evidence of a change in mechanical properties only when the temperature is above 100° C. The approximate measurements are

$$\sigma_{200°}/\sigma_{20°} \sim E_{200°}/E_{20°} \sim 0.35$$

T (°C)	σ_c (MPa)	E (GPa)	ν	$\Delta V/V$ max[1]
20	160	65	0,27	$0{,}7.10^{-3}$
100	155	68	0,30	$0{,}7.10^{-3}$
150	145	69	0,16	$0{,}8.10^{-3}$
200	135	54	0,16	$1{,}8.10^{-3}$

Table 53 : Characteristics of Auriat granite at different temperatures

The development of the cracking is shown by the reduction in the Poisson ratio and the increase in the change in volume of the samples measured during the test. An identical phenomenon was observed with samples held at 100° C for one month.

- Effect of temperature under triaxial loads

The triaxial tests employed are the conventional tests with

$\sigma_1 = P + \Delta$ and $\sigma_2 = \sigma_3 = P$ (P : lateral confining pressure).

. Compressibility

The compressibility of the granite is recorded during the increase in confinement pressure stage (first phase of the triaxial test). Figure 79 shows the curves for $P = f\ (\Delta V/V)$ for the material in different conditions (natural state, after one month at 100° C, after one month at 200° C). It can be seen that cracking is more evident with T = 200° C, but the most pronounced curvature on the graph does not readily indicate the values of the pressure at which the cracks are closed and the relevant crack porosity.

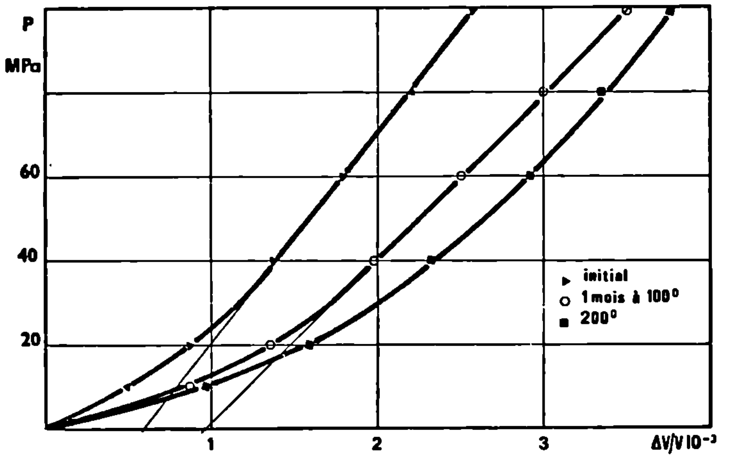


Fig. 79 : Compressibility of Auriat granite under triaxial load

. Failure behaviour

Table 54 provides the values of failure at T = 200° C for the stress σ_1 at different confinement pressures (with an indication of results at ambient temperature).

The differences, which can clearly be seen up to P = 50 MPa, drop with increasing lateral confining pressure.

P (MPa)	10	25	50	75	100
$\sigma_{1\ 20°}$ (MPa)	320	405	550	685	785
$\sigma_{1\ 200°}$ (MPa)	240	350	500	645	760

Table 54 : Rupture stress at different confinement pressure

Figure 80 gives the Mohr's envelope for Auriat granite at T = 200° C compared to that at 20° C.

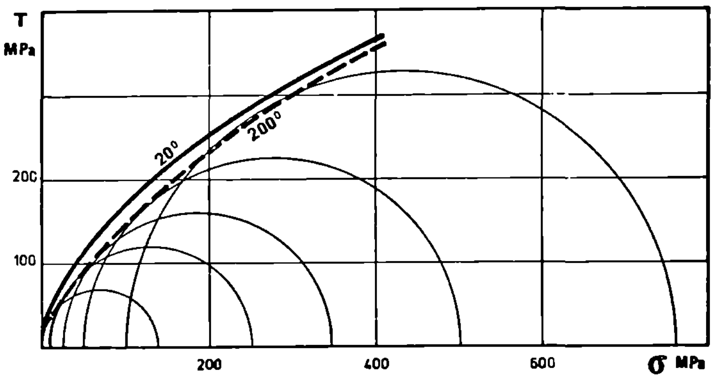


Fig. 80 : Mohr's envelopes of Auriat granite at 20° and 200° C.

Study of deep fracturing of granite formations

Contract : 148-80-7 WASF, CEA-BRGM, Orléans.

Scope and Objective

The aim of this research is to examine deep fracturing in granite rocks and compare it to fracturing observed on the surface, to find out the evolution of fractures from the surface downwards.

A definition of guides for extrapolating data from surface to depth is sought.

Progress and Results

- Bibliographic study

  This work concerns the Bassiès granite located in the Ariège Pyrenees and the Auriat granite located in the eastern part of the French Massif Central.

  In both of these granite massifs, the average strikes and the densities of the main subvertical fracture families hardly ever vary over 1000 m depth in the Auriat drillings (observations made in drillholes) or 1000 m altitude (from 2500 to 1500 m) for the Bassies granite.

  It appears also that the sub-horizontal fractures (dip $<$ 30°) may have developed inside the massifs over a depth of at least 1000 m with no significant increase in their average density, apart from the thin surface layer. Here, in fact, in the 80 m thick rocks lying under the present Auriat granite surface, the average linear frequency of the sub-horizontal fractures (2 fractures per meter in the massif) increases to 5 fractures per meter due to the rock decompression induced by the erosion.

- Structural analysis óf fractures

  . Photo-interpretation study and processing

  The interpretation of the panchromatic aerial photos was carried out over an area of 80 km^2 (9 km x 9 km) including the Margnac and Fanay-Augères mines sector.

  . Structural study of the Margnac and Fanay-Augères mines

  In the Fanay-Augères and Margnac mines, examination of the slight fracturing affecting the massif between the large faults was made by systematic recordings of the fractures. These recordings were taken in measuring stations 50 to 100 m long, distributed in the accessible galleries found at each level of the two mines.

  Among the parameters recorded, the most important are : the fracture type, the orientation (strike and dip), the thickness, the filling and the inter-fracture distance (distance between two consecutive fractures belonging to the same directional family).

Theoretical study of fracture sealing in granitic rocks by silica precipitation

Contract : 200-81-7 WASF, CEA-EMP, Paris.

Scope and Objective

The purpose of this work is to evaluate the precipitation of silica in fractures in relation to the decrease in the fluid velocity in a given temperature field.

Progress and Results

A theoretical simulation of a deep repository condition was performed. In this case, one considers a vertical fracture between the repository and ground surface.

The chosen temperature field lies between the repository and the surface. In this case, the temperature gradient due to the heat produced by the waste, is added to the geothermal gradient (figure 81).

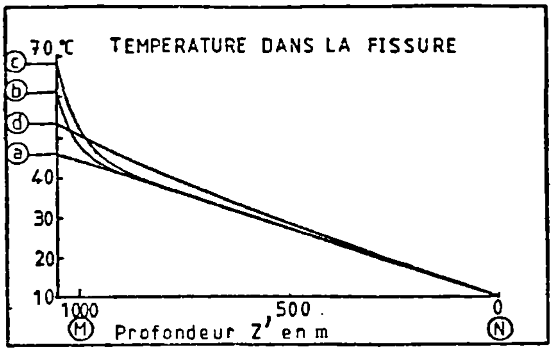


Fig. 81 : Temperature in the fracture between the waste (M) and the surface (N). a,b,c,d : for t = 0, 50, 100 and 1000 years.

The simulation considers amorphous silica for which the solubility gradient is the strongest.

The computed concentration is almost equal to the solubility (fig. 82) for any considered fluid velocity V of the fluid and kinetic constant of the reaction between silica and water.

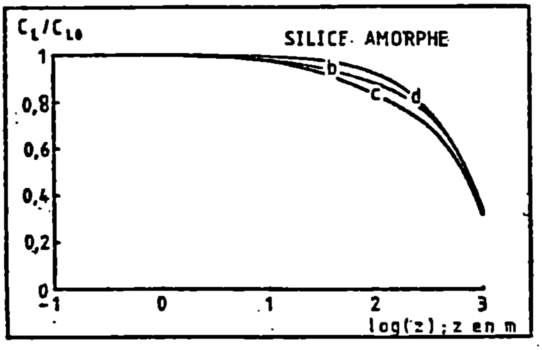


Fig. 82 : Silica concentration C_L versus the distance z from the heat source. C_{LO} : imposed concentration in z = 0. b,c,d curves for temperature fields of 50, 100 and 1000 years

The fluid velocity V was varied between 10^{-5} and 10^{-10} m/s and several values were considered for the kinetic constant of the silica-water reaction. These variations allowed to compute the precipitated mass in the different cases. It increases with the fluid velocity and the kinetic constant. For the maximum values of these two parameters the deposit width should be about 1/10 of the fracture width after 10 000 years (figure 83). However, this result must be carefully investigated.

The velocity of the fluid included in the fractures is a function of the fracture width. When the temperature decreases in the direction of the convective flow, the solution can become supersaturated and therefore precipitation of silica is possible. With the assumption of a constant fracture width, the numerical simulations show that precipitation cannot lead to sealing. However, it is difficult to conclude, since the kinetics of the geochemical reactions are poorly known and

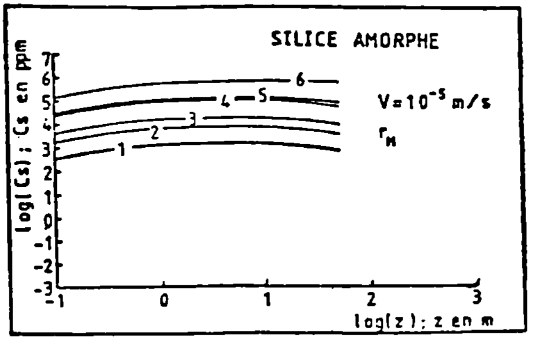


Fig. 83 : Precipitated mass (C_s) per unit of fracture volume versus the distance z from the heat source for the kinetic constant r_M and the fluid velocity V.
1 to 6 : curves for t = 10, 50, 100, 500, 1000 and 10 000 yrs.

since a small variation of any hydraulic or geochemical parameters can noticeably modify the phenomena.

Statistical study on the determination of the hydraulic conductivity in a fractured medium

Contract : 150-80-7 WASF, CEA-EMP, Paris.

Scope and Objective

The aim of the study is to try to link measurements of geometric properties of fractures to the values of the average equivalent permeability tensor of the medium.

It would make it possible, in the long term, to estimate the flow in fractured rocks from borehole measurements (geometry of fractures, also perhaps local permeability tests) and outcrop observations.

The work performed so far was oriented in two different directions : (i) theoretical studies of the statistical relationship between fracture properties and permeability for fractures of finite length; (ii) practical studies of the permeability and properties of two real sites, the Fanay-Augères uranium district and the cores of the Auriat site.

Progress and Results

The theoretical approach was oriented in two directions.

First, statistical considerations allowed the calculation of an upper boundary value of the equivalent permeability, in the case of a fractured medium, using statistics about density, length, aperture and area of fractures. This upper boundary value is at present applied to the data collected in the fractures of the deep boreholes at AURIAT.

A second line of investigation was developed using the concepts of percolation theory. The work has been geared to a generalisation in three-dimensions of concepts already developed elsewhere for two-dimensions. Two options are considered : (a) geometrical study of random finite fractures considered as "disks" and (b) description of the medium by solid blocks surrounded by fractures. None of these two approaches is considered as satisfactory and the research continues.

The above theoretical investigations are now being validated against in-situ experiments.

The statistical study of the fracture distribution in the Fanay-Augères district is now completed and a 3-D hydraulic model of the whole district has been fitted on the available hydrologic data (i.e. water levels, estimation of the infiltration rate, measurements of water extraction at each level in the mine). The permeability distribution, which resulted from the fitting of the model, is composed of two layers, one representing the upper 6 m of the granite (weathered zone), and the second for the lower 400 m of the granite. The first layer is assumed isotropic, with a permeability of 10^{-5} m/s, and the second anisotropic, with permeabilities in the principal directions of :

$$K_{xx} = 1{,}6\ 10^{-8}\ \text{m/s}$$
$$K_{yy} = 1{,}5\ 10^{-8}\ \text{m/s}$$
$$K_{zz} = 6\ \ 10^{-9}\ \text{m/s}$$

These results are coherent with permeabilities measured by packer tests on a new borehole drilled on the site.

The work will continue with attemps to link this fitted average permeability to the one determined by applying the theoretical results from the above mentionned theoretical approaches to the geometrical data on the fractures collected in Fanay.

The influence of fluid-rock interaction on the rheology of salt rock and on ionic transport in the salt

Contract : 153-80-7 WASNL, University of Utrecht.

Scope and Objective

This research investigates the potential for solutes to migrate through stressed saltrock. Solute transport depends on the permeability, which is related to dilatancy during slow plastic deformation of the salt. This permeability could increase noticeably above a stress level at which the dilatancy transition point is reached.

This behaviour is affected by fluid pressure, mean stress and temperature, as well as composition of the salt.

Progress and Results

The research program will be performed on a specially designed testing apparatus with the capability of measuring sample dilatancy and permeability in association with rheological parameters under different values of confining pressure and temperature. Controlled composition pore fluids can be forced through the specimen under accurately controlled hydraulic gradients. This apparatus was commissioned in 1982.

In the mean time a large number of simple dead-weight uniaxial creep experiments have been performed on artificially prepared salt samples, grain size 350 µm, at atmospheric pressure and room temperature. These experiments show that the addition of saturated brine to dry loaded salt causes strongly dilatant cataclasis accompanied by a 2 to 3 order decrease in load bearing capacity of the column. Permeability increases 6-7 orders of magnitude. Stratification of the brines to avoid double diffusive convection was carefully avoided. The creep behaviour of the salt column was described by a power law with a stress exponent of about 1.5 and we suspect deformation is controlled by a solution mass transfer process along grain boundaries (eg. "pressure solution").

These conditions were rather extreme, and work is in progress to determine the relevance of these phenomena to the waste disposal problem.

Suitability of the Konrad mine for the disposal of radioactive wastes

Contract : 145-80-7 WASD, GSF, Braunschweig.

Scope and Objective

This contract is a feasibility study of the disused iron-ore mine Konrad for the final disposal of LLW and decommissioning waste from nuclear power stations. This study was terminated in 1982 with the compilation of the Final Report. The technical conceptions developed within the frame of the project are to be considered as important aids in the construction, operation and decommissioning of the waste repository.

Progress and Results

- Petrographical and geochemical investigations

  In continuation of sorption experiments laboratory investigations were performed to determine the transport of radio-nuclides in practically impermeable clay-stones (permeability coefficient < 10^{-9} m/s) by diffusion.

  The specimen were compressed with 10 kp/cm^2. According to this compression the rock density ranged between 2,1 and 2,2 g/cm^3 and the free water content between 10 and 15 wt% (original rock density : 2,2 to 2,35 g/cm^3, H_2O : 6 to 11 wt%). The diffusion constants were determinated for strontium, iodine, caesium and water. The constants determinated ranged for water marked with tritrium between 3,5 and 6,5 x 10^{-6} cm^2/s, for iodine between 2,0 and 3,5 x 10^{-6} cm^2/s, for strontium between 0,4 and 1,5 x 10^{-6} cm^2/s and for caesium between 0,5 and 1,1 x 10^{-8} cm^2/s. The distinctly lower diffusion constants for the elements strontium and caesium, in comparison with water, indicate a sorption behaviour of the rocks, which is specific for the elements investigated.

- Hydrogeological and hydrochemical investigations

  In the scope of the hydrological field investigations the groundwater temperatures and the electrical conductivity in quarternary aquifers were measured in 49 observation tubes and wells within a radius of 5,5 km around the Konrad mine. The values determinated for the electrical conductivity of the quarternary groundwater range from between 100 to 2000 µS and thus correspond to those of fresh non saline groundwater.

  In the ventilation test gallery the most important result so far is that the little moisture content of the rock mass is mobilized only insignificantly by mining activities, which cause a certain degree of rock desintegration near the galleries.

  In the second phase following now the gallery is ventilated. It is beeing expected that the natural moisture content of the iron-ore formation evaporates so that the ore dries up within a certain distance from the gallery.

After a two years preparatory period, the installation of a mine ventilation monitoring system was completed. Ten underground monitoring stations were installed and fitted with temperature/moisture gauges as well as with ventilation air velocity gauges. The measuring data are transmitted to the meteorological observation station at the surface.

- Rock mechanical investigations

On all previously and newly set up monitoring stations the deformation behaviour of the galleries in iron-ore was further measured, in particular in new galleries excavated by machines.

In 1982 the development of a trial disposal gallery has begun. In sections the upper half of the U-shaped gallery was opened up first before the lower half was cut. This became necessary in order to reach a total hight of 6 m and to minimize the rock deformation. Parallel to the rock mechanical investigations in the gallery a microseismic monitoring apparatus for the identification of sudden deformation movements in the surrounding rock strata was acquired for this test.

For a stability analysis of the underground workings the relevant formation parameters of the confined disposal area were determined parallel to the in-situ-measurements. In-situ permeability measurements similar to the hydro-frac method were carried out in two galleries. First tests with an improved borehole-probe supplied plausible results for depths between 2,70 m and 23,9 m. The measurements are being continued within the zones of rock deformation around testing galleries of various size and shape.

- Seismic investigations and tiltmeter measurements

Investigation of the regional and local seismicity is done by the two stations Asse and Konrad situated 18 km apart. Seismometers have been installed at 750 m below surface in the Asse mine resp. at 1200 m in the Konrad mine. Seismic activity was not detected in the region of Southeast Lower Saxony for the year 1982. These measurements also revealed that the amplitude of vibrations underground are reduced by a factor of 2 as compared to its value on the surface.

Investigations of the seismic noise show how strongly this is dependent on traffic and industry.

Two sudden tilts in the long-term drift determined by tiltmeter measurements during the year were not registered at the seismic stations. The question is whether these effects were strictly limited to the near field of the station or happened outside the frequency range of the seismic station.

- Technical disposal investigations

The disposal tests with inactive waste containers were continued. A considerably less advantageous chamber utilization was experienced with the stacking of pallets than with the stacking of single drums. The experiments have proved that a filling capacity of 70 % can get reached in the disposal chambers if single drums are stowed in a tight order (fig. 84). Based on these tests detailed figures for the annual disposal capacity as well as for the total capacity of the repository were specified.

The development was undertaken of a special container system for packing bulk decommissioning wastes. Six types of containers measuring 1,6 m in width with side dimensions of 0.8, 1.2, 1.6 and 2.4 m are planned. The development of suitable backfill materials for filling stations, transport galleries and disposal chambers was continued with laboratory investigations. As to the compressive strength the comparatively best results were produced by crushed iron-ore of a grain size distribution of 0,25/8 mm mixed with 30 % of blast furnace slag. For the use in cast dams, e. g. for the sealing of disposal galleries, crushed iron-ore with a maximum grain-size of 6,3 mm is well suited. The material is well compressible in the galleries and chambers either by technical means or by the rock mechanical convergence observed in the mine workings.

- Investigations of waste products

Ready-mixed concrete and Portland cement were used as conditioning materials.

The investigations carried out illustrate the necessity for a corrosion protective coating of the waste casks. A considerable cor-

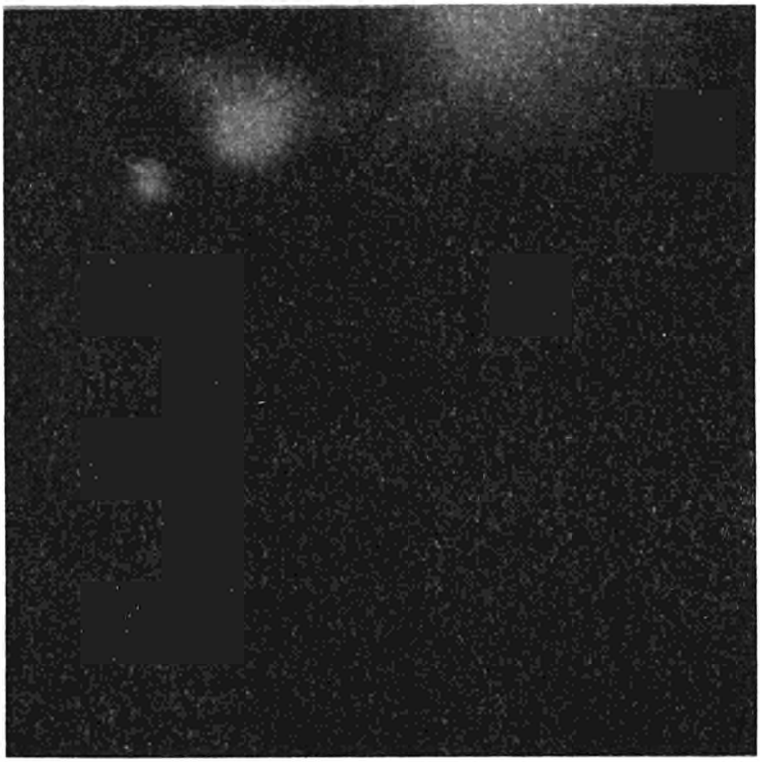


Fig. 84 : Inactive 400 l-waste drums stacked to the full height of the disposal test gallery (behind) and in two layers (in front), covered with iron-ore gravel for ramp construction

rosion protection is achieved for example by means of an epoxy-resin coating which is used by the Kernforschungszentrum Karlsruhe.

For the further characterization of low-level wastes concreted waste concentrates from nuclear power stations were examined regarding their leaching behaviour.

- Radiological investigations

  In the scope of establishing site data at Konrad the natural radionuclide contents of the iron-ore and mine atmosphere were measured; 13 nCi Ra-222 resp. 1,1 nCi Rn-220/m^3 are yielded in the ventilated mine atmosphere.

Geoprospective study of a repository site

Contract : 222-81-7 WASF, BRGM, Orléans.

Scope and Objective

The performance analysis of a repository system necessitates the prediction of the site's natural geological evolution. This evolution is conditioned by a number of factors such as seismic activity, tectonics, climatic changes, and above all by the interaction between these factors.

The aim of this contract is to study these factors and their interactions, in order to build a forecasting model which than can be applied to specific geological sites where radioactive waste disposal is planned.

The study comprises two parts :

- inventory of significant factors and assessment of their effects. This assessment, based on the recent Quaternary period, is quantitative when possible.
- Ranking and combination of these factors into a predictive model with deterministic and probabilistic capabilities.

Progress and Results

- Analysis of factors

Several specific factors were the subject of detailed studies in 1982 and the main results are summarized as follows :

. Climatic evolution

For three million years, the terrestrial environment has been undergoing the influence of a climatic crisis, the causes of which are still discussed. 700 000 years ago, the paroxysm of this crisis was caracterized by the development of big ice-caps in the northern hemisphere.

Considering the amplitude and the frequency of the Quaternary climatic changes, it is difficult to imagine that the glacial crisis should be over. It seems therefore quite reasonable to admit the probability of at least one new glacial age during the next 100 000 years, with uncertainty about its starting date and future effects. Some of them may however be estimated. A total melting of the ice-caps would lead to a 80 m rise of sea-levels. On the contrary, a new glaciation comparable to the previous one would induce the growth of polar ice caps, thus bringing down the sea-levels by about 120 m, with drastic consequences on the erosion of landscapes.

. Vertical movements of the earth's crust

Vertical movements are due to numerous causes : volcanism, isostatic compensation of deglaciated areas, geoidal shape variations, earth-tides, pro-seismic dilatancy, earthquakes.

A series of data about the above causes was compiled according to the type of geotectonic province. It could thus be shown that velocity of vertical movements range from 1 to 10^6 mm per millenium, in some paroxystic cases, the velocity of uplift or subsidence of specific areas can reach 1,000 m per millenium.

. Tectonic activity

Tectonic analysis, the in situ measurements of stress and the earthquake focal phenomena show that, from the lower Quaternary to the present, the Western European continental plate has been subjected to NNW to SSE convergent stress. A study of the arrangement of European and African plates in the Western Mediterranean shows that the entire region is undergoing a period of continental collision. The change in the process implies a westerly continental drift of the Spanish plate, a movement which could take several million years.

On the Western European scale, the most likely hypothesis during the next 100 000 years is the persistance of the present stress trending approximately N-S. On the other hand, on a local scale, reorganisations of this stress are possible, owing to the presence of tectonic or lithological heterogeneities.

. Salt diapirism

When subjected to certain conditions, a salt bed under a sedimentary overburden may produce one or several diapirs. This possibility is the result of the relative ease with wich salt undergoes plastic deformation.

This transition is essentially conditioned by temperature (as a function of geothermal gradient and overburden thickness), by pressure on the salt bed (as a function of overburden density and thickness) and by salt purity.

Once salt has become plastic, the intervention of a trigger factor induces upward diapiric movement. The main trigger factors are : geostatic pressure variations, tectonic pulses, irregularities in the deposit's geometry.

Once diapirism is instigated, the salt upward movement is mainly controlled by the differential of geostatic pressure, resulting from overburden load changes and by the density contrast between the salt and the overburden.

Modelling of these processes is still in progress.

- Interaction between the factors

This modelling part is performed with an increasing degree of complexity.

. The general framework consists of the main computer programme CASTOR (Construction Automatique de Scenarios d'évolution d'un site de STOckage de Radionucléides = Automated construction of evolution scenarios for a radio-nuclide disposal site).

The CASTOR simulator is made up of a principal program written in FORTRAN IV and controls a time iteration loop, from 0 to 100 000 years.

At each iteration the program involves specialised subprograms, simulating different natural mechanisms which determine the evolution of a site :

climatic variation, morphological variation, geomechanical variation, variation of the hydraulic characteristics such as rock mass permeability, erosion, etc.

Some of these mechanisms operate according to the forseeable laws presented above; they are called "controlled mechanisms". In other cases, where these laws are impossible to identify, the mechanisms are simulated by an interactive dialogue with the user (eg. the initiation of a glacial phase).

The mechanisms simulated in this way can interact between themselves.

. An example of subprogram is given here and refers to the time variation of rock mass permeability. This submodel assesses the influence of various geological events on the permeability of a fractured rock mass at great depth (up to 1.000 m).

Two sites have been investigated : the granite of Fougères and the limestone of the upper Jurassic in the Nivernais.

Two types of geological events have been recognized as the most likely to cause drastic changes in the state of stress and thus in the permeability : a glacial age, and an increase of surface temperature.

In both cases, the induced variations of stresses have been found, for three time periods (300, 10 000 and 100 000 years), using maximum assumptions on the extent of these events.

The changes in permeability were then computed using a programme (PERTRI) based on the modelling of the mechanical behaviour of fractures.

The results obtained are still under examination.

2.2.5. MIGRATION OF RADIONUCLIDES

Knowledge about migration of radionuclides does not only depend on sorption studies within the repository and in the host rock, but also on other research areas, such as the chemical characterisation of rock and groundwater and the hydrology and hydraulic properties of host rock (§ 2.2.4.). Assessment of its long-term effects requires extrapolation and modelling of the experimental results (§ 2.2.6.). During 1982, the Commission took the initiative for a coordinated action from 1983 onwards on Migration of Radionuclides in the Geosphere (project MIRAGE).

A large part of the reported work is concerned with nuclide transport in groundwater through fracture flow in granite. Migration studies in clay are limited, mainly due to efforts on a proper characterisation of clay and clay water in situ (see § 2.2.4.). Migration in salt is reported in § 2.2.2. Migration experiments on complete waste are foreseen in clay and in a so-called intergral migration experiment for clay and granite. Migration studies in ocean sediments are reported in § 2.2.8.

Reported contracts :

Migration of radionuclides in clay formations

Contract : 144-80-7 WASB, part 5, SCK/CEN

Objective and Scope

The objective is to determine the retention of radionuclides on Boom clay and when practicable, their solubilities in the interstitial fluid of the clay rock.

All techniques and relevant data mentioned in part 4 of this contract are put to use to conduct these tests under strictly controlled conditions. In addition, direct migration tests are being performed on thick clay parts. The experiments are carried out with Am, Pu and U.

Progress and Results

Solubility tests were conducted in synthetic interstitial solution. The carbonate composition guarantees the pH buffering, while Eh buffering is obtained by addition of ground FeS_2 or with $FeCO_3$ precipitate. The drawbacks of this Eh simulation were readily apparent (sorption on the precipitate, surface passivation of FeS_2 by an oxide film). However these tests confirmed the magnitude of the solubilities evaluated by Allard, taking into account actual parameters like Eh, pH and carbonate concentration. These underlined the relevance of conducting sorption and diffusion work at the tracer level. For Am, Np and Pu the following solubilities were respectively found : 2×10^{-7}, 10^{-8} and 10^{-10} molar.

From these tests a procedure has been developped to carry out subsequent sorption experiments with Boom clay under strict anaerobic conditions : mixtures preparation is taking place under controlled atmosphere (25 ppm O_2); samples are transferred exclusively through septa;

septa vials are stored immersed in N_2 saturated water, leaving the bath just the time needed for manipulation. All chemically abundant waste elements (mostly trivalent elements and uranium) are taken under consideration in this programme, one of the goals being to assess the influence of the waste "ensemble" on the migration of the most toxic radionuclides. With this purpose in mind experiments, conducted by this method with 233 U, have shown that Kd = 0 for uranium on Boom clay under in situ conditions. Formation of negatively charged colloïdal particles of U^{IV} are likely, but this question needs further examination.

The work done at the University of Leuven (Prof Cremers) has shown unequivocally the importance of small amounts of sesqui-oxides $Fe_2 O_3$ and $Al_2 O_3$ on the sorption of Eu. Sorption factors (K_D) sharply increase with the Fe_2O_3 content. This observation clearly stresses the need to remeasure actinide sorption on optimally-stored clay samples where Fe_2O_3 may well be totally absent. Also shown is the radical difference in the sorption mechanism for Sn, Cs and for Eu. As a consequence it may be asserted that in the process of migration of HLW material stable cesium and alkaline earths will not interfere on the migration of trivalent species.

A method of direct diffusion measurements in clay gels has been extensively tested on Cs and Eu at the University of Leuven in view of its application on actinides at the SCK/CEN. It is based on the measurement of the activity diffusing out of a specimen of gel into a stirred "infinite" bath of zero activity, which is separated from the gel by a semi-permeable membrane (such as cellulose acetate). In order to respect the boundary conditions (zero activity in the bath) the solution contains in suspension a very strong sorbent acting as a scavenger with respect to the solution. Regularly the sorbent is allowed to settle and dipped into a counting well to measure the cumulated gamma activity.

The system is perfectly tight and anaerobic. The demonstration was made of measurements down to 10^{-10} cm^2 sec^{-1} for the diffusion coefficient.

Migration of radio-nuclides in clay

Contract : 208-81-7 WASI, ENEA, Casaccia

Objective and Scope

Contribution to the understanding of migration of radio-nuclides in clay as a result of diffusion phenomena.

Progress and Results

In preceding reports the results of the accomplished methodological studies and application to synthetic clays are described. In the course of 1982 the diffusion capacity in clays belonging to various italian clay basins has been determined. ^{137}Cs, ^{85}Sr and ^{131}I are the radio-nuclides used in the conducted experiences. All the samples used for the determination of D and Kd values are now under examination in order to acquire data relating to mineralogical, chemical and granulometric compositions and geotechnical characteristics.

Clay samples have been collected from six basins aged from miocene to pliocene and pleistocene. The analytical data of D here reported have been obtained by means of a planar source and Kd's are obtained in batch.

Data obtained by means of a semi-infinite solution are presently under elaboration. The here reported data show a small variation of diffusion capacity between the different examined clays. The lowest values correspond to miocenic clay of Garigliano Valley.

BASIN	AGE	DIFFUSION COEFFICIENT D (cm^2/sec^{-1})		
		Cs^{137}	Sr^{85}	I^{131}
Vasto	pp	$2,09.10^{-8}$	$1,16.10^{-7}$	$1,74.10^{-6}$
Monterotondo	p	$1,93.10^{-8}$	$1,80.10^{-7}$	$3,43.10^{-6}$
"	p	$1,87.10^{-8}$	$1,59.10^{-7}$	$2,82.10^{-6}$
"	p			$2,58.10^{-6}$
Val d'Era	pp	$1,10.10^{-8}$	$1,66.10^{-7}$	$2,38.10^{-6}$
Garigliano	m	$7,70.10^{-9}$	$9,07.10^{-8}$	$1,43.10^{-6}$
Crotone	pp	$5,63.10^{-9}$	$2,23.10^{-7}$	$2,00.10^{-6}$
Trisaia	p		$1,58.10^{-7}$	$4,70.10^{-6}$
"	p			$3,56.10^{-6}$
"	p			$3,49.10^{-6}$

pp=plio-pleistocene p=pliocene m=miocene

Table 56 : Measured diffusion coefficients in italian clays

BASIN	AGE	DISTRIBUTION COEFFICIENT Kd
		Sr^{85}
Vasto	pp	336.37
Monterotondo	p	60.12
Val d'Era	pp	39.83
Garigliano	m	12.75
Crotone	pp	52.06
Trisaia	p	63.8

pp=plio-pleistocene p=pliocene m=miocene

Table 57 : Calculated distribution coefficients for Sr-85 in italian clays

Nuclide migration studies in granite

Contract : 209-81-7 WASUK, part 1, UKAEA, Harwell.

Objective and Scope

Study of migration phenomena were concerned with nuclide-rock interactions and the determination of formed species, with physical and chemical properties of rock and, indirectly related to migration-phenomena, with groundwater dating.

During the year the experimental programme changed its emphasis from high level wastes to intermediate level wastes.

Progress and Results

- Nuclide - Rock Interaction

  A set of experiments has now been completed in which the interactions between leachates from simulated high level waste and materials such as concrete and granite have been studied. The leachates were obtained by immersing samples of simulated vitrified waste doped with ^{237}Np and ^{99}Tc in water for 150 days at 40° C. The Tc leached into the aqueous phase was exclusively anionic in form. There was some evidence that small particles of concrete and granite sorbed a small amount of Tc, but otherwise the interactions of the leachate with these materials was nil. The Np leached into the aqueous phase was about 80 % cationic in form with the remainder associated with particles or colloids. Although some sorption on granite was observed, the most significant effect occured when the leachate was contacted with concrete; the amount of Np in the aqueous phase fell by 70 % or more and the residual Np-activity was entirely particulate or colloidal in nature.

  The colloidal species from these experiments were examined, using the electron probe analyser. This showed that the colloids in the size-range 0.1 to 10 µm were fragments of the gel layer on the surface of the corroding glass. The composition of the colloids, like that of the gel layer itself, was depleted in sodium and silicon with respect to the waste elements.

A first series of experiments involving magnox (i.e. magnesium alloy hulls) encapsulated in cement is nearing completion. Samples have been leached with water in the presence of clay, sandstone and slate. For comparison, experiments with no geological media present have also been performed. $\beta\gamma$-activity (e.g. ^{134}Cs, ^{137}Cs, ^{60}Co) has been leached into the aqueous phase, but the amount of α-activity found is extremely small. Sorption is shown by all three geological media, particularly clay which apparently removed about 90 % of the β-emitters leached into the aqueous phase.

The leaching behaviour of naked magnox swarf is also being investigated. The amount of total β-activity appearing in the water increases when concrete is present in the system, presumably a consequence of the high pH ($\sim$ 12) which results.

However, the Cs nuclides do not show this effect, and in fact the concentration of Cs appearing in the water is slightly less when concrete is present.

- Physico-chemical effects

  . Permeability

  Permeability measurements have been made using the techniques developed for various samples of a range of rocks of both high and low permeabilities. The results obtained show permeabilities varying from 2×10^{-16} m^2 for sandstones to 4×10^{-18} m^2 for granites. Reproductibility from sample to sample of nominally the same rock varies by factors of about ten.

  . Diffusion coefficients and porosity

  The study of diffusion into granites has continued using iodine as the diffusing species.

  The experimental method used involves maintaining a concentration difference across granite specimens and measuring the initial, varying, and later, steady, diffusion rates. Further developments of the analysis of the transient measurements allow some information about the division of porosity between 'through' and 'blind' pores to be obtained.

The relevance of this work is that it allows a more reliable or credible model of retardation of radio-nuclide transfer from a repository to be developed.

- Field experiments

No field experiments on nuclide migration, as such, were carried out during this period.

- Groundwater dating

Uranium series disequilibrium methods have been applied to groundwater studies at the test site at Altnabreac, Caithness, as part of a general hydrological study. Surface waters and deep groundwaters have been clearly identified by their uranium concentrations and $^{234}U/^{238}U$ values and proposed mechanisms for $^{234}U/^{238}U$ enhangement indicate considerable residence times (of the order of 10^5 years) for the deeper groundwaters. Uranium isotopes have also proved sensitive indicators of intrusion of drilling waters and have shown that considerable times are required following disturbance for return to steady-state geo-chemistry.

Integral migration tests

Contract : 253-81-7 WASUK, UKAEA, Harwell.

Scope and Objective

The purpose of these tests is to assemble in the laboratory all the essential components relevant to a repository and the near-field geosphere in such a way that experiments involving groundwater flow can be carried out as realistically as possible. Migration rates of important nuclides can be measured and this type of experiment should reveal if any especially mobile nuclide is present.

Progress and Results

A preliminary experiment based on simulated vitrified high level waste has been completed after operating for six months. The glass was doped with ^{99}Tc, ^{137}Cs, ^{241}Am, ^{237}Np and a mixture of Pu nuclides. Aqueous leachate from this glass was caused to flow by gravity through five columns of crushed granite arranged in parallel. A combination of different flow-rates and particle sizes was studied in this arrangement. The columns also contained samples of iron oxide (corroded canister) and concrete (back-fill). Daily samples of the water emerging from the columns were taken and monitored for α, β and γ activities. Most of the α-activity in these samples was associated with suspended particles, but in the case of the β-activity only 30 % was retained by the smallest filter used (0.05 µm pore). Plans are being made to measure the distribution profile of nuclides along the columns.

The next stage in the programme is the construction and operation of the main Integral Migration Test apparatus, which should be ready for commissioning early in 1983. It will consist of six independent modules, each of which will contain about 8 columns arranged in parallel. Each module contains a contactor vessel in which a sample of intermediate level waste (e.g. hulls encapsulated in cement) is leached by groundwater which then flows through the columns. The water chemistry can be varied between the different modules. About 50 % of the columns will be operated with crushed rock such as sandstone, shale, granite, and slate. The remaining columns will be devoted to tests with clay. However, the relative impermeability of most clays introduces certain practical problems into flow experiments and some further development is needed before clays can be introduced into the integral migration tests.

The Eh of the groundwater is an important variable in the water chemistry. The development of an electrolytic cell for Eh control in a flowing system is nearing completion.

Study of the "scale-effect" in radio-nuclide transport in fractured media

Contract : 147-80-7 WASF, CEA-EMP, Paris.

Scope and Objective

The aim of the study is to get a better insight of hydrodynamic dispersion phenomena which occur in fractured media (granite). In this kind of heterogeneous media, the dispersion coefficient, which represents the spreading and dilution of a contaminant plume moving through the medium, is a function of the averaged distance travelled by the contaminant in the medium. This phenomenon is termed "scale-effect".

Neglecting this effect may have detrimental consequences. On the one hand, measurement of a supposed constant dispersion coefficient by small-scale, in-situ experiments, will give values which are systematically underestimated and uncorrectly describe the true physical mechanism. On the other hand, repository safety analyses using underestimated dispersion coefficients will result in prediction where the flux of radio-nuclides reaches the biosphere later than in reality and is less diluted than in reality, at least for the first arrival.

The present phase of the research is a theoretical study of the scale-effect in heterogeneous media. A second phase, to begin in 1983, will consist of in-situ tracer experiments in a fractured formation to validate the theoretical concepts previously developed.

Progress and Results

A first step of study was completed in 1981, in which the theoretical study of the scale-effect was done in two dimensions. The fractured medium was represented by an equivalent porous medium, the fracture pattern being accounted for by the introduction of a markedly anisotropic permeability. Flow velocity fields were randomly generated using Monte-Carlo techniques and particles were moved inside the medium, neglecting diffusion. From the statistics of the spatial distribution of the particles, as functions of time, the variation of both the longitudinal and transversal dispersion coefficients, as a function of the average travelled distance, could be established. It was shown that the obtention of an "asymptotic behaviour", i.e. a constant value of the dispersion coefficient after some travelled distance, depends upon the properties of the random velocity field. This first stage thus allowed to establish the methodology for the study of the scale-effect.

The second stage, carried out in 1982, consisted in developing the work in three-dimensions, as the restriction to two-dimensions could lead to systematically biased conclusions. In particular, the time mixing phenomena, which are essential, can only be dealt with in a three-dimensional analysis.

A numerical approach generalized the work done in two-dimensions. The medium is discretized into a set of 10 x 10 x 100 cubes, the direction of flow being parallel to the longest side. Various travel distances are accounted for by considering the medium as "cyclic", i.e. particles leaving the medium at the dowstream end and re-enter it instantaneously at the upstream end.

Conservative flow velocity fields are selected by Monte-Carlo techniques; particles are moved by convection, molecular diffusion is neglected. The statistics of the spatial distribution of particles are analyzed, as functions of time, for various velocity fields. These velocity fields could also be generated by selecting realisations of a random permeability field and solving the flow equation numerically by a three-dimensional finite element program. This approach allows the study of :

- the existence of an asymptotic behaviour, depending on the hypothesis made about the flow velocity field
- the principal direction of the dispersion tensor (a three-dimensional generalization of the scalar dispersion coefficient), as function of time and of the flow velocity field. It will thus be investigated whether or not these principal directions remain constant, and

whether or not they are the same as the direction of the average flow velocity. This latter point is still a matter of controversy and needs clarification.

Study of physico-chemical behaviour of actinides

Contract : 210-81-7 WASF, CEA, Fontanay-aux Roses.

Scope and Objective

Study of the fixation of the actinides Np and Pu on argillaceous barriers is complicated because of the polyvalency of these actinides. Careful control of Eh and pH in the batch-type sorption experiments is essentiel to obtain reproducible results. The picture is further complicated by complexing reactions, producing solid particles within the solutes. Detection methods for these solid particles, especially at very low concentrations, remain to be developped.

Progress and Results

- K_D measurements

  Earlier work began on retention studies geared to the Np (V)/bentonite system, yielding partial results for plutonium retention. This work was continued in greater depth to confirm the results previously obtained.

  Fig. 86 is an example of the discrepancies that can be observed : in curve 1, v and m remain constant, while the pH is adjusted by adding H^+ ions; in curve 2, v and m remain constant, while the pH is regulated by adding OH^- ions; in curve 3, the H^+ concentration and v remain constant, while the pH is adjusted by varying the mass of clay (which is basic in nature). In this case, the pH obtained is stable and reproducible. The latter method was systematically adopted in further measurements.

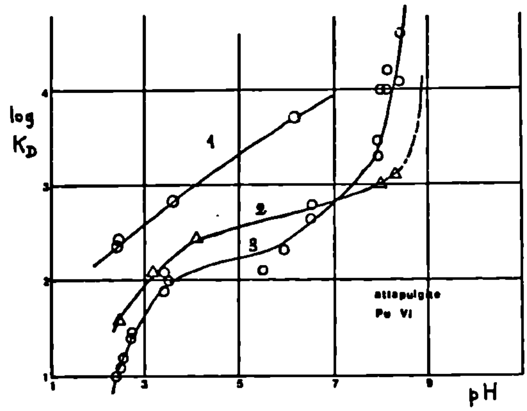


Fig. 86 : Retention of Pu (VI) by attapulgite :
influence of the different experimental conditions.

Fig. 87 sets out in summary form all the readings taken with the plutonium/bentonite system. The retention curve for Pu (III) was obtained in a reducing medium and that for Pu (IV) in an oxidizing medium. As far a Pu (VI) is concerned, the plutonium was maintained at that valency by the presence of a very slight excess of Ce^{4+}. Each curve was plotted on an average from some 50 experimental readings.

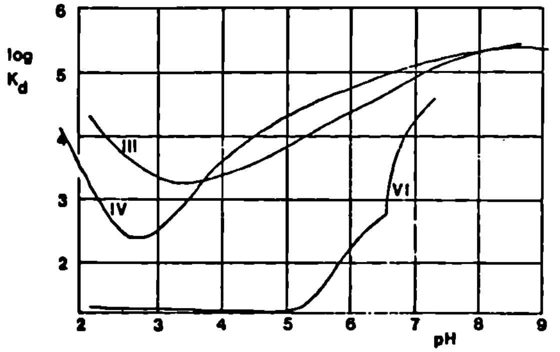


Fig. 87 : Plutonium retention by bentonite versus pH, for valencies III, IV and VI.

The parallel study with attapulgite is practically completed; only the behaviour of Pu (III) in a reducing medium has yet to be investigated.

- Studies on complexing reactions

A method of preparing polymerized Pu (IV) solutions was developed. These present a characteristic absorption spectrum that enables them to be identified at high concentrations; more sensitive measurement techniques (use of lasers, for instance) are under investigation.

Progress is being made in the study of the carbonate complexes of Np (V) through the use of a potentiometric method that Grenthe applied to the carbonate complexes of uranium and of the lanthanides.

The study of the complexing of Pu (VI) by humic acids was tackled by means of absorption spectrophotometry. A recent article by Sullivan indicates the existence of absorption bands in the near infrared region, which are due to interactions between plutonyl and humic acids. Our own experiments reveal plutonyl/hydroxyl absorption bands that can also be observed in the spectra from pH 4 upwards in the absence of humic acids. This prompted the study of the hydrolysis of Pu (VI).

The equipment necessary for separating humic or fulvic acids by the gel chromatography method was installed and the initial tests with Sephadex and TSK gels were started.

Research is continuing on the application of laser techniques to develop a sensitive method for the specific detection of ions in solution. The thermal lensing technique appears to be between 100 and 1000 times as sensitive as optical absorption spectrophotometry in the case of uranium. Experiments were carried out at Ispra with the participation of the CEA-FAR's laser spectroscopy laboratory.

Lastly, the critical review of literature on complexes of transuranic elements was completed and has revealed that numerical values for the complexing constants and even data relating to the nature of the species are lacking in very many cases.

- Eh-pH diagrams

Fig. 88 shows the distribution of the various forms of Pu and Np at infinite dilution (i.e. in the absence of precipitation), as far as can be estimated in the light of current data. As regards neptunium, it can be seen that there is a high probability of the occurrence of Np (V) in an oxidizing medium and of Np (IV) in a reducing medium, whereas in the case of plutonium the co-existence of the four degrees of oxidation can be observed : Pu (VI) in an oxidizing medium, Pu (III) in an acid reducing medium, Pu (IV) in an alkaline reducing medium and, lastly, Pu (V) in an intermediate zone. These diagrams of course merely constitute a basic outline that will have to be modified, when the necessary data are available, to allow for complexing by an-ions such as carbonate. The areas bounded by dotted lines on the diagrams are precisely those for which the hydrolysis (complexing by OH^- ions) is not fully understood.

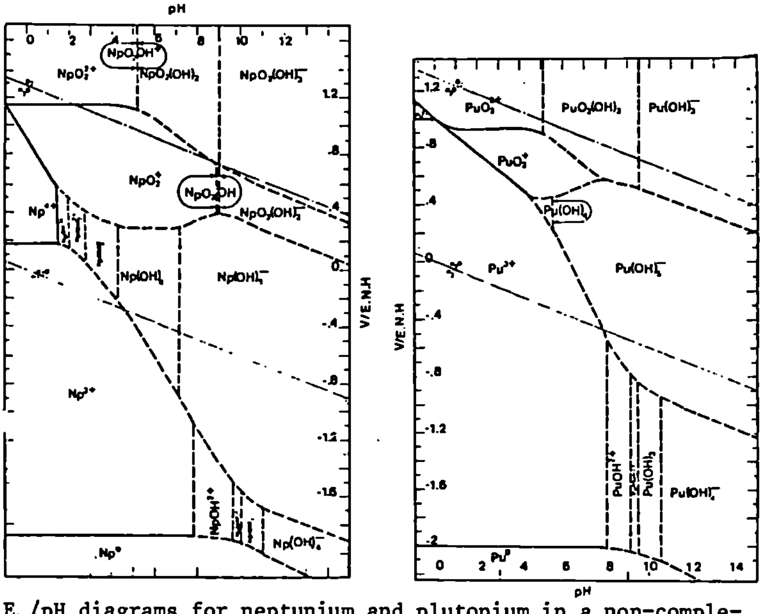


Fig. 88 : E_h/pH diagrams for neptunium and plutonium in a non-complexing medium under conditions of infinite dilution, i.e. in the absence of equilibria involving solid phases.

Research on the retention of radio-elements on the fracture surfaces of granite

Contract : 203-81-7 WASF, CEA-Cadaracha.

Scope and Objective

Experimental work during 1982 was re-oriented. It is now directed towards a comparative study of sorption on granite of radio-nuclides, especially the actinides, under oxidizing and reducing conditions. The aim of this new series of column experiments is to establish the importance of simulating reducing conditions, which will occur in radioaction waste repositories at great depth.

Progress and Results

- Description of the experiments

  The simulation in the laboratory of deep groundwater needs the complete desoxygenation of the solutions, their chemical reduction and the degassing of the solid samples. The experimental device must not only reduce these materials but also maintain them in a reduced state. This device is placed in a glove box and maintained under neutral atmosphere by nitrogen - circulation.

  The testing of the oxygen content in the box is made with a polarographic probe. The Eh - pH measurements, are carried out by a pH meter, a milli-voltmeter with a three electrode apparatus allowing the pH - Eh measurement by simple commutation.

  The desoxigenation of the media is not sufficient to reach the low Eh-potential likely to exist in deep groundwater. It is necessary to impose a drastic chemical reduction. Several chemical reducers have been tested (hydrogen on nickel de Raney, Fe Cl_2, hydroxylamine, ascorbic acid, hydrazine). For considerations of feasibility and performance, this reduction is done by ascorbic acid 10^{-1} M in acid media and by hydrazine, 1 M in alcaline media. It is possible to change the pH of these solutions without changing the reducing power; it is however necessary to experiment after 1 or 2 days of stabilization.

The actinides have been counted by liquid scintillation; comparative measurements have shown that the adjonction of the reducer in basic solution has an influence, not on the counting rate, but on the form of the peak (flattening of the peak). This effect disappears if the counting is undertaken in a gel instead of a scintillating liquid. That is why calibration and controls of the counting methods are needed in order to have accurate comparative measurements of the actinides in the two media.

- Results

Several experiments have been carried out with Pu in columns of quartz sand (grain size 0,1 mm) using the injection-impulsion method. The experiments have been carried out in both oxidizing and reducing media at pH 9 with the same initial source. In oxidizing conditions (350 mV/ENH) the Pu is strongly taken up on the head of the column, only a small part of the Pu get through the column, without any retention, like a tracer of the water; this "mobile form" represents 2 % of the initial concentration. In reducing conditions with hydrazine (- 200 mV/ENH) the greater part of the Pu, 60 % of the initial activity, gets through the column.

- Preliminary conclusions

There is a strong difference between the behaviour of the Pu in oxidizing and reducing conditions. These experimental results verify previous theoretical considerations. Further experiments will be performed to complete and improve these observations. They will be performed with Am and Np on Auriat-granite.

2.2.6. MATHEMATICAL MODELLING

This chapter deals with contracts specifically aimed at developing or improving computer codes as calculation tools for (a) repository design and (b) prediction of groundwater flow and radio-nuclide migration.

The bulk of the work consisted in the improvement of finite-element thermo-mechanical codes for description of the stress-strain behaviour of excavation in salt. The remaining portion of the work was related to the modelling of groundwater flow in fractured media, as well as retention of radio-nuclides in the pores of the rock matrix.

All these programmes were covered by a review of computer programmes suitable for studies related to radioactive waste disposal; the resulting document will be presented in the form of a "Programme Directory".

Reported contracts :

Review of computer programs available for use in radioactive waste disposal studies

Contract : 219-81-7 WASUK, Atkins Research and Development, Epsom

Scope and Objective

The overall objective is to establish which of the large number of existing computer programs used in studies on radioactive waste disposal may be recommended to analyse various problems related to the post-closure phase of facility operations. A Program Directory will be produced giving detailed information on programs which may be applied to the study of the following topics :

- Nuclide inventory
- Corrosion and leaching of waste package
- Temperature distribution and stresses within the facility
- Groundwater flow and radio-nuclide migration in the geosphere

The following chemical, physical and thermal effects will be covered in relation to the above topics :

- Geochemical near field interaction
- Sorption
- Diffusion
- Hydrochemical properties of the host medium
- Thermal effects on the properties of the host medium

It is also anticipated that a need may be identified for the modification of certain programs and for the development of new programs to cover aspects for which the existing programs are inadequate. Suggestions will be given as to whether or not suitable computer programs can and should be developed to include these areas.

Progress et Results

Visits to and correspondance with various relevant companies, research centres, universities and government departments in Europe and the USA was made. This has enabled a list to be compiled of the most suitable individuals and organisations to be contacted and subsequently letters have been sent requesting references and copies of program manuals. Response has been generally quite good and the literature supplied by these contacts, together with the information obtained by Atkins own literature search, has enabled the program review process to be carried out.

A style and format for each program entry in the Directory was proposed and accepted. It was agreed that the Directory should concentrate on a smaller number of the most relevant computer programs for detailed reviews but all other programs, identified as being in use in this field, will be listed in the Directory with some brief information about each.

The following numbers of programs have now been reviewed and will be entered in the Directory as follows :

- Detailed Reviews : 55 programs
- Summary Reviews : 110 programs
- Tabular Reviews : 65 programs
- Total System Analysis Codes : 5 programs

Other reviews and comparisons of programs have been investigated, including INTRACOIN, ONWI, NRC, OECD/NEA, NTIS. The NRC Directory (first stage published in July 1982) is the closest to the present study but the contents are strongly biased towards USA programs.

Improvement of the computer codes for the calculation of temperature fields after disposal of HLW in salt

Contract : 266-80-7 WASD, part 2, KfK, Karlsruhe.

Scope and Objective

Work was continued to enlarge the applicability of the computer code MAUS (mechanical analysis of underground storage) and to develop the temperature calculation program system FAST-STEP.

Progress and Results

- Development of Maus-XY (plane-strain and plane-stress problems)

  On the basis of the former code Versions MAUS-ED (for plane-strain problems) and MAUS-ES (for plane-stress problems) a new code version (MAUS-XY) was developed and handed over during the year under review. The code MAUS-XY includes, compared with MAUS-ED and MAUS-ES, improvements such as restart capability, simulation of excavation and filling processes, and a stress-strain-law for crushed salt.

- The birth of elements capability

  The actual stress-strain-state at any time and at any place in a salt dome is a direct consequence of the complete dome load histoty. In order to assess the stress-strain-state in the surroundings of a HLW repository with an adequate accuracy it is therefore important to model the entire load path, i.e. the excavation of caverns and shafts, the back-filling of the remanent volume of the charged chambers, and the complete time-dependent thermal loading. With regards to these points the modelling capability of the computer code MAUS has been improved by the addition of a simple algorithm that simulates the birth of elements.

- Examinations to the stability-problems of MAUS

  Because of the pronounced creep-properties of rock-salt, extended viscoplastic strains can occur near boreholes or cavities.

In this case the applicability of MAUS is limited, because stability problems arise. During this year extensive work was done in searching the cause of the stability problems.

A lot of simple testing calculations pointed out that there seems to be no way to avoid the instabilities by using any correction-algorithm. But it seems to be promising to use finite elements with higher quality concerning the formulation of the matrices (e.g. intergration-scheme).

· Development of the temperature calculation program system FAST-STEP and test calculation

The current computer programs for the thermal layout of a high level waste repository are based upon simplifications like

- the unit cell concept (the boreholes are filled simultaneously and the disposal area is of a very large extension), or
- the assumption of temperature independent thermal properties (time-dependent filling of the disposal area by superposition of temperature fields).

These simplifications lead mostly to conservative results. In order to get more realistic temperatures it is necessary to choose a calculational method that avoids the above idealisations. Like in neutron diffusion calculations of large power reactors a step by step calculation procedure with the following features was developed :

- The disposal area is calculated in four successive steps. In the first step the disposal fields are considered as smeared heat sources. In the second step an arbitrary disposal region consisting of single plate-sources is considered. In the third step a plate-source consisting of coarsened boreholes and in the last step a single borehole in its real dimensions is calculated.
- The single calculation steps mentioned above are connected in the way that each calculation (exept the first) has time-dependent boundary temperatures, which are calculated in intermediate steps with special interpolation programs from the results of the preceding calculation step.

. The single calculation programs are based on the coarse-mesh-method and work in three-dimensional cartesian geometry.

The ensemble of these programs, called FAST-STEP, has been tested by the calculation of an appropriate test-problem. The results show clearly the influence of the time-dependent filling of the disposal area.

Development of methods of computation and performance of model computations for thermomechanical interactions of the salt and borehole casing or waste canisters

Contract : 266-80-7 WASD, part 3, KfK, Karlsruhe, RWTH, Aachen.

Scope and Objective

The following thermomechanical problems were studied :

- Thermally induced borehole closure and stresses around a 300 m deep borehole in an HLW-disposal field with and without brine pressure.
- The surface uplift above a spent fuel repository.

Progress and Results

- Thermomechanical model calculation in and around an HLW-borehole

  Calculations were concerned with the closure of an HLW-borehole in the presence and in the absence of hydrostatic pressure resulting from a hypothetical brine inrush and the stress and deformation fields in the vicinity of the in situ heater tests.

  The finite-element model was axial-symmetric and the vertical and horizontal boundary conditions were considered to be hydrostatic ($\sim$ 21 MPa).

  The influence of the hydrostatic fluid pressure (σ_F = 12 MPa) on the borehole wall was analysed in case of an accidental flooding of the disposal field.

The computations performed up to now showed a rather large effect on the closure rate of the radial discretisation and type of element chosen (4 and 8 node isoparametric elements). Some further tests are under way.

For the "Hexagone experiment" in the salt mine Asse (temperature test 6), several temperature and stress-strain calculations were performed. Under the constraints that the maximum temperature does not exceed 200° C and 230° C resp., the thermomechanical analysis made clear, that under the model assumption there are no cracks or local failure to be expected in the 'cold' surroundings.

Temperature calculations pointed out that 210 kW heaters would increase the maximum temperature up to more than 1200° C within the heating period of 145 days. This is not realistic because the melting point of rock salt is 800° C.

Calculations of a 120 kW variant are performed at present and first results were already made available.

As the temperature experiment 5 load path has a very complex structure with a step-by-step growing sequence, the computer calculations were performed by means of the recently implemented restart facility of MAUS. With this it is possible to store the results of a successfully accomplished part of the calculation and to continue with modified control parameters.

· Surface uplift above a spent fuel repository

For two variants of repository accommodating spent fuel elements, the thermomechanical loading, i.e. the stresses and deformations in the system consisting of salt dome, surrounding rock and cap rock, were analysed with the help of simple models. The computations were made for a 2D(xy)-model assuming a plane strain condition (i.e. zero strain in the Z-direction). The results of the thermomechanical analysis show a considerable dependency on the initial state (i.e. the initial uplift rate) of the system salt dome/surrounding rock. The comparison of the two variants shows that the uplift is approximately proportional to the surface density, i.e. to the mean heat release per unit of base area in the repository.

A further computation for a HLW-repository of comparable capacity resulted in a similar maximum surface uplift, occuring however at substantially earlier time.

Development and application of rock-mechanical computer codes on the strength behaviour of heated and unheated rock-salt

Contract : 130-80-7 WASD, part 9, GSF, Braunschweig.

Scope and Objective

Objective of this task is the numerical prediction of stress and reaction of the salt rock during mining activities and storage of hot radioactive waste. For numerical calculations involving the finite element method and - if necessary - the difference method, computer codes are employed which run on high-capacity computers. These programmes must take into account the creep behaviour of salt as well as fracture and failure criteria at different temperatures.

Progress and Results

- Improvement and adaptation of existing programmes

  At the end of 1982 three computer programmes were available for the development and numerical treatment of physico-technical models in the field of rock-mechanics. They are the programmes ANSALT, ADINA and MAUS. Since November the programme ANSALT, which was developed by Control Data GmbH, can be used for first trial calculations. Special features of this programme are automatic time stepping and the possibility to implement user-defined constitutive laws.

  To improve handling of ADINA, pre- and post-processor programmes are being developed. By this means the input is simplified and output may be presented graphically. It is planned to extend these programmes in such a way, that ANSALT input and output data can also be processed.

Access to high-capacity computers at Frankfurt and Hannover, on which rock-mechanical calculations are performed, will be possible by means of a terminal station which is located at the Institute. The most important part of the equipment has already been acquired.

- Development of failure criteria

To discuss the possible occurrence of cracks caused by the disposal of radioactive waste in rock salt, failure criteria and laws must be known. A failure criterion, which is supported by theoretical investigations. was formulated. It can be fitted to measured data which are obtained from other parts of the programme. A flow chart was prepared which explains how to integrate a particular failure law into a computer programme. Existing cracks can be treated by "joint" elements, which are implemented in the programme MAUS.

The programme ANSALT offers equivalent "gap" elements.

- Completion and verification of a suitable constitutive law

Experiments are being performed permanently at the Institut für Tieflagerung and - by order of the IfT - at the Bundesanstalt für Geowissenschaften and Rohstoffe (BGR) in order to improve on the creep law for rock salt under the special consideration of the temperature dependency.

The law is first verified by trial calculations of cylindrical samples in order to obtain correction parameters for the measurements.

A constitutive law for backfill material was formulated. To fit the parameters, extensive experimental investigations are still required. This law, which contains a visco-plastic component, allows for the calculation of load cases in back-filled disposal storage rooms.

- Application of FE-codes

The "Hexagone experiment" (temperature test 6) serves as a preparation for the trial disposal of a hot radioactive waste container. By arranging heaters in a hexagonal scheme, similar to a final waste disposal site, the thermal and mechanical behaviour of rock salt can be simulated. Considering the important problem of crack formation caused by heating the surrounding rock, calculations with MAUS were done. The results show that outside a cylindrical surrounding of approximately 60 cm diameter the stresses are always below failure stresses.

In order to complete frac-experiments, performed in the Asse mine to obtain information on stress state and fracture behaviour of the rock, calculations were done to investigate the change of the stress field before and during the process of fracture. The relation between borehole pressure and the components of the stress tensor at the edge of the borehole was set up.

To easily obtain graphic representations of the Asse mine, a file is being furnished with coordinates of the Asse mine. With these data the graphic programme GRAPLOT can plot the desired view perspectively from any side. Sixteen floors have been written into the file so far.

- Geomechanical data base system

  Experimental laboratory and in situ investigations produce vast amounts of data requiring considerable expenditure of money and manpower. For this reason it is of great importance to secure these data and to make them readily available when needed. Care must be taken that the data can be searched for, retrieved and updated. A suitable data base system was designed and partially realized.

Development of computer programmes for temperature analysis and deformation behaviour in a salt dome

Contract : 226-81-7 WASNL, part 1, ECN, Petten.

Scope and Objective

This task aims at developing and validating finite-element computer codes (TASTE for temperature distributions and GOLIA for stress-strain analysis) to be used in repository design and, later, in performance studies.

Progress and Results

The already developed codes were used to calculate the stress-strain behaviour of a "prototype cavern" in the Asse salt mine. This work was carried out in cooperation with GSF and KfK.

With respect to the deformations of the cavern three geometric schematizations have been analysed :

Model 1 : An infinite long cylindrical cavity in an infinite salt space.

Model 2 : A spherical cavity in an infinite salt space.

Model 3 : A geometrical exact representation of the cavern and shaft in a half infinite salt space.

Due to the fact that the cavern is situated in the same salt dome and at the same depth as the ECN borehole, it is assumed that the creep equations derived from the borehole convergence are valid for the cavern too (see § 2.2.2. contract : 142-80-7 WASNL, part 1).

The most important results of the analyses, the radial convergence of the cavern, is given in fig. 90.

From this figure it can be concluded that the simplified model 2, with a radius of 12.06 m, gives a very good approach of the results from detailed analyses. This could be expected regarding the rather good geometrical approach of the cavern with a spherical cavity with a radius of 12.06 m.

From a comparison of the results of model 2 with R = 16 m and R = 12.06 m, it appears that the radial convergence is linearly dependent on the radius R. The comparison of the results of convergence measurements and the analytical results shows rather big differences. The main cause of these differences is the fact that in reality creep deformations and stress changes occur already during the excavation of the cavern.

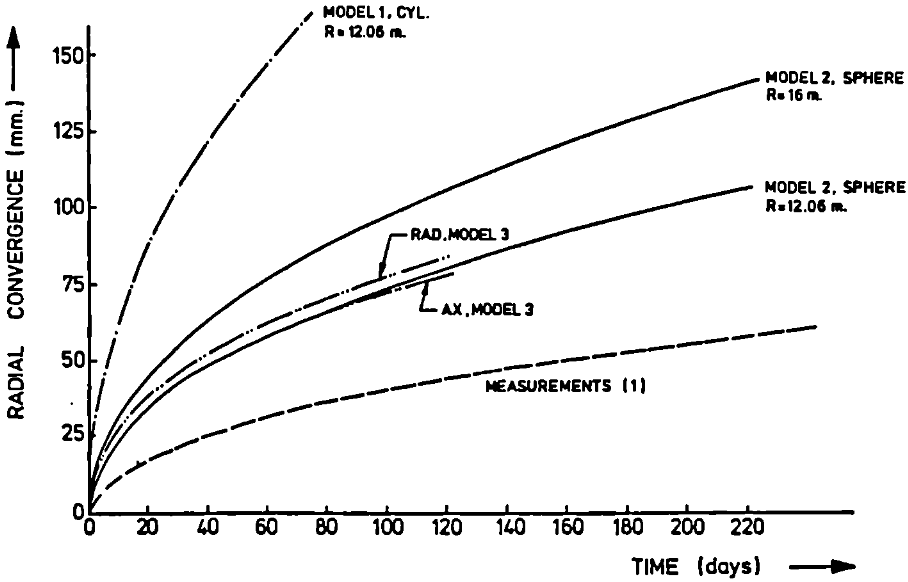


Fig. 90 : Calculated vs. measured radial convergence of the prototype cavern.

Mathematical modelling of groundwater flow and radio-nuclide migration in crystalline rock

Contract : 209-81-7 WASUK, part 2, UKAEA, Harwell.

Scope and Objective

This work concerns the development and verification of models for radio-nuclide migration in fractured rock.

Progress and Results

- One-dimensional radio-nuclide migration models

  The majority of safety analyses of radioactive waste burial have used one-dimensional models which include the effects of advection, longitudinal dispersion, equilibrium sorption and radioactive chain decay. It has been pointed out that poorly sorbed nuclides will be significantly retarded by diffusing from the water flowing through fractures into the stagnant water in the micropores of the rock matrix. A one-dimensional model which includes this effect, in addition to the ones mentioned above, is needed for performing generic safety analyses.

Such a model (NAMID) has been developed by solving the Laplace transformed equations analytically and then inverting this solution numerically.

In order to make reliable safety assessments with such models it is necessary to test them against field experiments on the transport of tracers in groundwater. To this end, a radial flow version (NAMRAD) of the above model has been developed and used to analyse and experiment on the transport of sorbed and non-sorbed (I^-) tracers through a horizontal fracture zone in crystalline rock. The experiment was performed in Sweden and its analysis forms part of the international INTRACOIN comparison project. The model includes the effects of radial advection, hydrodynamic dispersion within the fracture, kinetic surface sorption and diffusion into the rock matrix with equilibrium bulk sorption. The last two were found to be vital in fitting the experimental results.

-

Diffusion will occur from water bearing fractures into the surrounding rock. It is now accepted that this will be a significant factor influencing radio-nuclide migration, particularly of non-sorbing species. To obtain information about this diffusion it is convenient to do laboratory studies on thin rock samples. It is important to know whether this information is directly relevant to large-scale rock formations.

A new 'dual porosity' model has been developed to improve agreement with experiment. In it the porosity is divided into two parts, a 'dead-end' part and a 'through-transport' part and diffusion in the two parts is treated separately.

The new model indicates that the conventional theory, which implicitly averages over the pore structure, is accurate except where details of the diffusion process are of importance over length scales of the order of a centimeter or so.

A related laboratory experiment is proposed to look at the processes controlling the movement down an idealized fissure.

- Flow in fracture networks

In many rock masses the groundwater flow occurs predominantly through an interconnected fracture system. By using a probabilistic model of the fracture system incorporating statistical information on fracture positions, orientations, lengths and apertures, the length scale required before a porous medium description is valid, was investigated. The length at which macroscopic permeability is meaningful depends on the statistical parameters and on the fracture density and generally lies between ten and twenty times the average fracture length.

Some investigations into the dependence of the permeability on the fracture statistics at a fixed size have been started. These have shown that above the percolation density the permeability is proportional to the excess density (that is the fracture density minus the percolation density).

A computer program to look at hydrodynamic dispersion in fracture networks has now been developed. It has shown that a diffusion like model can be made to fit a single experiment fairly easily but the parameters vary significantly from experiment to experiment. The size-dependence of this variability and the relationship between the fracture statistics and the dispersion parameters is being studied.

- The program NAMTAR

The computer program NAMTAR (numerical assessment method for the transport of active radio-nuclides) is being developed to model the migration of radio-nuclides released from a waste repository in rock. All the important physical processes affecting the migration will eventually be included and are being added one by one to the program. They include not only advection by the water flowing through the rock and radioactive decay, but also molecular diffusion, hydrodynamic disperson by the flow, complex chemical effects (collectively known as sorption) and diffusion into the non-flowing water in the microscopic rock pores. Recently progress has been made on including non-isotropic velocity-dependent dispersion, as the dispersion parallel and transverse to the flow are different. In addition work has been done on the inclusion of a more complex boundary condition at the repository.

· The program NAMMU

The computer program NAMMU for modelling fluid flow in porous media with heat sources, has been used by the National Radiological Protection Board and the Institute of Geological Sciences to model the groundwater flow.

Development of NAMMU has continued with the addition of some new post-processing options. This enables the user to obtain cross-section plots or time evolution plots of pressure, temperature and velocity and velocity vector plots in addition to the original contour, streamline and pathline plots. The program has also been modified to use the GHOST80 graphics package.

2.2.7. REPOSITORY DESIGN

The two reported contracts have both been concerned in 1982 with calculations work in support of the design studies.

Engineering studies for a waste disposal facility in clay

Contract : 225-80-7 WASI, ENEA, Casaccia.

Scope and Objective

The main goals of these studies are the following :

- determination of the most suitable geometry of a repository in clay, using parametric studies;
- assessment of technical feasibility of the repository on the basis of present underground engineering techniques.

Progress and Results

The main achievements for this activity are :

- thermal analysis for different layouts of waste repositories in clay formations;
- a preliminary thermo-mechanical analysis of the far field.

For the thermal analysis some basic assumptions on generation and properties of waste canisters have been defined.

The repository layouts are based on two concepts :

- a matrix of deep boreholes;
- a conventional mine.

For various waste canister geometries the inter-dependence of parameters such as age of waste, distance between canisters and maximum temperature rise in the clay, has been investigated.

For the thermal calculations an existing computer code has been adapted and improved.

The main preliminary conclusions of this work indicate that disposal of radioactive wastes in clay formations would be possible even if the maximum temperature rise in the host medium is limited to 80-100° C. However the relatively low thermal conductivity of clay would require delay times before disposal in the range 30 to 50 years. Significantly younger wastes could be emplaced if the maximum acceptable temperature in the clay were between 150 and 200° C.

From a thermal viewpoint repositories based either on a matrix of boreholes or on a conventional mine layout seem to be feasible. For a repository based on the matrix of boreholes capable of accomodating all high-level and cladding waste generated by a nuclear power programme of 10 000 Mwe x 30 years, between 100 and 150 km of boreholes would be required. The same amount of wastes in a repository based on a conventional mine concept would require between 10 and 20 km of galleries.

For the thermo-mechanical analysis the preliminary calculations have been carried out with a finite element technique.

However the uncertainty about the mechanical behaviour of clay materials at the depth of a few hundred meters is a serious drawback for this study. The conclusion of this phase of work is that a more reliable thermo-mechanical analysis will be possible only when experimental data will become available.

Design work on a HLW repository in a salt dome

Contract : 226-81-7 WASNL, part 2, ECN, Petten.

Scope and Objective

The successful dry-drilling experiment in the ASSE-II mine has shown that a repository with 300 m long boreholes is feasible. The studies in this contract will be focussed on the one-layer mine concept. This design study includes some calculations used as bench marks or validation. This work is complementary to that reported under part 1 of this contract (see § 2.2.6.).

Progress and results

In accordance with the design work on a repository for nuclear waste disposal in salt domes some stress-strain calculations are performed with respect to the closing and sealing of boreholes (see fig. 91). The influence of the nuclear waste in boreholes and the influence of galleries on the stress-strain state in the surrounding salt are treated separately. For each case creep calculations are performed with the finite element program GOLIA. A cylinder of salt around a borehole is modelled by a finite element mesh and the salt, subjected to a thermal load from the nuclear waste, can move only upwards. Boreholes with canisters are simulated with finite continuous line sources, each showing a monotonic decreasing time dependent heat capacity. The numerical results show a strong local disturbance caused by the waste. In axial direction the domain of influence on the stress state extends to about 2.5 m beyond the boreholes. The domain of influence is defined as the area in which one or more stress components deviate 1 MPa from the undisturbed situation, i.e. the elastic solution. Within this area no tensile stresses occur, hence from a mechanical point of view no cracks will be formed.

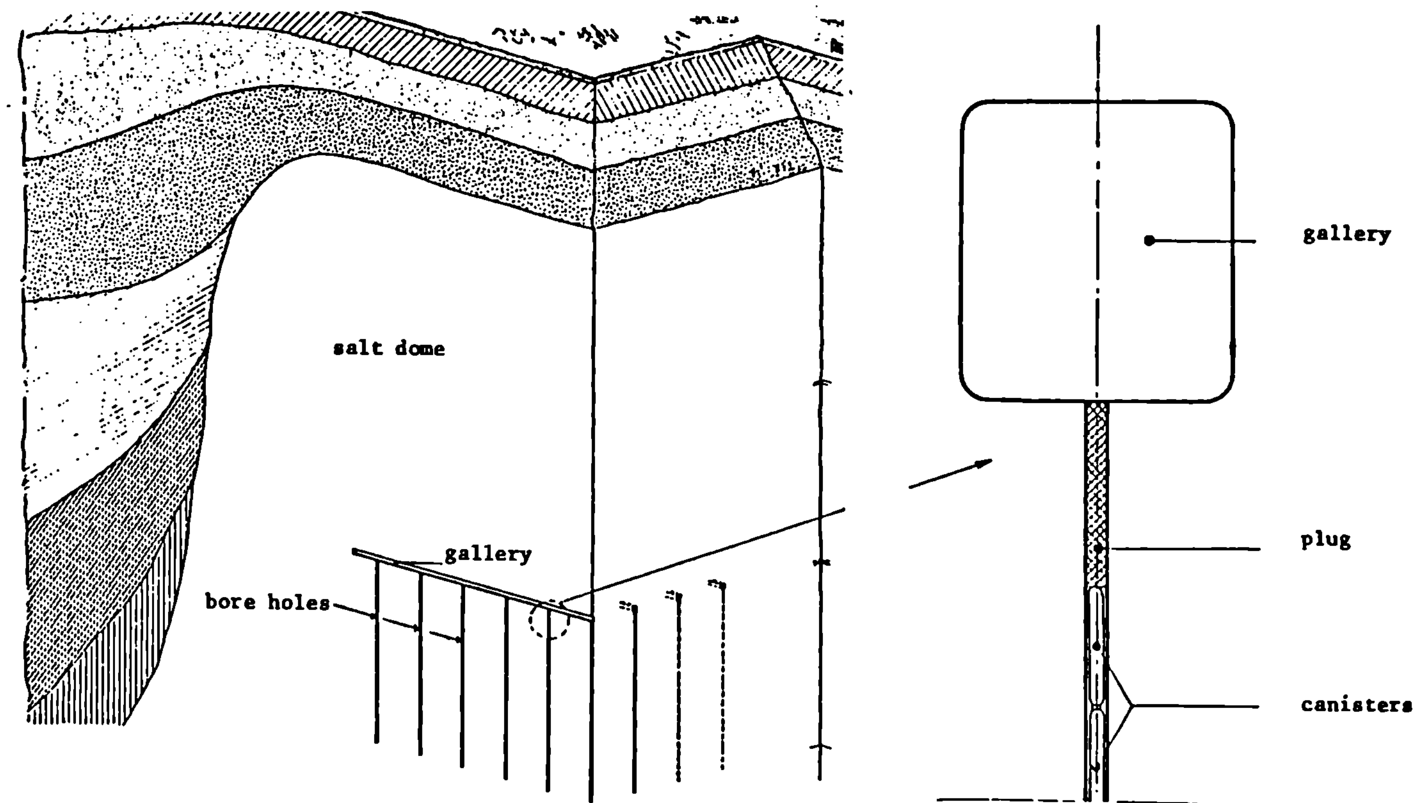


Fig. 91 : Salt dome with disposal holes

2.2.8. DISPOSAL INTO THE SEA-BED

Ocean sediments are considered as being a possible option for waste disposal. In reference to the division of the activities in this field by the NEA Seabed Working Group*, the following research areas are covered in the CEC cost-sharing programme :

- Sediment and rock : behaviour of sediments under elevated temperature and sorption characteristics of the sediments are examined.
- Physical oceanography : research is centered on deep sea currents important for sediment disposal, radio-nuclide transport and dispersion processes excluding the biological chain.
- Engineering studies : main aspects of the feasibility of waste disposal operations are dealt with from port facilities through to final in-sediment positioning and verification of the waste package isolation system.

Progress is reported on five contracts in this field. Support of research of three contracts (NERC/IOS, Delta Institute and CEA Cadarache) ends in 1982 and their final reports are in preparation.

For the second phase of the programme (1983 - 1984) a major reorientation is taking place, focussing on engineering studies needed for the assessment of the emplacement technique.

Reported contracts :

* see also Publications reference (12).

Properties of ocean sediments in relation to the disposal of radioactive waste

Contract : 257-81-7 WASUK, NERC/IOS, Wormley.

Scope and Objective

The objective is to assess the properties of sediments at possible ocean disposal sites in relation to the emplacement of canisters of radioactive waste and the retention within the sediments of radionuclides eventually released from the canisters. In particular the aim is :

- to discover which sedimentary conditions offer the optimum physical situation for emplacement;
- to investigate the chemistry of sediments;
- to study the behaviour of natural actinides in pelagic sediments.

Progress and Results

Work on the physical properties of sediments has concentrated on three topics :

- Continuation of laboratory measurements of sediment properties and of the development of instrumentation for in situ measurements.
- Participation aboard USS "Glomar Challenger" in leg 86 of the Deep Sea Drilling Project (DSDP), including physical properties measurements on high grade hydraulic piston corer samples.
- A study of open burrows in distal turbidites.

Laboratory measurements of permeability and consolidation characteristics of deep sea sediments are well advanced. Development of apparatus for in-situ measurement of hydraulic gradients continues.

IOS participation in DSDP had as its primary objective to obtain undisturbed samples for laboratory tests, especially from red clays that have undergone natural loading. The organization and equipment of the DSDP programme is such as to provide unique quality of sediment samples and an unrivalled set of parallel measurements. This work is still going on.

Careful sampling and observation has revealed the presence of open burrows up to 2 m deep in some sediments. These have been studied in detail and their possible effect on sediment permeability evaluated theoretically.

Studies of sediment chemistry and mineralogy and of the behaviour of natural actinides has concentrated on North East Atlantic carbonate sediments, mainly those collected earlier in 1982 during RRS "Discovery" cruises 125 and 129. Two cores are particularly important because complementary in-situ pore water samples are available.

Results of measurements are available on cores from the following areas :

<u>Cape Verde 1</u> : Only the uppermost 50 cm of a single Kasten Core is useful : work is still in hand.

<u>Cape Verde 2</u> : Three cores have been studies and it seems probable that oxygen is present in the sediments to at least 10 m depth.

<u>Great Meteor East</u> : Pore water studies show that molecular oxygen falls to zero at 30 cm depth. Studies of two of the three cores collected show that about 95 % of the thickness sampled is made up of redeposited

material, probably from shallower water. There is evidence of remobilization and reprecipitation of manganese.

Migration processes in marine sediments caused by heat sources

Contract : 258-81-7 WASNL, Delta Institute for hydrobiological research, Yerseke.

Scope and Objective

The investigations concern simulation experiments with the objective to study diffusion and convection processes in point-source heated sediments and the change of sorption capacities of marine sediments due to elevated temperatures.

The programme can be separated into four items :

- measurements of sorption coefficients as function of temperature;
- correlation of sorption coefficients with sediment properties;
- heat convection experiments;
- mathematical modelling.

Progress and Results

For the evaluation of sub-seabed disposal of hot canisters with high-level radioactive wastes the estimation of the factors, that determine any return of radio-nuclides from the buried sources to the sediment-water interface, is important. These factors are the sorption coefficients and related diffusion coefficients, and the convection factor. K_d studies were carried out accompanied by mathematical simulation studies.

In a series of initial experiments the methodology was tested to determine a method to study the effect of temperature on the adsorption. Cadmium and Atlantic sediments were used for this purpose. A range of concentrations of cadmium was applied to the sediments at several temperatures. These experiments showed a decrease in adsorption at elevated temperatures, which could be explained thermodynamically. The reaction enthalpy was found to be fairly constant in the temperature range 27° C to 75° C and calculated as - 460 $Jmol^{-1}$.

The first determinations of K_d of Pu and Eu (a nuclide with about the same chemical characteristics as Am) with the same sediment as used for the Cd experiements did so far not show any significant decrease in K_d. Ongoing experiments deal with the adsorption of Np, Am and Pu with two different sediments from selected disposal sites in the Atlantic.

Earlier determined sorption data for 10 radio-nuclides with some 30 major ocean sediments from all over the world were used for a statistical analysis. K_d values were correlated with chemical, physical and mineralogical characteristics of the sediments. It followed from these analyses that only the mineralogy had a significant correlation with K_d. Multiple regression analysis showed the impact of specific minerals on the K_d of some radio-nuclides. In this particular study the radio-nuclides Pu, Np and Am were not taken into account, although these nuclides are important in the safety assessment calculations of high-level radioactive waste disposal in the seabed. On the basis of similarities of chemical properties, extrapolation of 'behaviour' in seabed sediments might be possible.

In order to predict the effect of heat sources in marine sediments, convection experiments have been carried out in large and small cylindrical vessels filled with ocean or simulated ocean sediments and with a heat source in the middle.

Simultaneously mathematical models have been used to assess the effect of the heat source in the corresponding experiments. All these models are based on the Boussinesq approximation.

The results of these convection experiments, steered and followed by model calculations, demonstrated that in pore water convection of

10^{-11} m s^{-1} can be archieved at temperature differences of 70° C, (0.3 mm yr^{-1}, for Rayleigh number 10^{-6}).

The combined results allow model calculations on the relationship between the safe-burial depth and release from the seabed, and both the temperature related K_d's and convection coefficients. An inverse square root relationship was found so far for the increase in burial depth and the K_d's or apparent diffusion coefficients, convection excluded. The impact of convection will be an additional factor.

Although the limited amount of results only allow premature conclusions, reduction of K_d's, due to heat, seems to be a possibility for some radioisotopes.

Sorption and migration of radio-nuclides through ocean sediments

Contract : 259-81-7 WASF, CEA, Cadarache.

Scope and Objective

To provide data required to assess the feasibility of emplacing radioactive wastes in sub-seafloor geologic formations, the sorption of radio-nuclides by and the migration of radio-nuclides through samples of Abyssal sediments collected in the North Atlantic are being investigated. The main research areas are :

- determination of distribution or sorption coefficients (Kd) for several Abyssal sediments of various physical and chemical characteristics;
- detailed study of sorption and desorption of long-lived beta emitting radio-nuclides to and from typical sediments;
- study of the biological availability of radio-nuclides.

Progress and Results

The influence of the temperature on retention has been studied in the laboratory at normal pressure. The tests combined :

- four redio-nuclides : Np, Pu, Am, Cs
- five temperatures : 4, 15, 30, 50, 80° C
- two sediments : CVI-KA 4, CV2-KA5 from the Cabo Verde plain
- the sea water of the meditarrenean sea
- Kd measurement by the batch method : 20 ml of water and 0,5 g of sediment.

After equilibrium of sorption, the reversibility has been evaluated by desorption measurements.

Americium : In all cases the retention is very strong (Kd > 10^5 $cm^3 . g^{-1}$), the sensitivity of the counting rate of the activity remaining in solution does not allow to establish an influence of the temperature.

Plutonium : The retention increases with temperature from 4° to 30° C and remains constant above 50° C. At 50 and 80° C the K_d's are nearly equal for the two samples (between 3000 and 3700 $cm^3 . g^{-1}$). The desorption is too weak to be measurable at low temperature, but it increases with temperature; this is probably a resolubilisation effect.

Neptunium : The retention of the cation NpO_2^+, probably dominating in oxidzing conditions, is notable and there is a distribution of the activity between the solid and liquid phases. The temperature plays an important role; the K_d's are higher at 30 and 50° C (between 1200 and 2700 $cm^3 . g^{-1}$ relating to the material) than at 4 and 15° C (300 to 500 $cm^3 . g^{-1}$). This retention is partialy reversible.

Cesium : The retention of the cation Cs^+ decreases with temperature from 4 to 30° C (500 to 300 $cm^3 . g^{-1}$ for CVI-KA4), but it increases strongly at 50 and 80° C (4200 and 7300 $cm^3 . g^{-1}$). The same influence has been found with CV2-KA5 and, for verification, with a pure clay, illite, in sea water. The desorption of the Cs is partially reversible for the range 4 to 30° C (reversibility rate between 60 and 80 %).

On a sediment cope from the Cabo Verde site, sorption coefficients and geochemical values on facies of this core have been measured.

The Kd measurements have been made for the Americium and Cesium with 200 cm^3 of sea water and 0,100 g of sediments at 15° C. For Am, the K_d's are constant and very high, whatever the facies (5 to 8.10^5 cm^3 . g^{-1}). The mean Kd for ^{137}Cs without carrier is 268 cm^3 . g^{-1}. It decreases for ^{135}Cs from 268 to 8 cm^3 . g^{-1} (3,5 . 10^2 to 3,5 . 10^6 pCi . l^{-1}). For all concentrations the desorption of Cs is easy.

In order to define the geochemical properties of the sedimentary layers of the abyssal plain of the Cabo Verde, the analysis of metallic trace elements in several levels of a core of sediments has been undertaken. The elements As, Ba, Br, Ca, Co, Cs, Cz, Eu, Fe, Hf, K, Na, Rb, Sb, Sc, Ta, Tb, Th, U, Yb, Zn, Ce, La, Nd, Nb, Zr are measured; this work is in progress.

Lagrangian current measurements and large-scale long term dispersion rates

Contract : 255-81-7 WASUK, Ministry of Agriculture, Fisheries and Food, Lowestoft.

Scope and Objective

Large-scale long term current measurements are possible by deploying long range neutrally buoyant acoustic floats, called SOFAR floats.

Listening stations have been developed which can be moored at sea and left to record signals from the free drifting floats. A suitable spaced array of such autonomous listening stations (ALS's) would make it possible to track flocks of SOFAR floats as they drift anywhere in the North Atlantic.

The aim of the programme is to extend measurements to the eastern basin of the North Atlantic; it has been demonstrated that the SOFAR floats are the only means presently available of building-up population statistics relating to large-scale, long term dispersion processes.

Progress and Results

The SOFAR float experiment is due to take place in the eastern North Atlantic Ocean late 1984 until 1986. The launch site was selected as being 41° N, 14 - 15° W over the Iberia Abyssal Plain. An initial cluster of six floats will be launched 25 km apart at 3000 m depth and then the remaining floats will be launched singly at nominally six month intervals thereafter, thus converting the initial patch experiment into a plume experiment.

In order to follow the movement of the SOFAR floats, there needs to be an edequate coverage of autonomous listening stations (ALS) to receive the acoustic signals. During 1982 sound ranging trials were performed to measure the sound propagation characteristics of the experimental area. From the results obtained, it was concluded that signalling from the floats between 500 and 3500 m depth is entirely reliable for ALS's at 669 m and 1925 m depth to ranges of at least 1000 km in the summer. This may be reduced in winter to 250 km, which will have implications for the positioning of the ALSs.

The programme is integrated with similar experiments performed by the Institute of Oceanographic Sciences (IOS, Wormley, UK) and Woods Hole Oceanographic Institution (WHOI, USA).

Feasability study of the offshore disposal of radioactive waste

Contract : 256-81-7 WASUK, Taylor - Woodrow Constr. Ltd, Southall.

Scope and Objective

The study concerns the disposal of vitrified waste in drilled holes in ocean sediments.

The aim of the study is to carry out an engineering appraisal of the disposal of radioactive waste in this manner with a view to establish technical and operational feasibility and giving guidance on the economics of installing and running the scheme.

Progress and Results

Phase 1 of the study has now been completed. In this part of the study the emphasis was placed on establishing the reference criteria, assessing the principal problems and evaluating potential solutions.

Taking as reference criteria the maximum expected quantity of waste as 400 m^3 of glass per year and the disposal location near the Great Meteor Sea Mount, the preferred solution that emerges is as follows.

- Drilling

  For reasons of safety as well as convenience, the holes would be formed in a separate operation from the disposal. A large drilling ship of a type similar to the "Discoverer Seven Seas" would be employed. After jetting in the casing of the upper part of the hole and the reentry cone, drilling would be carried out without a riser, using water as lubricant where possible.

- Offshore structure

  Two forms of structure are currently being evaluated, a large concrete platform of a semi-submersible form, and a barge designed not to respond to the prevailing sea conditions. The displacement of each would be of the order of 250.000 tonnes.

- Transport and offloading

  The radioactive waste would be transported by a number of supply vessels of a type common in North Sea operations, but equiped with dynamic positioning. Each vessel would be capable of carrying 1000 tonnes and would be offloaded by conventional cranes assisted by some form of motion compensator, during calm weather only.

- On board handling

  From their storage area on deck, flasks would be transferred to a submerged unloading cell where the individual canisters would be removed under remote control, and assembled into strings of 100 - 200 m in length. The wet cell method offers considerable savings in weight and cost over the dry cell method, as well as reducing the risk of contaminating the lowering system. Fig. 93 indicates a possible layout for the unloading cell.

- Lowering, emplacement and backfilling

  Canisters would be lowered on the end of drilling pipes which would also be used to place any backfilling material. Cementitious grout has been identified as the most suitable backfilling material. After canisters have been placed, the top 200 m or so of the casing would be cut out.

- Station keeping

  A study commissioned from Brian Watts Associates has shown that the power required for station keeping is of the order of 36 MW for the concrete semi-submersible.

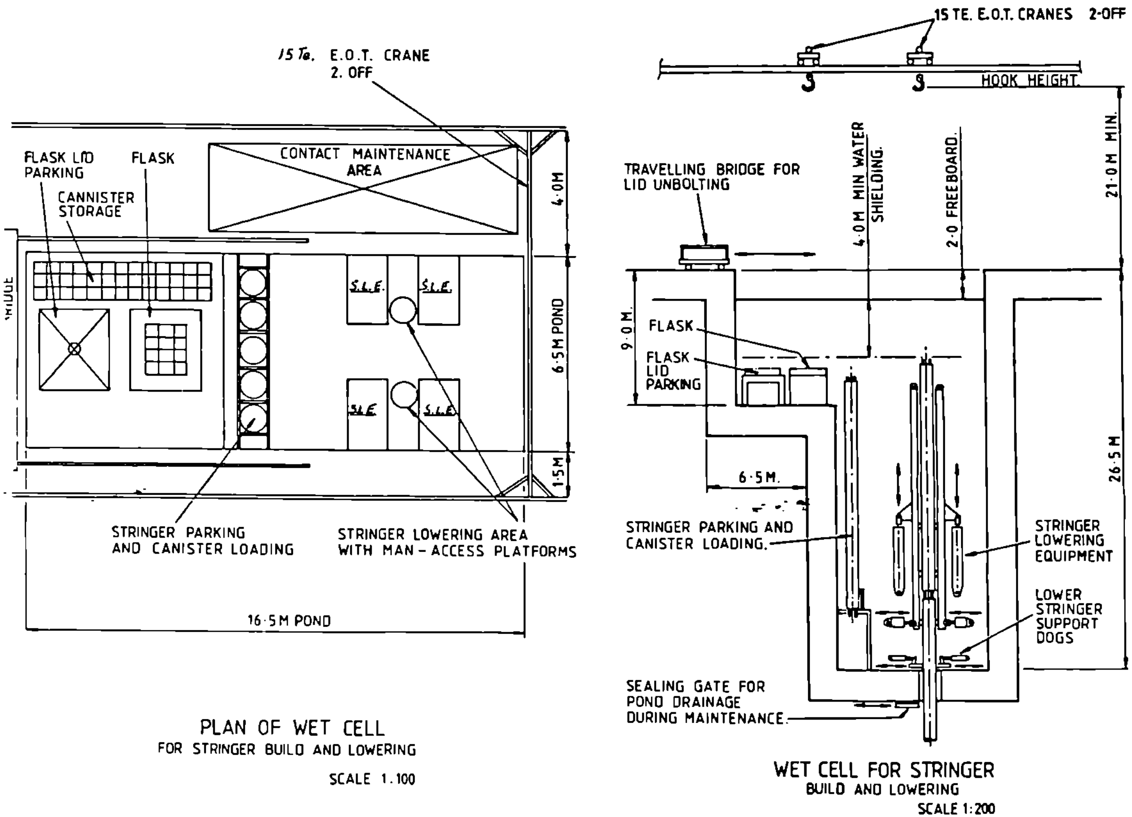


Fig. 93 : Possible lay-out of submerged unloading cell

2.2.9. DEVELOPMENT OF SITE ASSESSMENT TECHNIQUES

This chapter covers methods and techniques developed to gain a better insight of large-scale rock properties, with particular attention paid to

- deep and shallow hydrogeology of fractured rock formations (borehole and airborne measurements);
- remote assessment of sediment permeability by use of sonic wave velocity measurements;
- characterization of deep features of clay basins using informations gained on surface;
- detection of fractures at some distance from exploratory boreholes in granite, and not only in its immediate vicinity.

The following contracts are reported :

Development of techniques for the assessment of geological formations

Contract : 128-80-7 WASUK, part 3, NERC/IGS, Harwell.

Scope and Objective

This part of the contract aims at developing new methods with a view to better characterize typical features of crystalline rock hydrogeology :

- a special borehole geochemical probe for the analysis of groundwater geochemistry without sampling, i.e. without perturbation of the local conditions;
- a special sinusoīdal pressure borehole testing method for the determination of fracture and matrix permeabilities;
- a thermal infrared airborne linescan technique for determination of groundwater discharge points, i.e. of better characterization of shallow groundwater hydrogeology.

Progress and Results

- During the year the development of the borehole geochemical probe has continued. Eh, oxygen, chloride ion, conductivity and pH electrodes have been completed and pressure tested along with the associated electronics. In order to provide maximum flexibility of operation the surface electronics are provided with a microprocessor controller and a video display for the results, as they are fed to the data logger. Although the probe and its control electronics have been completed, field testing has not yet taken place.

- Over the contract period IGS has been developing a new technique involving cross-hole sinusoidal pressure testing to measure the hydraulic properties of low hydraulic conductivity crystalline rock. The initial appraisal covered two basic configurations : that of a point source and that of a line source within homogeneous isotropic porous media. A programme of further analysis development has been undertaken to cover a number of situations such as a line source with interacting slabs of porous rock, a point source in anisotropic homogeneous rock and a point source with interacting blocks of porous rock. These "dual-porosity" analyses introduce an interesting facet of sinusoidal testing : the possibility of changing the frequency of the signal in order to investigate either the diffusivity of the fracture system only or of the whole system (fractures and matrix). A field test of both the theory and the experimental equipment was carried out in December 1981, using two adjacent boreholes in a quarry in Cornwall, and results have been analysed over the present contract period. Positive signals were obtained from 7 receiver zones of one borehole as a result of sinusoidal pressure fluctuations generated within a 7 m zone of another borehole 25 m away. Of the 7 positive signals obtained, 2 were interpretable using a model involving cylindrical flow in a homogeneous porous medium, but in order to interpret the other 5 the model had to consider cylindrical flow in a fissured porous medium broken up into slabs between 20 and 40 mm in thickness.

- The thermal infra-red linescan survey was successfully completed during February 1982. The total coverage achieved during the survey was about 270 line km. Because of duplicate coverage of some areas the total area surveyed was about 63 sq. km. The photographic records identified three general categories of groundwater discharge in the Altnabreac area. These are : distinct point discharges emanating into the headwaters of streams or along the stream bank sides; groundwater discharges into the beds of the streams or rivers; and springs which manifest themselves as the thermal anomalies on the surfaces of Du Lochs.

Where the thermal anomalies are particularly distinct, the somewhat subjective analysis of the data presented on the preliminary photographic records has been satisfactory. However, where more detailed results were required a digital image enhancement technique was used. The most useful technique is to identify a spring discharge zone on the image, determine the spectral and temperature ranges of the zone and then to identify all other zones on the image with the same characteristics, to the exclusion of all superflous information. Colour coding the resulting image enables considerable detail to be highlighted. The thermal infra-red linescan technique has not only proved that it is fully capable to identifying groundwater discharge points, it has also demonstrated that the groundwater component of the streams and rivers in the Altnabreac area is higher than previously expected.

Remote assessment of permeability/thermal diffusivity of ocean sediments

Contract : 263-81-7 WASUK, University College of North Wales, Anglesey.

Scope and Objective

The aim of this study is to examine the feasibility of predicting marine sediment column permeability and thermal diffusivity by remote geophysical observations. To this end the standard soil consolidation apparatus (the oedometer) has been redesigned to allow a study of the consolidation behaviour of marine silts and clays, in association with observations of P- and S- wave velocities, electrical resistivity and thermal condictivity. A suite of samples from a deep sea environment are currently being studied in this modified apparatus.

Progress and Results

- The modified consolidation cell (fig. 94)

  The cell design closely follows the classical lines of the standard consolidation or oedometer cell. Around this basic unit the elements required for the various geophysical measurements are integrally housed : the P- and S- wave transducers above and below the porous discs confining the sample, resistivity electrodes. A thermal conductivity needle probe (or temperature sensor) can be inserted.

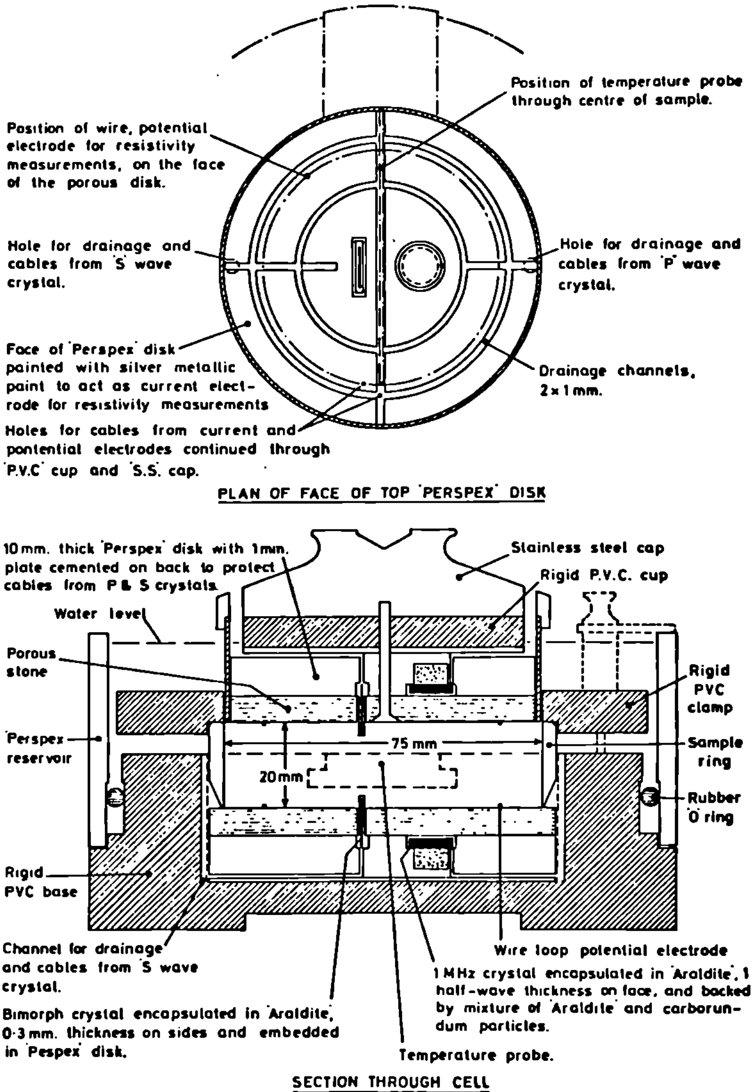


Fig 94 The modified consolidation cell

- The measuring systems

  The consolidation behaviour of a sample is monitored via a micrometer dial and a linear variable displacement transducer, as pressure is applied on the sample. Electrical resistivity measurements are made in an attempt to improve the accuracy of the permeability prediction from the geophysical measurements. Thermal conductivity measurements are achieved by use of a specially designed needle probe.

- Results

  Initial results show that the inclusion of the geophysical elements in the cell has a minimal interference effect on the consolidation behaviour of samples. The thermal conductivity measuring system has overcome the problems imposed by the size of the sample and the need to restrict the temperature variation of the sample. A suite of samples from a deep sea environment is now being tested and detailed data analysis is in progress.

Deduction of some characteristics of large deep clay deposits by low cost surface survey

Contract : 239-81-7 WASI, ENEA, Casaccia, Italy.

Scope and Objective

This work aims at forecasting general mineralogical and sedimentalogical characteristics of deep clay deposits from observations on surfacial outcroppings. Special items are :

- assessing regional distribution pattern of different, if existing, clay mineralogical associations;
- assessing possible relationships between parent rock of clay formations and mineralogy derived from sediments;
- assessing structural and sedimentological variations of clay bodies according to evolution of the basins.

Progress and Results

Previous work has shown that :

a) clay mineralogic associations show a regional distribution pattern, i.d. the effectiveness of many mineralogic provinces at the italian scale is demonstrated;

b) other than from depositional mechanisms the mineralogic differential distribution pattern is due also to the lithologic nature of parent rock of the clay.

These results account for the possibility of forecasting general mineralogic composition of deep clay bodies starting from observations at surface.

During 1982 further investigations have been directed towards two types of basins prevailing in the italian territory :

a) seaward open basin with only one border formed by gentle mountainous reliefs, widespread in the eastern adriatic side of the Appennine chain;

b) tectonic very deep basins, of graben type, widespread in the western thyrrenic side of the Appennine chain.

For the first type two basins have been considered, Vasto, in the Adriatic area, and Crotone in the Ionian area. They differ for the mineralogic nature. For the second type the Val d'Era basin, in Tuscany, has been selected. Complementary zones have also been examined. The main results are :

- the regional characteristics of the composition of different basins is further confirmed, as well as the influence of parent rock in causing different mineralogic composition of derived clay;
- slight mineralogic and granulometric variations have been however recognized in the single basins both in horizontal and vertical directions.

The research programme will be concluded by the general evaluation, now under-way, of the collected data. Complementary investigations are also in progress on geochemical, geotechnical, microtextural and paleontologic characteristics in the most significative situations of the clay basins.

Development of a geophysical methodology for site assessment

Contract : 264-81-7 WASF, BRGM, Orléans.

Scope and Objective

The aim of this research is to characterize the fracturation in depth at different scales :

- close vicinity of the boreholes (centimetric to metric scale) : use of classical borehole logging (electrical and nuclear probes mainly);
- decametric scale : use of dipole-dipole electric and electro-magnetic probes to assess the continuity of the fractures encountered in the vicinity of the boreholes. An "investigation width" of decametric order can be reached;
- cross hole measurements : cross-hole "mise à la masse" technique gives an idea of the continuity of the main fractures joining two boreholes.

Progress and Results

The whole field work has been carried out on the site of Auriat (Creuse - France), where two deep boreholes in granites (500 and 1000 m) were available. Nuclear and electrical borehole logging has been done throughout the total lenght of the two boreholes. The electrical and electromagnetic dipole-dipole survey covers the same area. The cross-hole "mise à la masse" has been applied to the common non-cased parts of the two boreholes (250 - 500 m) which are rather close (10 m) to each other. Seventeen transmitting points have been choosen on main fractures in any of the two boreholes, while the measurements were made continuously in the receiving borehole for each of the transmitting points.

Borehole logging

The gamma-gamma and neutron logging results have been transformed into density and neutronic porosity logging. Cross-plot correlation between the different physical parameters deduced from the logging, and the fracturation (number of closed and opened fractures per meter, on samples) show the interest of normal resistivity (16 and 64"), gamma-gamma, and neutron logging for the detection of the fracturation on granites. The normal resistivity results have been interpreted using a tabular model, which has been applied to give the theoretical response of other electrical arrays (especially dipole-dipole). The coincidence between the theoretical and field loggings gives an idea of the tabularity of the granite.

Dipole-dipole methods

The electromagnetic probe reveals its too low frequency, regarding the high resistivities encountered in Auriat (10 to 50 000 ohm.m). Its interest is thus less in this case than the electrical dipole-dipole probe, which enables to characterize the lateral extension of the different fractures.

Cross-hole "mise à la masse"

This technique has proved its feasibility in the field. The records show much information, especially the comparison from a transmitting point to another. Interpretation with a conductive layer inside a homogeneous half-space helps to understand the field results, although more interpretation (two or three-dimensional) would reveal itself particularly necessary in this case. As a result, an estimate of the fractures intersecting the two boreholes can be given.

Development of a borehole probe for measurement of permeability and hydraulic pressure in rocks with low permeability

Contract : 261-81-7 WASF, CEA-Télémac, Asnières.

Scope and Objective

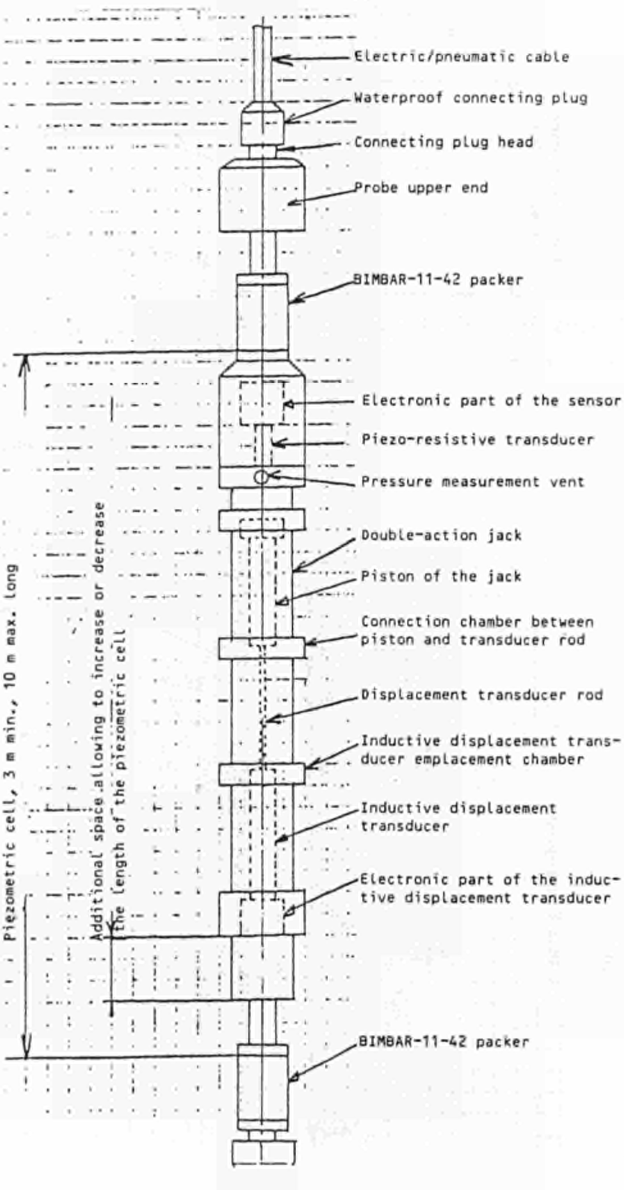
This new method of hydraulic measurement in deep boreholes shows two particular aspects :

a) a special equipment of the tested borehole. In order to avoid perturbations of the local hydrogeology by the borehole itself (i.e. mixing of waters from different levels), the borehole is cased and cemented except at discrete locations where testing will occur later. At these locations, the casing is perforated and a connection is established between casing and borehole wall by a porous material. Prior to testing, the internal side of the perforated casing is covered by a rubber sleeve, kept in place by the weight of the water column filling the borehole (fig. 95);

b) a special testing method. Conventional packer testing is used to measure water pressure and permeability at the selected locations, the pressure of the groundwaters is transmitted to the measuring cell through the rubber sleeve, the stiffness of which is negligible. This again avoids risks of interference between several tested levels (fig. 96).

Two kinds of measurements can be made :

- water head at specific locations : the pressure of the groundwater and in the packered interspace are equilibrated and a pressure transducer gives the direct measurement of the water head;
- permeability measurement : a given volume of water is extracted "instantaneously", which induces a drop in pressure. The relationship between pressure change and time in the packered interspace (i.e. at the borehole wall) allows the calculation of the permeability.



'ig. 95 : The measurement probe

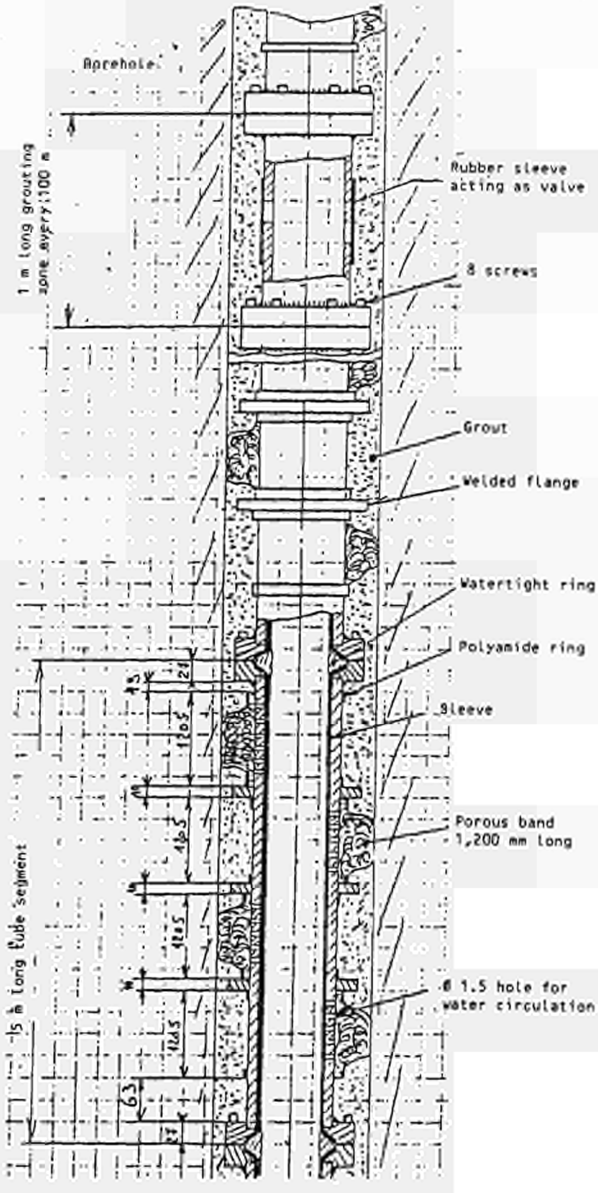


Fig. 96 : Schematic section of the equipped borehole

Progress and Results

The development of the borehole equipment and the measurement devices is underway; subsequently, testing will be performed on a selected borehole in a granite formation down to 500 m deep.

- Equipment of the borehole

  The borehole casing will be made of several steel sections, each being 5 m long, internal diameter 76 mm assembled by screwed flanges. At specified locations, these sections will be performed and covered by a porous material, which will ensure the continuity between the borehole wall and the casing. Some special latex foam has been selected with a view to its resistance to abrasion, mechanical strength and permeability. Between sections the casing will be cemented to the borehole wall with a special waterproof cement grout still under development; this grout could be charged with chemical admixtures or bentonite.

  The rubber sleeves will be fixed on the internal side of the perforated casing sections at the time when they are manufactured. A prototype series of these sleeves is being produced.

- Measurement devices

  The probe, inserted between the inflated packers, comprises a volumetric pump activated from the surface, a piezo-resistive pressure transducer and a displacement transducer which allows the determination of the water volume being pumped out. All these devices, together with the inflatable packers and connection cables to the surface, are still under development.

  The surface unit, including monitoring and electronic recording devices, will be manufactured later on.

2.3. PERFORMANCE AND SAFETY EVALUATION OF RADIOACTIVE WASTE DISPOSAL IN GEOLOGICAL FORMATIONS

This chapter is subdivided in two parts :

- The safety analyses, which cover studies being site oriented. These studies represent the follow-up of the previous programme on the clay formation at the site of Mol and on the salt dome of Gorleben.

- The PAGIS action (performance assessment of geologic isolation systems), which has been launched by the Commission at the beginning of 1982 in agreement with the ACPM of the Plan of Action "Waste Management and Disposal", as described in the 1981 Annual Report, pp. 292-293.

  This action aims to collect, pool and make use of the available information for the performance assessments and the safety evaluations. It thereby aims to use commonly agreed safety approaches and harmonized methodologies in the calculation of long term release of radionuclides from nuclear waste repositories.

  The five contracts signed in 1982 cover the first phase of PAGIS, which aims at the selection of basic data and models, at the definition of release scenarios and at the development of appropriate methodologies.

  No R&D work is included in this phase.

  Four reports are concerned with progress in data collection referring to HLW repositories in clay, salt, granite and sub-seabed

  A common scheme has been adopted and the collection and selection work has been subdivided in several tasks.

  A fifth report deals with the horizontal problem of modelling the radio-nuclide migration in the biosphere for the three continental formations and, appropriately adapted, for the sub-seabed.

The following contracts are reported :

2.3.1. SAFETY ANALYSIS

Safety analysis of waste disposal at the Mol site

Contract : 144-80-7 WASB, part 6, CEN/SCK, Mol.

Scope and Objective

Long-term safety analysis studies on possible nuclear waste disposal at the Mol site were focussed upon two scenarios selected previously : the glacial erosion scenario (in cooperation with JRC-ISPRA) and the base scenario of the normal natural evolution of a clay repository.

Progress and Results

A preliminary glacial erosion scenario was already developed last year. For the sake of scientific soundness and acceptability by the scientific community the glacial erosion scenario has been reworked after experts opinion confrontation. Main outputs of this experts opinion confrontation are that the geological sampling (time and area), used as reference, are of prime importance for putting together a glacial erosion scenario and that the time sequence of the different glacial dynamic phases needed to be revised.

Calculation of the consequence of a glacial erosion action upon a HLW repository underlying the Mol-site is planned for beginning 1983. For taking into account the uncertainties associated with the parameters involved, the latin-hypercubic sampling is foreseen. This technique has already been studied by the JRC-ISPRA.

For the repository evolution analysis still most effort was devoted to modelling aspects and especially to the evaluation of the importance of assumptions, related to geometry and pulse type of the source term.

Thus a refinement of the analytical solutions in the migration model was performed, together with calculations for different parameter sets.

All computations indicated that for the Mol-site extremely low release rates of radio-nuclides are to be expected at the clay-aquifer interface. Refinements in the model will thus probably not bring about any significant changes. However, these refinements may be required because the migration model is to be used for the base line scenario, in conjunction with abnormal scenarios (e.g. faulting, glaciation, human intrusion, etc.) and because the base line scenario should reflect as true as possible the phenomena involved.

The results of this activity will be essential for the clay option in the action PAGIS (see contract 272-82-75 WASB). For this action CEN/SCK already collected data for clay sites in Belgium (Mol), United Kingdom and Italy. A selection was also made for a reference repository design and (together with the secretaries of the other options) a set of reference data for the solid HLW was selected. A comparative study was undertaken in order to evaluate available models for dose calculations, geosphere transport and leaching.

Safety study for the disposal of radioactive waste in the salt dome at Gorleben

Contract 270-81-7 WASD, Hahn-Meitner Institute, Berlin.

Scope and Objective

The aim of this research work is to identify release scenarios for the planned repository in the salt dome of Gorleben and to evaluate the corresponding consequences. The results of these works shall demonstrate the possibility to perform a site-specific safety analysis. They will also provide data which will subsequently be used in the action PAGIS (see contract 273-82-75 WASD).

In order to identify scenarios which may effect the integrity of the repository, those processes will be simulated and analysed, which

a) are predictable to a large extent (e.g. behaviour of the salt dome under the influence of a repository), and

b) whose tendencies can be estimated relatively well within a reasonable time frame (projection of the tendencies observed for the past into the future evolution of the site).

The method used here is essentially a deterministic one. Uncertainties are to be estimated by suitable statistical methods.

Progress and Results

- Test of the applicability of information on the site and the technical concept for mathematical models

  On the basis of the actual state of planning for the Gorleben repository first correlations have been made for the mechanisms with which the release of radio-nuclides from a brine-flooded repository can be modelled. Mechanisms which are taken into account are : thermally induced convection, diffusion and expulsion of brine caused by the creep behaviour of salt (convergence).

  The barrier models established with these first correlations have been used to evaluate the release of selected radio-nuclides (Sr-90, Tc-99, I-129, Cs-137, Pu-239) in view of demonstrating the applicability of the proposed procedure.

  After the evaluation of the nuclide release from the disposal formation the distribution of the nuclides in the geological layers over the salt dome will be calculated including effects of convection, dispersion, diffusion and sorption. First two-dimensional calculations have given 900 years of time for a convective transport from the point of release to the edges of the salt dome. Three-dimensional calculations will be used in connection with field data (determination of the age of deep groundwaters, borehole measurements of groundwater velocities) to support the data on water flow.

Assuming a ratio I-129/Tc-99 of about 1 to 500 (curie per weight unit) in the disposed waste, the annual individual dose from each of these radio-nuclides will be in the order of 100 m rem if the near-surface groundwater around the repository is used for drinking purposes.

The experiences with the applied procedure have been found satisfactory. Data used in certain fields (convergence processes, permeability of backfill and sealing material, solubilities) are not yet sufficiently reliable.

- Development and exemplary demonstration of a site-specific and self-consistent analysis for the post-closure period of the repository

  As for scenarios of the type "water intrusion into residual hollow space of the mine" a time interval for the possible occurance of this scenario will be defined on the basis of convergence calculations. Intrusion of water into residual space is no longer possible if this space has been closed by convergence. The necessary calculations with respect to convergence are being started now.

  Geological events leading to a release of nuclides will be deduced from results of consequence calculations under the assumption of conceivable scenarios like subrosion. For the latter scenario the definition of a consequence model has been started, which allows to establish time intervals within which these events show sizable consequences. From this, parameter domains for the subrosion rate can be deduced and conclusions can be inferred, identifying parts of these domains where a more detailed knowledge of the subrosion rate is required.

  Events which took place in the North-German Lowland in the geological past are being investigated by a geohistorical analysis. Events taken into consideration are glacial times, tectonic events, epirogenese, halokinese and subrosion. The respective works have not yet been finished. There is the intention to extrapolate some chosen events into the future and to investigate their influence on the integrity of the salt dome.

  It is also planned to reach estimates for the extent to which the present hydrological conditions of the overlaying rocks can be changed by future geological processes. This should ensure that the long-scale considerations also take into account those geological situations which may, under certain circumstances, have the largest radiological consequences.

In view of preparing a consequence analysis for several release scenarios, the boundary conditions for this analysis have been fixed from the description of these scenarios. Scenarios for the further considerations of the threat to the repository due to influences from the waste and the mine are

- limited intrusion of brine (about 1000 m^3) into a closed section of the repository
- water intrusion through the main anhydrite at the beginning of the post-closure phase
- water intrusion through a future man-made drilling into the residual hollow space of the mine
- future solution mining of cavities.

2.3.2. PERFORMANCE ASSESSMENT OF GEOLOGICAL ISOLATION SYSTEMS (PAGIS)

Evaluation of the performance of clay formations in view of the disposal of HLW

Contract : 272-82-7 WASD, CEN/SCK, Mol.

Scope and Objective

In the framework of the PAGIS action, CEN/SCK Mol has been charged with the secretaryship of the clay option for the phase 1 of this action. It has also been one of the consulting interlocutors during the launching phase 0 of the PAGIS-action.

Contractually several tasks have to be fulfilled. Below a brief review is given of the progress make and the status of the work performed for the different tasks.

Progress and Results

Task 1 : Site selection

Its aim is to select for the PAGIS-action one or more argillaceous sites, covering the conditions that may be found in member countries of the European Community. On the basis of the European catalogue of geological formations presenting favorable characteristics for the disposal of solidified high level radioactive waste and in agreement with the ACPM of the Plan of Action "Waste Management and Disposal" and other bodies in the countries desiring to contribute to the clay option, the Mol site has been chosen as reference, while sites in the United Kingdom and in Italy will be the variants.

Task 2 : Site and regional data

This task covers the gathering of available data of the reference site and of the variants or alternative site conditions.

For the Mol-site as well as for the site conditions in the United Kingdom and in the Val d'Era-area, data have been compiled relative to the hydrology, geomorphology, lithology, tectonism, structural geology, etc.

A draft document has been prepared, dealing with the Mol-site conditions. Reports concerning site data from U.K. and Italy were provided by contributing parties from these countries.

Co-operation has been provided to the co-ordinating staff of the Commission in order to prepare an outline of the report structure concerning task 2, taking care of a systematic presentation for different site conditions.

Task 3 : Repository design data

A review has been performed of the repository designs made specifically for clay host formations.

The repository design worked out in the frame of a feasibility study coordinated by SCK/CEN, specifically for the Boom clay formation at Mol, has been selected as the reference case.

The repository concept selected consists of a parallel set of galeries, with HLW disposal holes at the bottom of these galeries.

The galeries will be lined in order to keep them open and in operation condition. Also a casing of the disposal holes is foreseen. The underground set of galeries is connected with the surface by a limited number of access and ventilation shafts.

A variant concept is also considered by SCK/CEN now. It differs from the previous one by the horizontal emplacement of the HLW within the galeries themselves. In this variant concept also MLW could be emplaced, together with the HLW, in the galeries. A preliminary design study of this variant concept has already been made. However no feasibility study, taking into account handling of the waste repository development, etc. has been undertaken yet.

Another alternative repository design has been developed in Italy by ISMES (Bergamo) for ENEA (Rome) and will be taken into account in PAGIS. It consists of a matrix of deep vertical disposal holes, drilled from the surface. Dimensioning calculations have been performed taking into account Italian clay site conditions and limitations by thermal loading.

Task 4 : Methodology

It was examined, together with the secretaries of the other options and the co-ordinating staff of the Commission, if a common methodology for the performance studies could be followed for the four options.

Applied to the clay option, the methodology proposed by the NRPB seems to be a good starting platform for the purposes of the PAGIS-action. Based on the knowledge already gathered by CEN/SCK Mol (see paragraph 2.3.1.), it is believed that the following two scenariois are of interest for the performance studies :

the normal degradation scenario (= base line scenario) and a faulting scenario (= abnormal, disruptive scenario).

Task 5 : HLW reference data

In collaboration with the secretaries of the other options and with the Commission, an attempt has been made to agree upon a common representative waste type (reference type), their sources, quantities, characteristics, properties and radio-nuclide content. The COGEMA solid HLW has been selected as the reference waste for the clay option.

Task 6 : Waste degradation

In order to evaluate and promote modelling efforts and data availability concerning the waste degradation, the clay option secretary participated to a CEC working party on solid high level waste (subject of § 1.5.).

At the JRC-ISPRA, the Commission is working out a geochemical model for waste degradation in argillaceous environments. This model may be used in PAGIS for the clay option.

On the other hand a literature review has been performed concerning the leach models and their associated R&D programs. As a conclusion of this review in 1982, it seems that there is only the Swiss LEACON-model and its associated programs, that constitute a progress compared to the earlier very simple models.

Task 7 : Canister degradation

In a similar way, as for task 6, the CEN/SCK participated to a working party on "Corrosion behaviour of HLW-containers" .(subject of § 2.2.3.). Research groups of CEN/SCK and JRC expressed their interest in developping and/or collaborating work on canister degradation modelling in argillaceous environments. It is expected that research on canister degradation under simulated repository conditions will provide soon valuable data.

Task 8 : Interaction of the repository with the host rock (nearfield)

In 1982 no specific near-field model has been developed by CEN/SCK, but modelling work performed by NRPB and JRC-ISPRA has been followed.

Task 9 : Interaction with the formation

The model for migration of radio-nuclides within a clay formation, developed by SCK/CEN earlier, has been reworked for several source term geometries and pulse types. Reporting is foreseen for 1983 (see contract 144-80-7 WASB, part 6).

Task 10 : Migration through surrounding geologies

For this task also a literature review has been made of the available geosphere transport models and associated programs. Several criteria have been handled for reviewing these : availability, program operation (language, in and output, etc.), validation and applications, numerics, etc. Provisionally the models/codes GETOUT, RANCH and MMT I D appear interesting for a first evaluation.

Task 11 : Interaction with the biosphere

This is a horizontal study which will be carried out by NRPB (see contract 276-82-75 WASUK). However a limited literature review of available biosphere models, applied to geological disposal, has been made by the clay option secretary.

Evaluation of the performance of salt formations in view of the disposal of HLW

Contract 273-82-75 WASD, HMI, Berlin.

Scope and Objective

National research work for waste disposal in salt has been or is being performed in Denmark, France, the F.R. Germany and the Netherlands.

The collection of the results of these investigations is the task of the secretaryship "salt", taken by the HMI as one of the four secretaryships of PAGIS, and is performed in close cooperation with the other interested parties in the Community.

Progress and Results

The components of the waste repository system (region, site, repository design, waste inventory and barriers) as well as the definition of events and release scenarios and of a methodology (including models and codes) are being selected for each country. The sites are defined either as reference or variant sites, each of them allowing still for parameter variations in order to take into account other similar formations which might be regarded as possible repositories by the E.C. countries.

The existing information (scientific background, data and assessment calculations) will be collected from all available sources like publications, expert advice and technical meetings. The data will be reviewed critically, in particular in view of a possible harmonization with those of other geological formations of their variability range and hence of their justification to be used for parametric calculations in PAGIS phase 2. They will be published in a final report at the end of PAGIS, phase 1.

The collected information has been presented in terms of the following 11 tasks :

Task 1 : Site selection

Reference site : in the F.R. Germany the salt dome of Gorleben has been selected as a potential repository and is being investigated more closely for its suitability for disposal of high level waste, preparatory to a licensing procedure. It will serve as reference site for the PAGIS calculations. A salt dome in the Netherlands, which is being closely investigated by the national institutions there has been chosen as a variant for PAGIS. Other variant sites are a deep lying salt dome in Denmark, for which a comprehensive report of 1981 exists, and a bedded salt formation in France.

Task 2 : Site and regional data

For the German reference site some regional geological and hydrological data have been collected. They will still be enlarged and supplemented by similar data for the other reference and variant sites. Moreover a common version of presentation for all-the four secretaryships is being prepared by the Commission.

Task 3 : Repository design data

The main guide-lines and their variability range for the design of the German reference repository have been prepared and will also be put into a common shape. The Dutch and French concepts will be the same, whereas in Denmark deep boreholes will be applied.

Task 5 : Reference high level waste data (inventory)

The German waste inventory has been summarized together with its possible variations. It will probably not differ much for the other sites. Hence a common inventory was agreed upon for PAGIS with corresponding variability of parameters.

The two available isotope-generation and depletion codes ORIGEN 2 and KORIGEN have been presented, so far without preference for any of them.

Task 4 : General methods for safety analysis

A normal evolution and some failure scenarios are available for the German and Dutch reference sites and have been stated together with the corresponding geological time frames. First steps have been taken in order to coordinate among the partners the methodology for the safety analysis. Codes for their calculation have been mentioned. Calculations are being performed in the German safety studies project PSE (see also contract 270-81-7 WASD) and by the Dutch partners. However, no reliable results are as yet available. Barriers which are effective against release of radionuclides from the repository are described in detail in the tasks 6 through 10.

Task 6 : Waste degradation

The first barrier for the high level radwaste, the glass matrix, has been investigated intensively with respect to its degredation. The German results have been collected and the tentative models described. The variability of parameters remains to be stated.

Moreover a paper for discussion with experts on HLW conditioning (§ 1.5) has been prepared in view of the choice of a waste degradation model.

Task 7 : Canister degradation

Data on the canister are given, but models of its degradation have not yet been developed to any considerable extent in Germany.

Task 8/9 : Interaction between host-rock formation and repository

The behaviour of salt rock as geological barrier under the defined scenarios, and of the technical barriers such as sealings and backfilling, is being studied intensively in Germany. The resulting data have been stated, but they must be supplemented in the course of time. The preliminary models describing the fluid and rock mechanical interaction exist.

Task 10 : Migration through the overlaying geosphere

Data and models for, and calculations (see 2.3.1.) of migration of the released radionuclides through the overlaying cap rock as a last barrier are cited, but reliable results could not be stated yet for the German site.

A migration questionnaire for required data has been prepared.

Task 11 : Interaction with the biosphere

Source terms have not yet been supplied; models are expected to arise from a horizontal study being performed by NRPB (see contract 276-82-75 WASUK).

Evaluation of the performance of granite formations in view of the disposal of HLW

Contract : 274-82-7 WASF, ANDRA, Paris.

Scope and Objective

Description of progress in the PAGIS-action by the secretary-ship for the granite option.

Progress and Results

Since the beginning of the PAGIS action phase 1, the secretary-ship for granite has gathered information covering the various sections of the evaluation of the isolation systems for vitrified high level wastes in granite.

This information will be completed by the results of the studies in progress and by data which depend on the options still open.

- Selection and definition of sites (Task 1 and 2)

  A description of the sites has been given in a report circulated to the PAGIS secretariat. Three reference types for granite sites were selected, namely :

  . Outcrop granite

  . Granite with a cover of various sediments

  . Coastal granite.

The selection made does not correspond to any real specific site, but the data and characteristics are representative of realistic situations in E.C. countries.

. Outcrop granite

The reference site corresponds to a massif of the "elliptic section cone type" which covers an area of 90 km^2 where granite can be found in two forms : one of medium-size grain (main facies), the other one of fine-size grain.

The mineralogical and chemical compositions of each variety of granite is described in the above-mentioned report as well as the structural data (pictures of fractures and lineaments).

The equivalent permeability (K) of the rock decreases with depth :

$$K = 6.10^{-9} \text{ m/s from 0 to 50 metres}$$

$$K = 10^{12} \text{ m/s from 540 to 1004 metres.}$$

. Granite with a cover of various sediments

Granite is covered with a sediment mantle of low permeability rock. Starting from the ground level to granite we find successively :

- limestone
- clay
- sand stone
- limestone in contact with granite.

The properties of the granite sub-mantle will be the same as those adopted for the outcrop granite. This site representation has been developed in cooperation with the Institute of Geological Sciences.

. Coastal granite

The granite of this massif spreads over :

- an emerged part of 60 to 100 km^2
- an underwater part set on a sediment layer, which is more recent than the underlaying granite. The underwater part with sediment layer is spreading over 500 km^2.

The emerged granite has two quite similar facies. The fracturation aspect of this part is not very visible (loess covered).

The emerged granite can be found at the edge of a sedimentary bassin where faults located at 60 km from the coast have been spotted during geophysical campaigns.

- Repositories design (Task 3)

Two types of repositories have been suggested in connection with the age of the high level waste at the time when the repository is closed. The first type is based on a closure-time of 30 years (case I), for the second one this age is 100 years (case II). The maximum temperature increase at the backfill/granite border equals 80° C, which is a conservative value according to the known data in granite formations.

In the case II the maximum temperature in the repository center equals 80° C (homogenous model). In both cases, the repository capacity is equal to 30,000 canisters (corresponding to 41,000 tons of reprocessed uranium).

Thermal calculations have been carried out. They show the significant role of canister spacings in a borehole and make it possible to determine the temperatures on and near the central shaft (thermal heterogenous model). The results of this study will be available in January 1983.

. Repository characteristics (Case I)

The repository is described in "charges thermiques admissibles" (Bibliography : ref. 15,16,17 and 18). It is located at a depth of 1,000 m and contains 5,040 shafts, each of them loaded with 6 canisters. These boreholes are 102 m deep and are drilled inside 72 tunnels (1,050 m long) in intervals of 26 metres.

The boreholes are filled with canisters separated by 15 meter high backfill layers. The backfill is a mixture of bentonite and quartz sand.

. Repository characteristics (Case II)

For the case of waste cooled during 100 years the way of placing containers has been modified and the repository surface reduced to

165.3 acres or 62 ha. The shafts are 30 metres deep and can contain 15 piled up canisters.

For this concept 22 tunnels 805 m long are required, at intervals of 35 metres; they are excavated at 700 metres depth.

- Safety assessment methodology

A common presentation of some scenarios such as glaciation, meteorite impacts and volcanic activity will be prepared by the four secretaries of PAGIS. The probability for such phenomena to happen will be determined by results given by NRPB and the JRC-ISPRA.

For granite the description of the normal evolution of the repository after closure will be provided; that is the case where no pertubating phenomena such as glaciation, meteorite impacts, etc. occur.

This evolution can only by described when a thorough knowledge exists of the fluid flows under temperature gradients, resulting from the decay heat from the waste. This is the main difficulty, because the determination of fluid flows is based both on the hydrological knowledge of the site and on disturbances produced by thermal effects. In the present state of this study the hydrology of the three sites has not been determined experimentally. To fill this lack of data a preliminary model of groundwater flow will be assumed.

The results of the available thermal computations allow the determination of the temperature distribution in the rock. This is a first step towards a description of groundwater flow perturbations.

- Waste description

The waste inventory has been drawn up on the basis of a PWR reactor (Fessenheim type). The results show the activity evolution, the thermal power of fission products and actinides per ton of reprocessed uranium. The composition of the glass used as reference is the one defined by COGEMA.

- The continuation of the study

A particular effort will be made during the next period in order to gather data for the tasks 6 to 10 (modelling of waste degradation, canister corrosion and migration of the radionuclides in the geosphere). At first, parameters such as flow and nature of groundwaters will have to be determined in order to select models for the behaviour of the various barriers.

Evaluation of the performance of sub-seabed formations in view of the disposal of HLW

Contract : 275-82-75 WASUK, NRPB, Chilton.

Scope and Objective

This contract forms part of Phase 1 of PAGIS and its aim is the collection and the critical review of all available data, and the development of methodologies and models, required for the subsequent radiological assessment of sub-seabed disposal.

Progress and Results

The work to be carried out has been divided into 11 tasks. Progress on each of these is reported below.

Task 1 - Site selection

Two or three reference sites are to be selected for inclusion in the assessment. A preliminary choice has been made from the sites in the North Atlantic ocean, which are currently being studied. The three suggested for inclusion are : Great Meteor East, King's Trough Flank and Southern Nares Abyssal Plain. This choice will be finalised when comments are received from experts in Community countries. The sites eventually selected will have differing sediment characteristics, so that the sensitivity of the predicted radiological impact of sub-seabed disposal to variations in sediment properties can be investigated.

Task 2 - Site and regional data

The available geological, hydrogeological and geochemical data for the reference sites are to be collected and assessed. Preliminary descriptions of all the possible sites have been prepared, using the data which are readily available. More detailed information on the reference sites is currently being collected and reviewed.

Task 3 - Emplacement concepts and data

The emplacement concepts, which have been selected for study, are the use of penetrators to place waste canisters at relatively shallow depths in sediments and the placing of canisters in deeper, drilled holes. Penetrator emplacement is being considered as the reference technique, with drilled holes as a variant for sensitivity analysis. Apart from the thickness of sediment cover, the main difference between the two techniques is in the emplacement geometry (horizontal and vertical spacings between waste canisters). Reference geometries for each technique, and variations for sensitivity analysis, have been suggested and will be finalised in consultation with appropriate experts.

Task 4 - Assessment methodology

The basic methodology to be used in assessing sub-seabed disposal is to be the same as that employed for disposal into the 3 types of continental geologic formations considered in the PAGIS project (salt, granite and clay). The outline of an appropriate methodology has been agreed in principle between CEC and the four PAGIS secretary-ships. The objective is to produce a comprehensive, probabilistic radiological assessment which will estimate the risks to both individuals and populations. The methodology is designed to include all relevant events and processes which may affect a repository, together with their probabilities of occurrence, as well as to estimate the uncertainties in the results. Work is in progress to develop the methodology in detail and to determine how it will be implemented for sub-seabed disposal assessments.

Task 5 - Reference high-level waste level

For sub-seabed disposal, all the high-level waste arising in EC countries to the year 2000 will be considered. Estimates of UK arisings are being obtained by the National Radiological Protection Board (NRPB), together with the parameters needed to calculate radionuclide inventories for these wastes. It has been agreed that, as far as possible, the same values for parameters such as percentage waste incorporation in glass and size of glass blocks will be used throughout the PAGIS work.

Task 6 - Waste degradation and Task 7 - Canister corrosion

Information on waste degradation (leaching) and canister corrosion in sub-seabed and deep ocean environments is being collected and reviewed. These data will be used in an integrated near-field model (see Task 8) to predict rates of release of radionuclides into far-field sediments. Advice on data and modelling is being sought from members of CEC Expert Groups.

Task 8 - Host geologic medium (near-field)

A model to predict the rates of release of radionuclides from the waste and their rates of migration through the near-field region of seabed sediments is being developed. This work is being carried out in parallel with other NRPB work on near-fiel modelling for geologic disposal assessments. Migration data for use in the model have yet to be collected and reviewed.

Tasks 9 and 10 - Far-field disposal medium and surrounding geologies

The model to be used to predict rates of radionuclide migration in the far-field will be selected from those in use or under development at NRPB (e.g. GEOS, SWIFT). Data for use with the model are currently being collected; these will subsequently be discussed with appropriate UK and other EC experts.

Task 11 - Biosphere modelling

The models to be used to predict the rates of radionuclide dispersion in the ocean, their rate of removal from the ocean via interactions with suspended and bottom sediments, and doses to individuals and populations via marine exposure routes, are currently being developed by NRPB, in consultation with UK experts. The ocean model is a compartment model of the Atlantic Ocean, and will interface with models for sedimentation, biology and coastal waters. Input data for the models are being collected and assessed.

Biosphere modelling for geologic disposal assessments

Contract : 276-82-75 WASUK, NRPB, Chilton.

Scope and Objective

To produce a mathematical model to predict the rates of movement of radionuclides through the biosphere and the doses to individuals and populations following releases of radionuclides from repositories in deep geologic formations on land. The model will be capable of being transferred to other organisations and will be compatible with models which predict rates of release of radionuclides from repositories in salt, clay and granite formations. The study forms part of Phase 1 of PAGIS.

Progress and Results

The structure of the proposed biosphere model is illustrated schematically in figure 98. The model will be of the compartment type and will be dynamic in the sense that it will calculte concentrations of radionuclides in the various compartments, and hence doses, as a function of time. In order to obtain adequate spatial resolution, and to simplify interfacing with geosphere models, the model is composed of local, regional and global compartments. The size and characteristics of these compartments may be specified by the user and can vary with time.

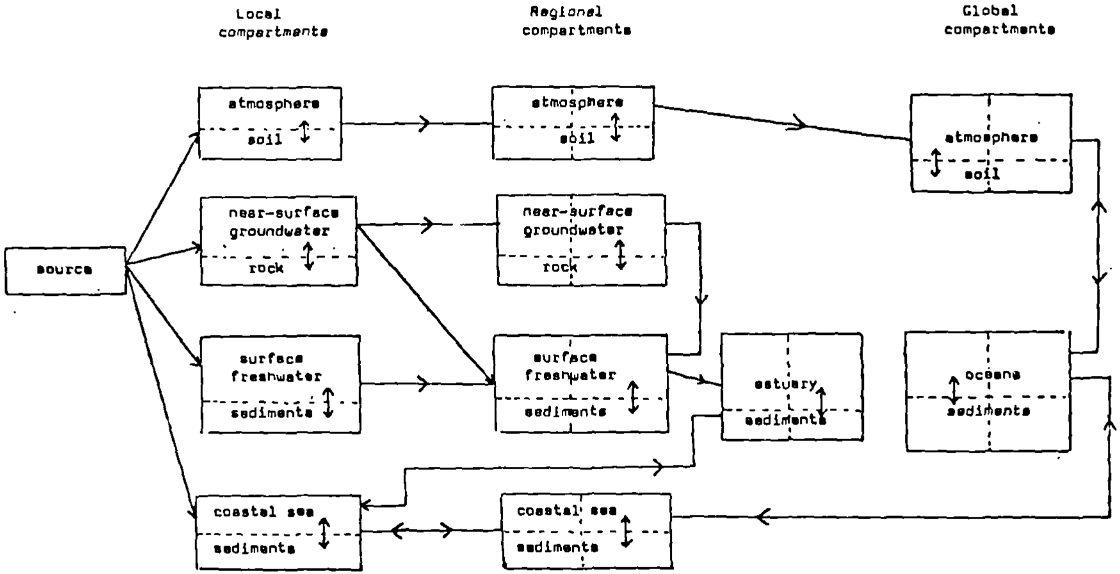


Figure 98 : Schematic diagram of biosphere model

The first stage in the development of the biosphere model has been to review the models which are available at the National Radiological Protection Board (NRPB) for predicting the rates of transfer of radionuclides through various parts of the environment and to determine which can be adapted for inclusion in the biosphere model. The review has concentrated on the transfer of radionuclides in the terrestrial environment and their dispersion in the world's oceans. The models currently in use at NRPB to predict the transfer of radionuclides in terrestrial foodchains were developed for assessments of releases from existing nuclear installations and deal only with relatively short timescales. Bearing in mind the uncertainties in biosphere conditions at long times in the future, these models are too complex for use in geologic disposal assessments and work has begun on simplifying them. The models will also require alteration since certain pathways which may be considered as "sinks" of activity in the short term (for example, the downward migration of activity deposited on the soil surface) may in the long term allow radionuclides to be recycled into man's environment (for example, transfer from soil to subsurface groundwater and thence into rivers).

The dispersion of radionuclides in coastal waters and their global dispersion in the world's oceans can be predicted by the computer code NOCEAN developed at NRPB. Again, because of uncertainties in long-term conditions, a simplified version of this model will be used, analogous to the simplification carried out for a previous assessment of the long-term radiological impact of a geologic repository at a coastal site. It has not yet been decided what modifications, if any, will be made to the Mediterranean regional model. A sedimentation model which takes account of return of activity from bottom sediments to the water column is being developed at NRPB and will be incorporated in the ocean dispersion models, as will exchanges between the oceans and the atmosphere on a global scale. The review of NRPB models will shortly be extended to include those developed to predict the atmospheric dispersion of radionuclides, and the global dispersion of long-lived nuclides.

In addition to the review of NRPB models a literature search is continuing in order to identify models which may be acquired and adapted for specific parts of the overall biosphere model. The search has concentrated on freshwater and estuarine environments for which appropriate models are not available at NRPB; several potentially suitable models have been identified. Work has started on defining the data requirements for the biosphere model and on writing the computer code.

APPENDICES

Page

BUDGET FIGURES

Total funding allocated to the R & D programme 1980 - 1984	43.10^6 ECU*
Contractual commitments taken as to 31/12/1982	$24{,}7.10^6$ ECU

* The European Currency Unit (ECU) is a weighted monetary unit, composed of the currencies of the EC member-states. Its conversion rate in July 1983 :

1 ECU	= 45,42 BFR/LFR	= 0,72 IRL
	= 8,16 DKR	= 1345 LIT
	= 2,27 DM	= 2,54 HFL
	= 75,54 DRA	= 0,58 UKL
	= 6,81 FF	($\approx$ 0,89 USD)

LIST OF REPORTED CONTRACTS

152-80-7	WASI	ENEA Casaccia	2.2.4	272
153-80-7	WASNL	Univ. Utrecht	2.2.4.	290
154-80-7	WASUK	UKAEA Harwell	2.2.4.	279
157-80-8	WASUK	UKAEA Harwell	1.6.1.	158
158-80-8	WASD	KfK Karlsruhe	1.6.1.	162
159-80-8	WASD	CEN/SCK Mol	1.6.2.	166
161-80-8	WASUK	NRPB Chilton	1.6.3.	169
162-80-8	WASD	KfK Karlsruhe	1.6.4.	174
163-80-8	WASUK	UKAEA-NRPB Harwell	1.6.3.	170
166-81-15	WASUK	AEE Winfrith	1.3.4.	97
167-81-2	WASB	CEN/SCK Mol	1.2.1.	48
168-81-2	WASD	KfK Karlsruhe	1.2.3.	68
169-81-2	WASD	NUKEM Hanau	1.2.1.	52
170-81-2	WASF	CEA Marcoule	1.2.2.	60
171-81-2	WASUK	UKAEA Harwell	1.2.2.	64
172-81-2	WASF	CEA Saclay	1.2.1.	56
173-81-2	WASD	KfK Karlsruhe	1.2.1.	58
174-81-31	WASI	ENEA Casaccia	1.3.3.	95
175-81-31	WASI	ENEA Casaccia	1.3.2.	90
176-81-31	WASUK	AERE Harwell	1.3.3.	93
177-81-31	WASD	KfK Karlsruhe	1.3.1.	74
178-81-33	WASD	KFA Jülich	1.3.1.	85
179-81-31	WASUK	AERE Harwell	1.3.1.	79
180-81-33	WASD	KFA Jülich	1.3.4.	100
181-81-31	WASF	SENA Chooz	1.3.1.	83
182-81-42	WASF	CEA Cadarache	1.4.3.	127
183-81-42	WASUK	AERE Harwell	1.4.3.	129
184-81-43	WASD	KfK Karlsruhe	1.4.3.	129
185-81-43	WASUK	AERE Harwell	1.4.1.	104
186-81-44	WASUK	UKAEA Springfields	1.4.1.	107
187-81-45	WASD	KfK Karlsruhe	1.4.2.	117
188-81-44	WASD	ALKEM Hanau	1.4.2.	120
190-81-42	WASB	SCK/CEN Mol	1.4.1.	109
191-81-44	WASI	AGIP Nucleare Bologna	1.4.1.	113
192-81-44	WASF	CEA Fontenay	1.4.1.	115
193-81-6	WASNL	Soil Mechanics Laboratory Delft	2.1.3.	192

194-81-6	WASDK	RNL Risø	2.1.3.	195
195-81-6	WASDK	RNL Risø	2.1.2.	189
196-81-6	WASF	CEA Fontenay-aux-Roses	2.1.2.	185
199-81-7	WASI	ENEA Casaccia	2.2.3.	263
200-81-7	WASF	CEA-EMP Paris	2.2.4.	286
202-81-7	WASF	CEA Fontenay	2.2.3.	264
203-81-7	WASF	CEA Cadarache	2.2.5.	316
204-81-7	WASUK	Mott, Hay & Anderson Croydon	2.2.3.	260
206-81-7	WASI	ENEA Casaccia	2.2.4.	269
208-80-7	WASI	ENEA Casaccia	2.2.5.	304
209-81-7	WASUK part 1	UKAEA Harwell	2.2.5.	306
209-81-7	WASUK part 2	"	2.2.6.	329
210-81-7	WASF	CEA Fontenay	2.2.5.	312
219-81-7	WASUK	ATKINS Epsom	2.2.6.	319
222-81-7	WASF	BRGM Orléans	2.2.4.	296
225-81-7	WASI	ENEA Casaccia	2.2.7.	333
226-81-7	WASNL part 1	ECN Petten	2.2.6.	327
226-81-7	WASNL part 2	"	2.2.7.	335
228-81-8	WASB	CEN/SCK Mol	1.6.4.	177
230-81-35	WASD	NUKEM Hanau	1.3.1.	77
231-81-31	WASI	AGIP Nucleare Bologna	1.3.2.	88
232-81-53	WASD	Fraunhofer Institut Würzburg	1.5	135
233-81-6	WASUK	NRPB Harwell	2.1.3.	196
235-81-13	WASDK	RNL Risø	1.1	35, 41
238-80-7	WASI	ENEA Casaccia	2.2.4.	274
239-80-7	WASI	ENEA Casaccia	2.2.9.	354
240-81-13	WASD	KfK Karlsruhe	1.1	23, 44
241-81-15	WASI	NUCLECO (Agip + ENEA) Milan	1.1	42
242-81-13	WASUK	Univ. Aberdeen	1.1	16, 34
243-81-13	WASUK	AERE Harwell	1.1	19
244-81-15	WASF	CEA Cadarache, Saclay Grenoble, Fontenay	1.1	13, 29, 32 37, 38
245-81-15	WASB	SCK/CEN Mol	1.1	18, 27, 43
246-81-2	WASD	KfK Karlsruhe	1.2.3.	69
248-81-7	WASUK	UKAEA Harwell	2.2.3.	250
249-81-7	WASF	CNRS Vitry s/S.	2.2.3.	257

250-81-7	WASD		KfK Karlsruhe	2.2.3.	247
252-81-7	WASF		CEA Fontenay	2.2.3.	254
253-81-7	WASUK		UKAEA Harwell	2.2.5.	308
255-81-7	WASUK		MAFF Lowestoft	2.2.8.	344
256-81-7	WASUK		Taylor-Woodrow Southall	2.2.8.	345
257-81-7	WASUK		NERC/IOS Wormley	2.2.8.	338
258-81-7	WASNL		Delta Institutt Ierseke	2.2.8.	340
259-81-7	WASF		CEA Cadarache	2.2.8.	342
261-81-7	WASF		CEA Fontenay	2.2.9.	358
263-81-7	WASUK		North Wales Univ. Anglesey	2.2.9.	352
264-81-7	WASF		BRGM Orléans	2.2.9.	356
266-80-7	WASD	part 1	KfK Karlsruhe	2.2.6.	233
266-80-7	WASD	part 2	"	2.2.6.	321
266-80-7	WASD	part 3	"	2.2.2.	323
267-81-6	WASF		CEA Cadarache	2.1.1.	184
268-81-55	WASF		CEA Saclay	1.5	137
270-81-7	WASD		HMI Berlin	2.3.1.	365
272-82-75	WASB		SCK/CEN Mol	2.3.2.	368
273-82-75	WASD		HMI Berlin	2.3.2.	372
274-82-75	WASF		ANDRA Paris	2.3.2.	376
275-82-75	WASUK		NRPB Chilton	2.3.2.	380
276-82-75	WASUK		NRPB Chilton	2.3.2.	383
277-82-53	WASD		HMI Berlin		
278-82-53	WASUK		AERE Harwell		
279-82-55	WASF		CEA Grenoble		
280-82-55	WASB		SCK/CEN Mol	1.5	153
281-82-53	WASDK		RNL RISØ		
282-82-55	WASI		ENEA Casaccia		
283-82-55	WASF		CEA Cadarache		
291-82-8	WASB		Univ. of Antwerp	1.6.1.	165
292-82-53	WASD		Fraunhofer Institut Würzburg	1.5	153
293-82-53	WASNL		University of Amsterdam		

SEMINARS, SYMPOSIA, CONFERENCES

(1) - CEC Seminar on "Conditioning and storage of spent fuel element hulls", Brussels 19 January 1982.
[proceedings edited by W. Hebel, G. Cottone, EUR 8250 (1982)].

(2) - Materials Research Society, fifth international symposium "Scientific basis for nuclear waste management", Berlin, 7-10 June 1982.
[co-sponsored by the CEC, proceedings edited by W. Lutze, North-Holland/Elsevier 1982, ISBN-0-444-00725-3].

(3) - IAEA/CEC/OECD international symposium "Conditioning of radioactive wastes for storage and disposal", Utrecht, 21-25 June 1982.
[proceedings : IAEA-SM-261 (1983)].

(4) - CEC seminar on "Methods of Krypton-85 management", Brussels, 29 June 1982.
[proceedings edited by W. Hebel, G. Cottone, EUR 8464 (1983)].

(5) - CEC/KfK seminar on "The acid digestion process for radioactive waste", Geel, 23 September 1982.
[proceedings edited by R. Simon, L. Cecille, EUR 8609 (1983)].

PUBLICATIONS

Previous annual reports : 1977 (EUR 5479), 1978 (EUR 6128), 1979/1980 (EUR 6650), 1980 (EUR 7652), 1981 (EUR 8272).

Seminars, etc. : see page 393.

Other publications (including published symposium papers) :

(11) - S. Orlowski, M. Bresesti, "Research and development action of the CEC in the field of radioactive waste management", IAEA-CN-42/424 (Vienna Conference, September 1982).

(12) - Seventh international NEA seabed working group meeting, La Jolla, CA, 15-19 March 1982, [proceedings Sandia report 82-0460. October 1982], including information on CEC seabed programme.

(13) - B. Huber, "Research on the management of fuel cladding waste", IAEA-SM-261/45.

(14) - W. Hebel, G. Cottone, "CEC research activities into the immobilization of volatile radionuclides from reprocessing", IAEA-SM-261/49.

Contract reports, synthesis-reports

- Admissible thermal loading in geological formation. Consequences on radioactive waste management methods. (Contracts 110-79-10 WASF, 111-79-10 WASB, 112-79-10 WASD).

(15)	Volume 1 : Synthesis report	EUR 8179 EN/FR	(1983)
(16)	Volume 2 : Granite formation	EUR 8179 FR	(1983)
(17)	Volume 3 : Sale formation	EUR 8179 DE	(1983)
(18)	Volume 4 : Clay formation	EUR 8179 FR	(1983)

(19) - R. De Batist et al., "Testing and Evaluation of Solidified High-level Waste Froms", Nuclear Science and Technology, EUR 8424,

(1983). Joint report of contracts n° 121-80-53 WASUK, 122-80-53 WASD, 123-80-55 WASF, 124-80-55 WASB, 125-80-55 WASN, 232-81-53 WASD, 268-81-55 WASF.

(20) - "Characterization of low and medium level radioactive waste forms", edited by R. Sambell, EUR 8663 (1983); joint report of contracts n° 235-81-13 WASDK, 240-81-13 WASD, 242-81-13 WASUK, 243-81-13 WASUK, 244-81-15 WASF and 245-81-15 WASB.

Contract reports, final reports of single contracts

(21) - M.G. Nicholas and P. Trevena (UKAEA, Harwell), Screening of materials for embrittlement by Rubidium , (contract 227-81-8 WASUK) EUR 8184 (1983).

(22) - G. Alonzo (CUREX, Saluggia), F. Castellani et al. (Univ. Pisa), Caratterizzazione del rilascio del radionuclidi in fase gassosa nel corso delle operazioni di taglio e di dissoluzione presso l'impianto pilota Eurex di elementi di combustibile irragiati in reattore di tipo Candu, (Contract 091-78-4 WASI) - EUR 7934 IT (1982).

(23) - E.F. Vansant et al. (Antwerpen Univ.), Occlusion and storage of Krypton in solids, (contract 234-81-8 WASB - EUR 8185 (1982).

(24) - R. Heremans et al. (SCK/CEN, Mol), Programme R&D relatif au rejet de déchets radioactifs en formations géologiques profondes. Etude d'une formation argileuse en Belgique, (Contracts 013-76-1 and 060-78-1 WASB) - EUR 7650 (1982).

(25) - B. Skytte Jensen (RNL Risø), Migration phenomena of radionuclides into the geosphere, - a critical review of available information. (Contract 066-78-1 WASDK) - EUR 7676 (1982).

(26) - Programme of research into the disposal of radioactive waste into geological formations (studies on crystalline rock). (Contract 059-78-1 WASUK), UKAEA, Harwell - EUR 7976 (1983).

(27) - A. Coudrain et al. (Ecole des Mines de Paris), Etudes des incidences du dégagement thermique en milieu fissuré suite à l'enfouissement de déchets nucléaires. (Contract 087-79-1 WASF) - EUR 8186 (1982).

(28) - Investigations par forages profonds du granite d'Auriat. (Contract 057-78-1 WASF) CEA/BRGM - EUR 8178 (1983).

(29) - Etude de conception générale d'une installation permettant l'évacuation de déchets radioactifs dans une formation granitique. (Contract 107-79-2 WASF) - Geostock, Paris - EUR 7620 FR (1983).

(30) - General conceptual design study for a high level radioactive waste repository in a granite formation. (Contract 107-79-2 WASF) Geostock, Paris - EUR 7620 EN (1983).

(31) - T.W. Broyd et al. (Atkins R&D, Epsom (UK)), A directory of computer programs for assessment of radioactive waste disposal in geological formations. (Contract 219-81-7 WASUK) - EUR 8669 EN (1983).

(32) - E. Smailos et al. (KfK, Karlsruhe), Korrosionsuntersuchungen an Verpackungsmaterialien für hochaktive Abfälle. (Contract 250-80-7 WASD) - EUR 8657 (1983).

(33) - G.P. Marsh et al. (UKAEA, Harwell). Corrosion assessment of metal overpacks for radioactive waste disposal. (Contract 248-81-7 WASUK) - EUR 8658 (1983).

(34) - I. Doeren et al. (ECN, Petten). Convergence measurements in the dry-drilled 300 m deep borehole in the Asse II salt mine. (Contract 142-80-7 WASNL) - EUR 8670 (1983).

(35) - P.J. Boreste et al. (UKAEA, Harwell). Nuclide migration and mathematical modelling. (Contract 209-81-7 WASUK) - EUR 8656 (1983).

(36) - F.T. Ewart et al. (UKAEA, Harwell). Migration of radionuclides through the geosphere. An integral migration experiment. (Contract 253-81-7 WASUK) - EUR 8659 (1983).

(37) - E. Korthaus (KfK, Karlsruhe). Abschliessende Verbesserung der vorliegenden Suchenprogramme zur Bestimmung der Temperaturentwicklung. (Contract 266-80-7 WASD) - EUR 8667 (1983).

(38) - R. Mueller, E. Korthaus (KfK, Karlsruhe). In-situ Untersuchung der Standfestigkeit von Versicheringen sowie Entwicklung und Erprobung einer Standard Konvergenzsonde. (Contract 266-80-7 WASD) - EUR 8668 (1983).

(39) - E.K. Duursma et al. (Delta Instituut, Yerseke). Migration processes in marine sediments caused by heat source. (Contract 258-81-7 WASNL) - EUR 8710 (1983).

<u>Nota</u> : a) Publications by the contractors and other references related to the reported R&D are not given here, but will be found in the final reports of each contract.

b) Many of this listed EUR reports are only appearing in 1983, as mentionned, but relate to accomplished R&D work of 1982, except of course the listed previous annual reports.

MEMBERS OF THE ADVISORY COMMITTEE ON PROGRAMME MANAGEMENT

Belgium	L. Baetslé
	M. Matthys
	P. De Meester
Denmark	K. Broderson
	B. Skytte Jensen
France	A. Barthoux
	M. Gras
	Y. Sousselier
Germany	K. Hübenthal
	H. Illi
	K. Kühn
	R. Kroebel
Greece	S. Amarantos
	I. Armyriotis
Ireland	J.D. Cunningham
Italy	A. Brondi
	A.G. Facchini
	G. Rolandi
	G. Russino
Luxembourg	P. Kayser
Netherlands	J.H. Alberts
	J.L. Baas
	B. Verkerk

United Kingdom	F. Feates
	K. Keen
	H.A. Taylor*
Commission	M. Girardi**
	S. Orlowski

* Who took, during 1982, the seat of Mr. Clelland

** Who took, during 1982, the seat of Mr. Bresesti.

ABBREVIATIONS

AERE	Atomic Energy Research Establishment
BAM	Bundesanstalt für Materialprüfung
BRGM	Bureau de Recherche Géologique et Minière
CEA	Commissariat à l'Energy Atomique
ENEA	Ente Nazionale per l'Energia Nucleare ed Energie Alternative
CNRS	Centre Nationale de la Recherche Scientifique
ECN	Energieonderzoek Centrum Nederland
EMP	Ecole des Mines, Paris
GSP	Gesellschaft für Strahlen - und Umweltforschung
HMI	Hahn-Meitner-Institut
IGS	Institute of Geological Sciences
IOS	Institute of Oceanographic Sciences
JRC	Joint Research Centre
KFA	Kernforschungsanlage Jülich
KfK	Kernforschungszentrum Karlsruhe
MAFF	Ministry of Agriculture, Fisheries and Food
NERC	Natural Environment Research Council
NRPB	National Radiological Protection Board
RNL	Risø National Laboratory
SCK-CEN	Studiecentrum voor Kernenergie - Centre d'Etudes Nucléaires
SENA	Société d'Energie Nucléaire Franco-Belge des Ardennes
UKAEA	United Kingdom Atomic Energy Authority

CEC	Commission of the European Communities
OJ	Official Journal of the European Communities
EC	European Community
ACPM	Advisory Committee on Programme Management
HLW (HAW)	High Level Waste (High Activity Waste)
LLW (LAW)	Low Level Waste
LLLW	Low Level Liquid Waste
MLW (MAW)	Medium Level Waste or Intermediate Level Waste
BWR	Boiling Water Reactor
GCR	Gas Cooled Reactor
PWR	Pressurized Water Reactor
BFS	Blast Furnace Slag
OPC	Ordinary Portland Cement
PZC	Pozzolana Cement

related titles of interest

RADIOACTIVE WASTE MANAGEMENT AND THE NUCLEAR FUEL CYCLE
An International Journal
Edited by D. R. Anderson, Sandia Laboratories, A. M. Platt, Battelle Pacific Northwest Laboratories and Francesco Girardi, Joint Research Centre, Ispra — ISSN : 0142-2405

RADIOACTIVE WASTE MANAGEMENT AND DISPOSAL
Edited by R. Simon and S. Orlowski — ISBN : 3-7186-0056-0

RADIOACTIVE WASTE ADVANCED MANAGEMENT METHODS FOR MEDIUM ACTIVE LIQUID WASTE
By K. W. Carley-Macauly, R. G. Gutman, E. W. Hooper, J. A. Jenkins, A. D. Turner, P. F. Wace, P. Chauvet, J. P. Gauchon and T. Dippel — ISBN : 3-7186-0060-9

RADIOACTIVE WASTE DISPOSAL INTO A PLASTIC CLAY FORMATION
A Site Specific Exercise of Probabilistic Assessment of Geological Containment
By Marco d'Alessandro and Arnold Bonne — ISBN : 3-7186-0084-6

MANAGEMENT OF PLUTONIUM CONTAMINATED WASTE
Edited by J. R. Grover — ISBN : 3-7186-0110-9

RESEARCH AND DEVELOPMENT ON RADIOACTIVE WASTE MANAGEMENT AND STORAGE
(First annual Progress Report of the European Community Programme 1980-1984)
Commission of the European Communities — ISBN : 3-7186-0115-X

ACTINIDE RECOVERY FROM WASTE AND LOW-GRADE SOURCES
By J. D. Navatil and W. W. Schulz — ISBN : 3-7186-0105-2

MIGRATION PHENOMENA OF RADIONUCLIDES INTO THE GEOSPHERE
By B. Skytte Jensen — ISBN : 3-7186-0120-6

MANAGEMENT MODES FOR IODINE-129
Edited by W. Hebel and G. Cottone — ISBN : 3-7186-0147-8

RESEARCH AND DEVELOPMENT ON RADIOACTIVE WASTE MANAGEMENT AND STORAGE
(Second Annual Progress Report of the European Community Programme 1980-1984)
Commission of the European Communities — ISBN : 3-7186-0148-6

CONDITIONING AND STORAGE OF SPENT FUEL ELEMENT HULLS
Edited by W. Hebel and G. Cottone — ISBN : 3-7186-0149-5

METHODS OF KRYPTON-85 MANAGEMENT
Edited by W. Hebel and G. Cottone — ISBN : 3-7186-0167-2

THE ACID DIGESTION PROCESS FOR RADIOACTIVE WASTE
Edited by L. Cécille and R. Simon — ISBN : 3-7186-0174-5

harwood academic publishers
chur-london-paris-utrecht-new york

ISSN : 0275-7273

ISBN : 3-7186-0191-5