INTERNATIONAL WORKSHOP ON THE USES OF BACKFILL IN NUCLEAR WASTE REPOSITORIES, CARLSBAD, NEW MEXICO, US, MAY 1998

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R&D Technical Report P178

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This report summarizes the proceedings of an international workshop on the uses of backfill in nuclear waste repositories that was held in Carlsbad, New Mexico, US, in May 1998. The Workshop was co-sponsored by the Environment Agency and the US Department of Energy (Carlsbad Area Office). The information within this document is for use by Environment Agency and US DOE staff and others involved in the management and disposal of radioactive waste.

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R&D Technical Report P178

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FOREWORD

The United States Department of Energy's Carlsbad Area Office (DOE/CAO) is responsible for the licensing and operation of the Waste Isolation Pilot Plant (WIPP), which is located near Carlsbad, New Mexico. The WIPP has been certified by the United States Enviromental Protection Agency to operate the first deep geological respository that was specifically constructed for the permanent disposal of transuranic waste. In May 1998, and in partnership with the Environment Agency of England and Wales, the DOE/CAO sponsored and hosted an International Workshop to provide a forum for discussion of the scientific bases for the use of backfills in nuclear waste repositories. The Workshop was attended by representatives from twelve countries, who discussed uses of backfills and barriers in the disposal concepts in their respective countries, the attributes of different backfills, and the selection, evaluation, and performance assessment of backfills. At the end of the Workshop, participants agreed that they would benefit from future interchanges on backfills. This interest has resulted in formation of an ad-hoc working Group to the Organization of Economic Cooperation and Development (OECD) Nuclear Energy Agency's Site Evaluation and Design of Experiments (NEA/SEDE). This working group will develop proposals for consideration by the NEA's Radioactive Waste Management Committee (NEA/RWMC) in April 1999.

During the past several years, the DOE/CAO has been involved in research on a variety of backfill materials for the WIPP, and is highly supportive of further interactions and collaboration in follow-on initiatives. We hope that this technical report of the International Workshop will be used to aid other nations in evaluating, selecting, and using backfill materials effectively.

Mr. Keith A. Klein, Acting Manager
United States Department of Energy, Carlsbad Area Office

FOREWORD

The Environment Agency of England and Wales has a duty to make arrangements for carrying out research and related activities in support of its work, and to make the results of this work available to others. The Agency sponsored and co-hosted an international workshop with the United States Department of Energy, Carlsbad Area Office, in May 1998, to consider the uses of backfill in nuclear waste repositories, as part of its Radioactive Substances research programme. The workshop provided a forum to discuss and determine the current state-of-the-art, identified requirements and strategies for representing backfills in performance assessment, and promoted international collaboration among organisations considering the use and assessment of backfill in radioactive waste disposal systems. The workshop was attended by experts from Asia, Europe and North America. A summary of the workshop proceedings and proposals for follow-on initiatives were presented at the OECD Nuclear Energy Agency's Site Evaluation and Design of Experiments (OECD/NEA/SEDE) meeting in September 1998. This resulted in a decision to form an NEA/SEDE ad-hoc working group to develop the proposals, for consideration by the NEA's Radioactive Waste Management Committee (NEA/RWMC) in April 1999.

Dr R J Pentreath
Chief Scientist and Director of Environmental Strategy

ACKNOWLEDGEMENTS

The success of the workshop was due to:

- the speakers, paper authors, and other contributors to the workshop; and
- the members of the Workshop Steering Committee: D G Bennett, M S Y Chu, S L Duerden, L Eriksson, D A Galson, A J Kane, M L Matthews and H W Papenguth.

In particular, the organizers of the workshop wish to express their gratitude to all those who participated in and contributed papers to the workshop, and to the various regulatory, disposal, research and other organizations that provided considerable in-kind support.

On behalf of all of the participants, the Workshop Steering Committee wishes to express its gratitude to the US Department of Energy, Carlsbad Area Office, for its hospitality in hosting the workshop.

This document has been prepared jointly by Galson Sciences Limited and Sandia National Laboratories for the Environment Agency of England and Wales and the US Department of Energy, Carlsbad Area Office. Work performed by Galson Sciences Limited for the Environment Agency has been made under the terms of Contract HOCO_293. Work performed by Galson Sciences Limited for the US Department of Energy has been made under the terms of Contract AP-2278 with Sandia National Laboratories.

EXECUTIVE SUMMARY

Most radioactive waste disposal programs are considering the use of repository backfill materials to enhance the containment of radioactive waste. A range of backfill concepts and materials are under consideration. The concepts include the use of backfills to provide well defined chemical conditions, favourable hydraulic conductivities, and/or desirable physical characteristics within the disposal facility. The materials currently under consideration in national programs include cements and blended cements, magnesium oxide, crushed salt, bentonite clay. Other materials are also under investigation (e.g., apatite, sand and gravel).

In the autumn of 1997, the Environment Agency of England and Wales and US Department of Energy agreed to co-sponsor an international workshop on the uses of backfill in nuclear waste repositories. The objectives of the workshop were to provide a forum:

(i) to identify key processes relevant to the selection, optimization, use and long-term behaviour of backfills in radioactive waste disposal systems;

(ii) to identify research issues that have been adequately addressed, significant remaining uncertainties, and future research requirements;

(iii) to identify requirements and strategies for representing backfills in performance assessment (PA); and

(iv) to promote international collaboration between organizations considering the use and assessment of backfill in radioactive waste disposal systems.

The workshop was held in Carlsbad, New Mexico, on 5-7 May 1998. The following general conclusions have been drawn from the workshop:

- A relatively small number of concepts exist for the use of backfill, and there is therefore some overlap between the research efforts of the various national programs. Synergistic benefit would arise from greater communication and collaboration between national disposal programs.
- Consensus exists as to the reasons why particular backfill materials may be selected, in terms of their desirable physico-chemical properties.
- Research into "new", potentially beneficial materials / backfill additives (e.g., phosphates, MgO) is on-going in a number of countries, but the status of research into these materials is less advanced than for the common materials being proposed for use as backfill for radioactive waste (i.e., clay, cement and salt).
- The radioactive waste disposal community has a good understanding of the technical aspects that need to be evaluated with regard to the use and assessment of backfill materials, and has a clear picture of the remaining technical uncertainties.
- Continued effort is necessary to investigate some of the remaining technical uncertainties and to improve the interface between research on backfill materials and performance assessment.
- Considerable similarities exist in the methods used by regulators of radioactive waste disposal in different countries. However, differences exist in the degree to which regulators rely on independent performance assessment in decision making, and in the extent of regulatory guidance provided to disposers.

- The development, testing and use of an internationally agreed reference methodology for backfill selection and optimization would build confidence in the repository development and optimization process. Development of such a methodology was initiated during the workshop. However, further work is required to develop, refine and test the methodology at international level.

- A need exists for a continuing forum to facilitate discussion, international collaboration and data exchange on near-field repository engineering and design issues. Such a forum could be designed to allow discussion on backfill-related topics that were beyond the scope of this workshop, and to ensure that prioritization of future research work is based on assessments of the safety of disposal.

Key Words: apatite; backfill; bentonite; cement; optimization; performance assessment; radioactive waste; repository; salt.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. WORKSHOP OVERVIEW

1.1 Workshop Rationale and Objectives

Most radioactive waste disposal programs are considering the use of repository backfill materials to enhance the containment of radioactive waste. A range of backfill concepts and materials are under consideration. The concepts include the use of backfills to provide well defined chemical conditions, favourable hydraulic conductivities, and/or desirable physical characteristics within the disposal facility. The materials currently under consideration in national programs include cements and blended cements, magnesium oxide, crushed salt, bentonite clay. Other materials are also under investigation (e.g., apatite, sand and gravel).

In the UK, the Environment Agency (and formerly Her Majesty's Inspectorate of Pollution) has funded a significant research program into the use of cementitious materials for disposal of low-level and intermediate-level radioactive waste (LLW, ILW). The Agency is currently assessing the disposal of cement-grouted LLW in shallow cementitious vaults at British Nuclear Fuels Limited's (BNFL) Drigg disposal site in Cumbria.

In the US, the Department of Energy (DOE) is responsible for the management and disposal of defense related transuranic (TRU) waste at the Waste Isolation Pilot Plant (WIPP), and for high-level waste including spent fuel at Yucca Mountain. The WIPP is a deep geologic repository mined in bedded salt near Carlsbad, New Mexico. The DOE investigated a wide range of potential backfill materials for use at the WIPP and has selected magnesium oxide (MgO).

In the autumn of 1997, the Environment Agency and the DOE agreed to co-sponsor a joint international workshop on the uses of backfill in nuclear waste repositories. The objectives of the workshop were to provide a forum:

(i) to identify key processes relevant to the selection, optimization, use and long-term behaviour of backfills in radioactive waste disposal systems;

(ii) to identify research issues that have been adequately addressed, significant remaining uncertainties, and future research requirements;

(iii) to identify requirements and strategies for representing backfills in performance assessment (PA); and

(iv) to promote international collaboration between organizations considering the use and assessment of backfill in radioactive waste disposal systems.

The workshop was hosted by the DOE in Carlsbad and was held on 5-7 May 1998. The workshop was attended by some 40 invited participants including regulators, implementors, managers of research programs, PA specialists, and leading backfill materials researchers from twelve countries.

1.2 Workshop Scope and Content

Workshop Scope

The conceptual basis for the use of backfill in radioactive waste disposal facilities varies depending on programmatic requirements. Different backfill materials offer a range of potential performance benefits depending on their chemical, hydrological and physical properties. In view of the interests of the sponsoring organizations, the emphasis of the workshop was on the use of chemical and hydrological/physical backfills and the disposal of LLW, ILW, and TRU wastes. However, the use of backfills in the disposal of high-level waste (HLW) and spent fuel was considered, and backfill selection and optimization were also important workshop topics.

Workshop Content

The workshop included 21 technical presentations, four thematic discussion sessions, and a session in which the participants divided into three working groups for in-depth discussion of selected issues (Appendix 1). The first day of the workshop comprised a series of presentations of national disposal concepts including the use of backfill (Appendix 2). The second day comprised four presentation / discussion sessions covering (Appendix 3):

- rationale for the uses of backfill and backfill material selection;
- status of research into backfill materials;
- representation of backfills in performance assessment; and
- approaches to regulatory evaluation of backfills.

The topics identified during discussion of the presentations on the second day were used to define the scope and objectives of three working groups that were convened on the morning of the third day to allow more detailed discussion:

- Working Group 1: Optimization and Backfill Selection

  Objectives

  - To consider the aims of backfills and the primary properties that influence the selection of backfill materials.
  - To consider how a systems approach to backfill selection and optimization might be employed.
  - To consider the stage(s) of a disposal program at which a backfill specification should be defined, and at what level of detail.

  Facilitators: David Bennett (GSL, UK), Alan Hooper (Nirex, UK).

  Working Group Members: Patrick Baudoin (IPSN, France), Richard Vann Bynum (SAIC, US), Margaret Chu (SNL, US), Allison Kane (SNL, US), Mark Matthews (DOE, US), Stan Patchett (WEC, US), Miashiro Shibata (PNC, Japan), Simcha Stroes-Gascoyne (AECL, Canada).

- Working Group 2: Chemical Backfills

  Objectives

  - To consider the primary objective, or function, of chemical backfills.
  - To consider the properties of chemical backfill materials that allow them to achieve their function and the secondary processes that may influence their function.

- To consider the level of understanding relating to chemical backfill materials and to identify significant remaining uncertainties and future research requirements.

Facilitators: Urs Berner (PSI, Switzerland), Susan Duerden (EA, UK), Fred Glasser (Aberdeen Uni., UK).

Working Group Members: Pat Brady (SNL, US), Bai Song Chen (CNNC, China), Eric Giffaut (ANDRA, France), Jim Krumhansl (SNL, US), Vern Rogers (RAEC, US), Della Roy (Penn. State Uni., US), Wolfgang Runde (LANL, US), Tsutomu Sato (JAERI, Japan), Vasili Sinitsyn (META, Ukraine), Divyesh Trivedi (BNFL, UK), Yifeng Wang (SNL, US).

- Working Group 3: Hydrological/Physical Backfills

  Objectives

  - To consider the primary objective, or function, of hydrological/physical backfills.
  - To consider the properties of hydrological/physical backfill materials that allow them to achieve their function and the secondary processes that may influence their function.
  - To consider the level of understanding relating to hydrological/physical backfill materials and to identify significant remaining uncertainties and future research requirements.

  Facilitators: Andrew Campbell (ACNW, US), David Savage (Quantisci, UK).

  Working Group Members: Wernt Brewitz (GRS, Germany), Luc Van Cauteren (ONDRAF/NIRAS, Belgium), Kwan-Sik Chun (KAERI, Korea), Yasuaki Ichikawa (Nagoya Uni., Japan), Frederic Plas (ANDRA, France), Bill Thompson (Golder Associates, US).

In the afternoon of the third day, the results of the working groups were presented to and discussed by the full workshop. This was followed by a plenary discussion focussed on identifying possible follow-on activities to the workshop.

1.3 Report Structure

This paper summarizes the objectives, scope, content, achievements, conclusions and recommendations of the workshop. Section 2 summarizes the use of backfill in radioactive waste repositories worldwide. Section 3 summarizes the discussions during days 2 and 3 of the workshop. Section 4 presents a set of recommendations for further work at international level.

The workshop agenda is reproduced in Appendix 1. Appendix 2 includes the national programmatic papers presented on the first day of the workshop and Appendix 3 includes the papers presented on the second day of the workshop. A list of participants is provided in Appendix 4.

2. BACKFILL IN RADIOACTIVE WASTE DISPOSAL

The conceptual basis for the use of engineered components in radioactive waste disposal facilities varies depending on programmatic requirements. This section summarizes the proposed use of backfill in a variety of national programs, based on the papers presented in Appendix 2.

2.1 Backfills with a Primarily Chemical Function

The potential range of chemical backfill materials is large. Many different materials may be used to buffer pH and control radionuclide solubilities, and to limit radionuclide migration by chemical sorption and (co)precipitation processes.

Notable examples of specific relevance to deep disposal include:

- The UK Nirex Ltd. Reference Vault Backfill (NRVB) - a mixture of 40% OPC, 15% lime and 45% crushed limestone. This backfill has been proposed for ILW disposal in the UK primarily to maintain a high-pH aqueous environment in the repository. The high pH lowers the solubility of key radionuclides. The high surface area of surface-active minerals in the NRVB promotes radionuclide sorption.

- Magnesium oxide. This backfill is to be used at the WIPP to buffer the pH of the repository to moderately basic conditions in order to reduce the solubility of key radionuclides. In addition, magnesium oxide will also act to consume carbon dioxide gas by the formation of relatively insoluble carbonate solids.

- Significant research is being conducted to investigate the potential uses of apatite as a component of repository backfills.

2.2 Backfills with a Primarily Hydrogeological Function

Clay backfills

Bentonite clay is the principal component of the backfill in many deep repository concepts hosted in crystalline rock or clay. The main use of bentonite is as follows:

- As a material to surround the canisters of waste within vertical or horizontal deposition holes. In disposal concepts hosted in crystalline rock, the bentonite is sometimes referred to as the "buffer" and fills the gap between the canisters and the host rock (Figure 1). Bentonite is used in this way in the Canadian, Finnish, French, and Swedish HLW disposal concepts.

- As a material to fill the void space within the tunnels and shafts. For disposal concepts in which the waste canisters are emplaced within disposal rooms and tunnels, the bentonite surrounds the canisters and separates them from the host rock. Bentonite is used in this way in the Canadian, French, Spanish and Swiss HLW disposal concepts hosted in crystalline rock, and in the Belgian HLW disposal concept hosted in clay.

Repositories hosted in clay may make use of the local host rock as the backfill. Repositories hosted in crystalline rock may use a mixture of the local host rock and bentonite clay to form the backfill.

In the Canadian disposal concept, both clay- and cement-based material have been considered for use as backfill. Clay is currently favored for the disposal rooms because of a desire to maintain a near-neutral pH adjacent to the waste containers. Mixtures including 90:10 sand to

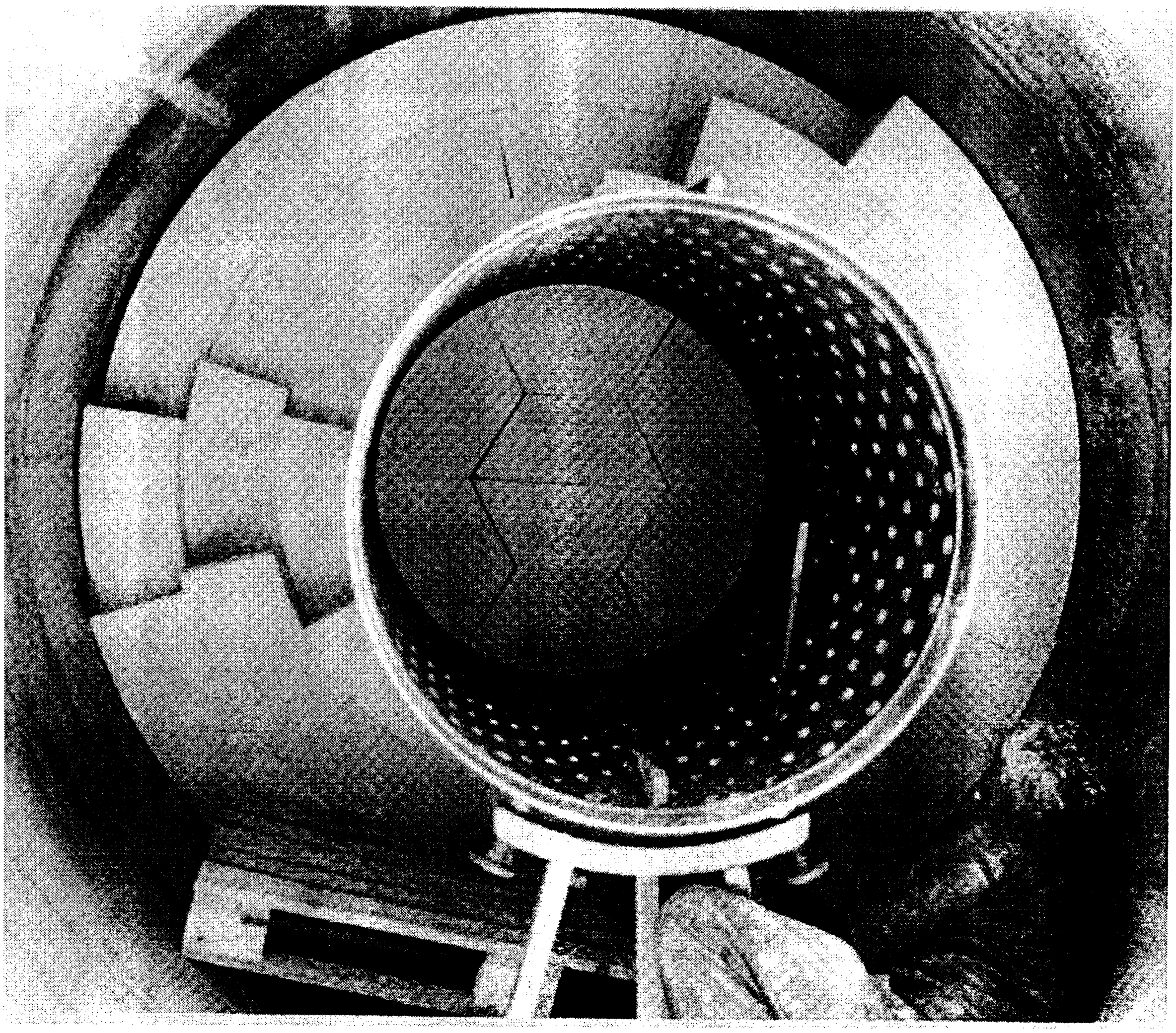

Figure 1. A trial installation of a bentonite buffer in a horizontal granite tunnel during the international FEBEX experiment at the Grimsel underground rock laboratory in Switzerland. The buffer is being emplaced as dry, shaped blocks of bentonite between the walls of the tunnel and a central cylindrical former. During the FEBEX experiments this central cylinder is occupied by an electrical heater, in a repository it would be occupied by a waste container (ENRESA 1998).

bentonite, and 75:25 crushed granite to clay, have been evaluated. Such mixtures have considerably lower swelling pressures than pure bentonite, thereby reducing complexity in their emplacement. However, at sufficiently high densities, the hydraulic conductivity of the mixtures will remain low, thereby maintaining their hydrological function. Such densities can be achieved by compaction, either in situ or prior to emplacement. Mixing other materials with the bentonite can also improve other performance characteristics of the backfill, such as resistance to erosion and thermal behaviour.

In the Canadian and Swedish disposal concepts, the backfill is to be emplaced within the disposal rooms and tunnels in two layers (Figure 2). For example, the Canadian concept includes a lower backfill of a 25:75 mixture of clay to granite, with a dry density of 2.1×10^3 kg m^{-3}, and an upper backfill of a 50:50 mixture of sodium bentonite and silica sand, with a dry density of 1.4×10^3 kg m^{-3}. In later studies, crushed granite was considered as an alternative to the silica sand in the upper backfill because the Fe(II) minerals in the granite would promote reducing conditions. This is desirable because it will help to ensure that technetium and other redox-sensitive radionuclides occur in their reduced, less mobile states.

Salt backfills

Apart from the MgO backfill material proposed to be used at the WIPP, the principal backfill material in salt-hosted repositories is crushed salt. Other countries with salt-hosted repository concepts include Germany and the Netherlands. However, the Netherlands has yet to select a specific site and the published PAs are generic. In Germany, radioactive waste disposal sites in salt exist at Asse, Morsleben and Gorleben.

In the reference design for the Gorleben repository, the repository is located 840 meters below the surface, and 540 meters below the top of the salt dome. HLW and heat-producing ILW canisters are emplaced in disposal boreholes, while the remaining waste is emplaced in storage chambers. The disposal boreholes are not backfilled, but are sealed at the top with a ten-meter plug of salt or salt-concrete. The shafts, disposal tunnels, flank tunnels and repository central field (the area between the shafts, and the disposal and flank tunnels) are backfilled with crushed salt. Disposal tunnels are sealed with salt-concrete. Finally, the shafts are backfilled with crushed salt and sealed to give bulk permeabilities which are assumed to be at least as low as the surrounding salt formation.

Cement backfills

The Swedish, Swiss and UK intermediate-level waste disposal concepts for ILW include cement-based backfills that are specifically designed to have high gas permeabilities.

2.3 Cementitious Components with a Primarily Structural Function

Structural cementitious components are commonly used in near-surface radioactive waste disposal repositories, such as Centre de la Manche and Centre de l'Aube in France, El Cabril in Spain (Figure 3) and Drigg in the UK (Figure 4). In such disposal systems cements are not used for backfill as such, but do feature in other repository components that may influence PA. Uses include:

- Structural components of the repository - for example, as vault walls and floors, roadways and drains.
- Waste containers and conditioning material within waste containers to cement the various waste forms and incorporate any liquid waste.

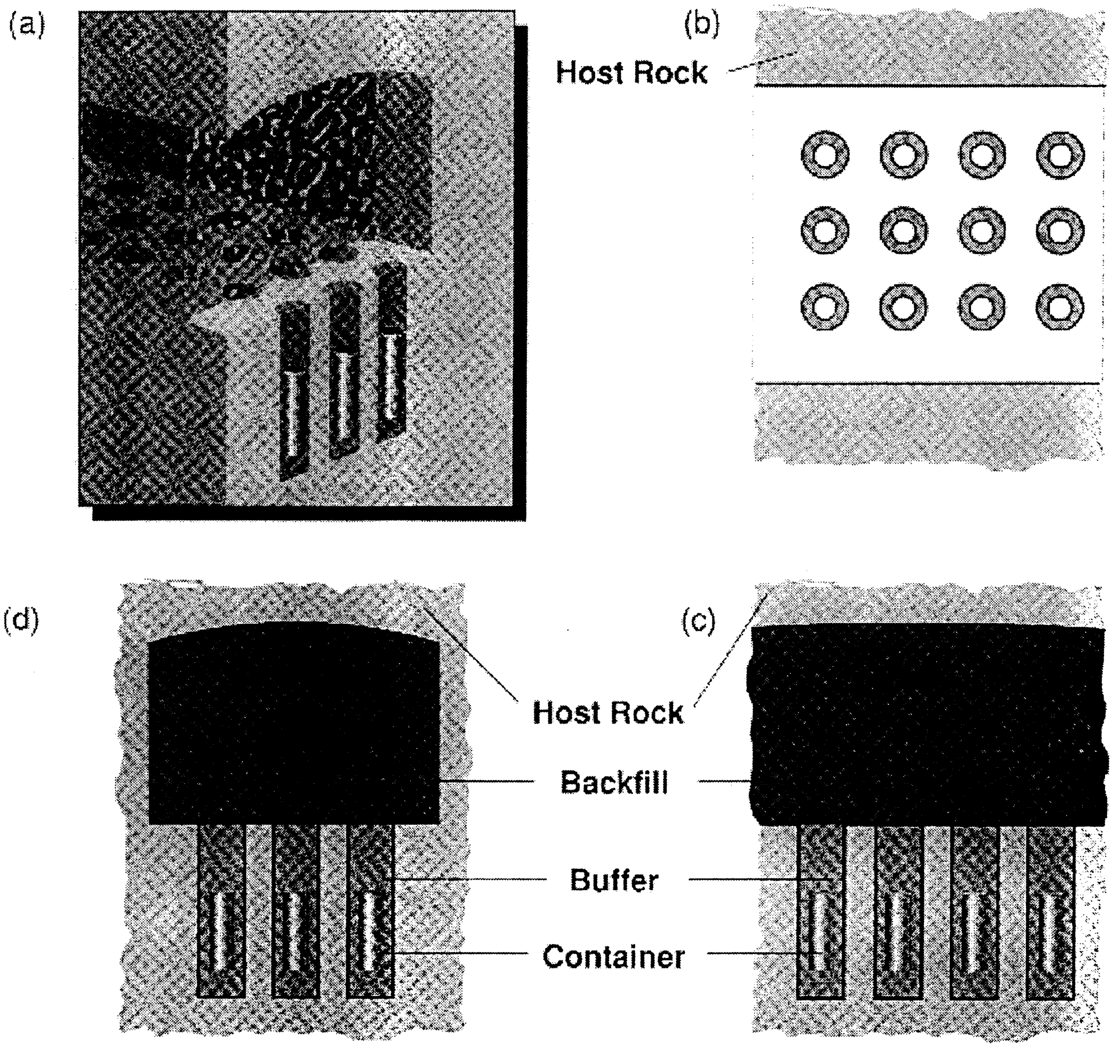

Figure 2. Four views of AECL's disposal room concept from the Canadian reference disposal system (AECL 1994). View (a) is a three dimensional view of part of a room. View (b) is an overhead view showing the pattern of boreholes drilled in the floor of the room. Views (c) and (d) are cross sections taken down the length and across the width of the room respectively. The waste containers are placed into the boreholes, surrounded by a thin layer of sand (not shown in the figure), which in turn is surrounded by a thicker layer of a low-permeability bentonite clay called the buffer. After closure, the remainder of each room is filled with a mixture of glacial lake clay and crushed rock called the backfill.

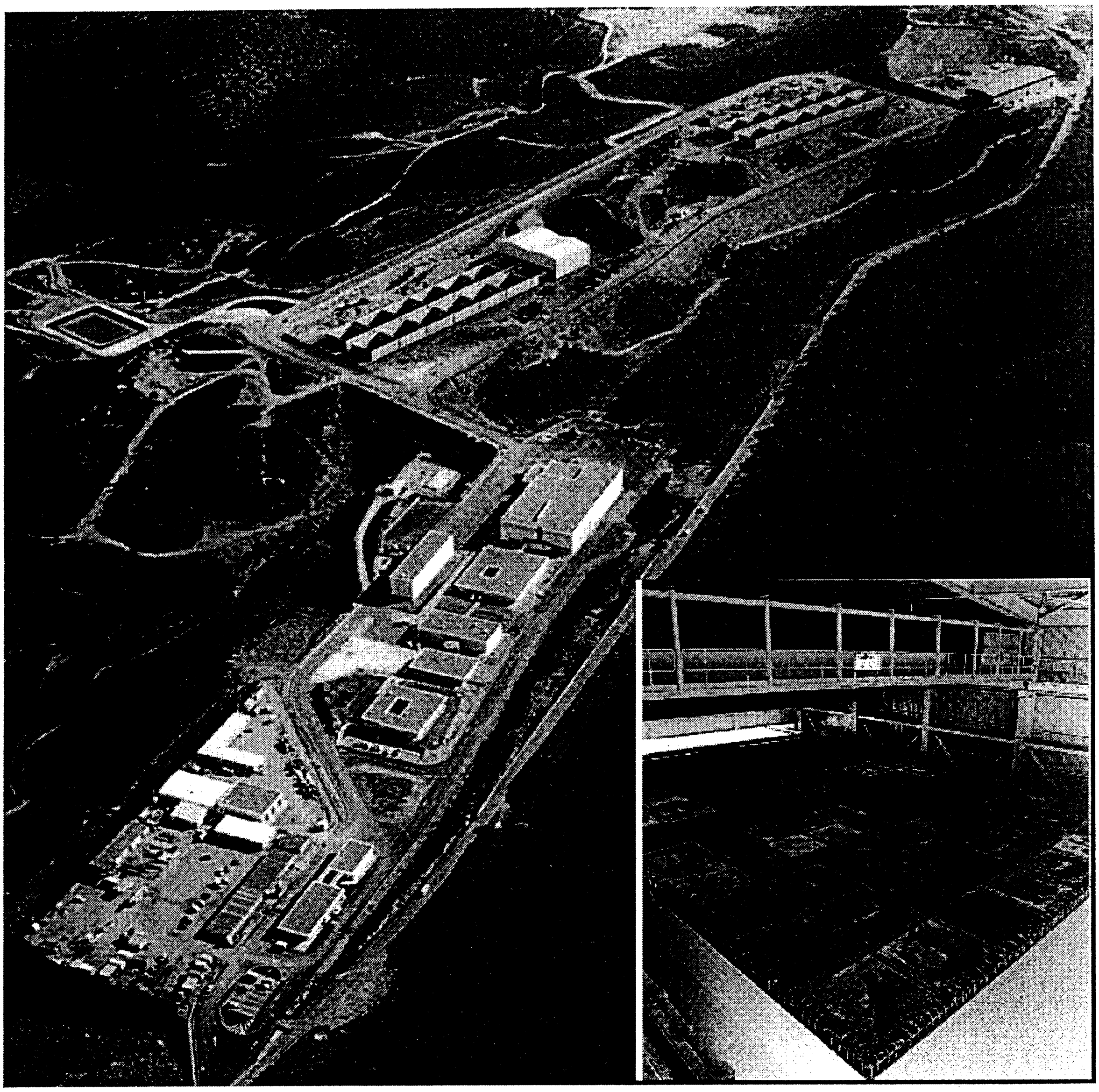

Figure 3. An aerial view of ENRESA's low-level radioactive waste disposal facility at El Cabril in Cordoba, Spain (ENRESA 1994). Two arrays of concrete disposal cells are visible in the top part of the main picture. The disposal cells are covered by a temporary roof (white) to limit the entry of rainwater while they are filled with waste. The inset shows waste in concrete boxes within a concrete disposal cell.

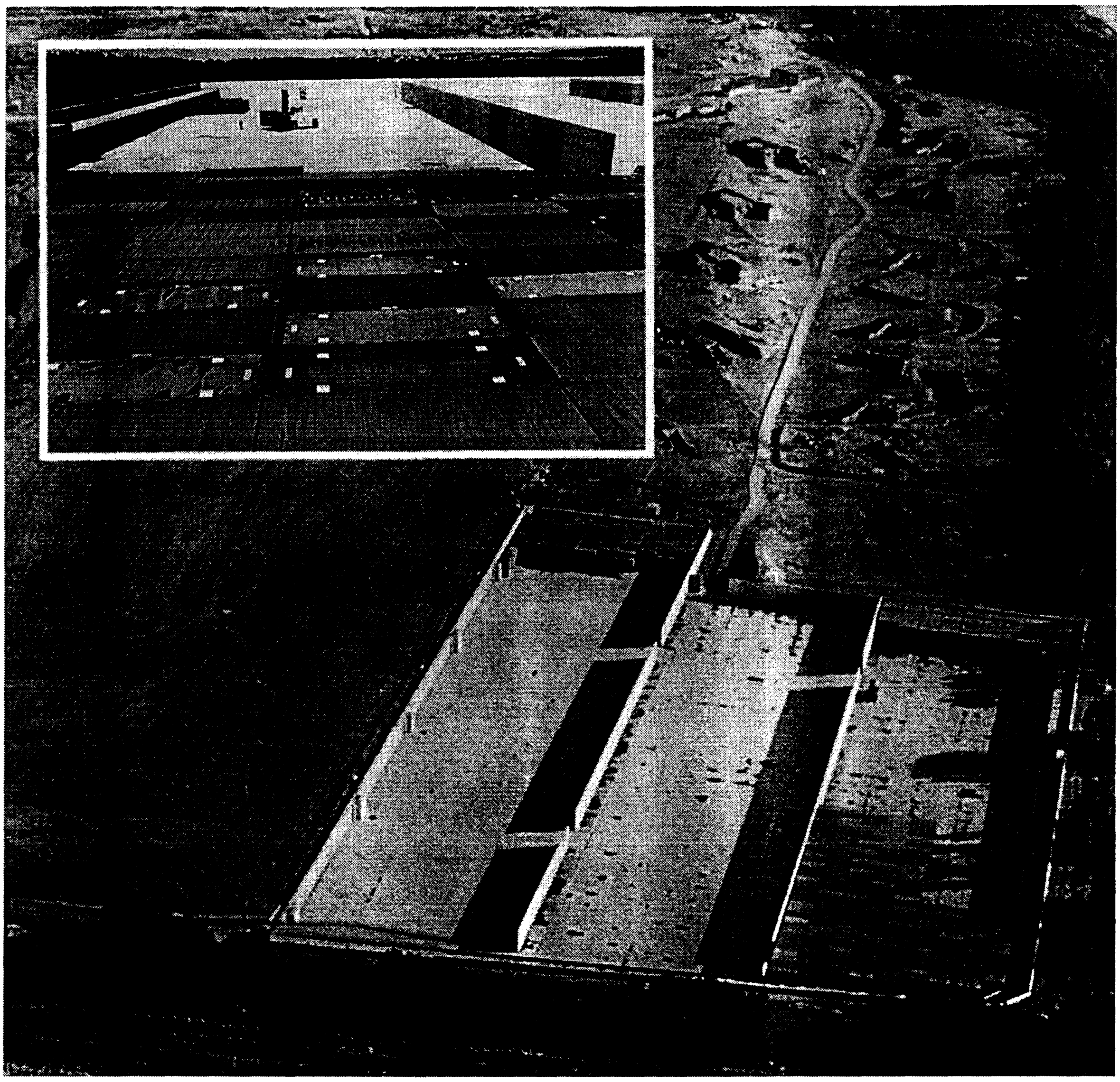

Figure 4. An aerial view of BNFL's low-level radioactive waste disposal facility at Drigg in north west England (CEC 1994). The bottom right-hand part of the main picture shows the concrete vault (known as Vault 8) which is divided into three sections by concrete walls. Super-compacted waste is loaded into steel ISO containers which are then filled with a fluid cement grout. Waste containers can be seen partially filling each of the vault sections. The inset gives a more detailed view of the tops of emplaced waste containers within the vault, and the emplacement method using a conventional fork-lift.

Deep disposal concepts in many countries also include cementitious materials as structural components. In addition to those uses noted above for near-surface repositories, cementitious materials may be used as:

- Structural components of the repository, for example, as tunnel supports, shotcrete and shaft linings.
- Tunnel, shaft and borehole seals.
- Fracture seals (grouts).

Different material formulations are required for these different roles according to the practicalities of emplacement and performance requirements. These formulations typically include blends of ordinary Portland cement (OPC) with pulverized fly ash (PFA) and/or other pozzolans, with or without superplasticizers. Use of cementitious materials as structural components will also strongly influence the chemistry of the repository environment.

3. SUMMARY OF WORKSHOP DISCUSSIONS

3.1 Key Processes in Backfill Selection, Optimization and Behaviour

The presentations of national disposal concepts summarized the requirements of backfills in terms of desirable properties for specific waste inventories and disposal concepts. The primary desirable properties of the different backfill types considered are set out in Table 1 and include:

Chemical Backfills

- *an ability to buffer the chemistry of the repository to conditions that favor low radionuclide solubilities.* Chemical buffering occurs through dissolution of backfill material into incoming groundwaters. Sufficient backfill needs to be emplaced so that the buffering effect occurs uniformly throughout the repository and is effective for an appropriate period. Backfill materials may be selected with the aim of conditioning one or more of the chemical variables that influence radionuclide solubility in the repository. Such variables include pH and pCO_2; and

- *an ability to sorb or incorporate radionuclides and, therefore, retard their release from the repository.* For example, some of the solid phases that form in hydrated cementitious materials, such as calcium-silica-hydrate (CSH) gels, may have a significant capacity to sorb particular radionuclides. Certain phosphate materials, such as apatites, may have a significant capacity to incorporate particular radionuclides within their structures through precipitation, co-precipitation, and/or solid solution processes.

Hydrological/Physical Backfills

- *hydraulic conductivities and diffusivities to minimize access of groundwater to the waste and limit radionuclide migration.* For example, certain clay-based backfill materials may eliminate advective transport processes, including colloidal transport. In salt-hosted disposal concepts, salt backfills may, after healing, attain hydrological properties that approach those of the host rock;

- *physical properties to ensure repository stability and/or to support waste packages;* and

- *thermal conductivities that promote effective dissipation of heat away from the waste.*

In addition to these desirable properties, a number of other considerations are important in the backfill selection process, including:

- properties and processes that may provide secondary benefits to system performance and those that are potentially detrimental to system performance;

- the practicalities and operational safety of backfill emplacement and backfill and waste retrievability;

- availability of quality assured backfill materials; and

- cost.

Table 1. Main physical properties influencing the selection of backfill materials.

Backfill Function	Property	Backfill Material				
		Cement	Clay	Salt	MgO	Phosphate
Chemical	Buffering/Poising Capacities	✓			✓	
	Solubility Control	✓			✓	✓
	Sorption Control	✓	✓			✓
Hydrological	Permeabilities (Water and Gas)	✓	✓	✓	✓	
	Diffusivities	~	✓	✓		
	Pore Size Distribution (Colloid Filtration)	~	✓			
Structural	Swelling Pressures (Expandability)		✓		✓	
	Creep Behavior			✓		
	Strength, Integrity	✓			✓	
	Voidage Reduction	✓		✓	✓	
Thermal	Thermal Conductivites		✓	~		

Optimization of the backfill selection process was considered by Working Group 1. A significant workshop achievement was the development in outline of a reference methodology, based on a systems approach, for backfill selection and optimization. This methodology is illustrated in Figure 5. Figure 5 shows a sequence of steps that may be followed during the selection and optimization process. A key feature of the methodology involves identifying and documenting the primary purpose of the backfill on the basis of its desirable properties and then, at a subsequent stage, evaluating the effects of secondary processes and backfill properties on system performance.

Incorporating these relatively simple ideas, the methodology involves the iterative use of performance assessment, at a number of key points in a repository development program, to evaluate the performance requirements of backfill and to assess the performance of the disposal system including particular backfill specifications. Evidence of optimization could be provided by obtaining a series of results from the PA studies that converge to a stable answer as the repository development program matures. Use of a structured and rigorous methodology would help to build regulatory and stakeholder confidence in the repository development and optimization process.

The Working Group illustrated how the methodology might be applied by considering a hypothetical example relevant to the deep disposal of spent fuel in a repository in fractured crystalline rock, backfilled with clay. The group recommended that the methodology be developed and applied to a range of backfill materials and disposal concepts.

3.2 Current Understanding of Key Processes

A series of papers summarizing the status of research into various potential backfills including cementitious materials, clays, salt, and phosphates was presented and discussed on the second day of the workshop. On the third day of the workshop, Working Groups 2 and 3 were tasked with identifying the primary properties of backfill materials that allow them to achieve their function, the secondary processes that may influence their function, research issues that have been adequately addressed, and significant remaining uncertainties and future research requirements.

The backfill materials were classified into two groups according to their primary properties: chemical backfills (e.g., cementitious materials, MgO), and hydrological/physical backfills (e.g., clay, salt, cementitious materials), respectively. This classification of the different backfill materials was consistent with the scope of the workshop; however, it meant that for some materials, relatively little time was available for detailed discussions of the secondary processes (e.g., the chemical retardation properties of clays).

The conclusions of the working group discussions are presented below and should be viewed in light of the workshop scope. Research issues identified for which a good understanding is available include:

Chemical Backfills

- An extensive, peer-reviewed literature exists on the reactions that may occur in cementitious materials and their thermodynamic properties at low temperatures (c. 25°C). This data allows an understanding of the pH buffering capacity and solubility of cementitious materials. Although kinetically-controlled processes occur as cementitious materials evolve, thermodynamic equilibrium models are generally appropriate for making long-term performance predictions.

- The capacity of MgO backfill to react with CO_2 has been demonstrated by experiment and simulated using thermodynamic modelling.

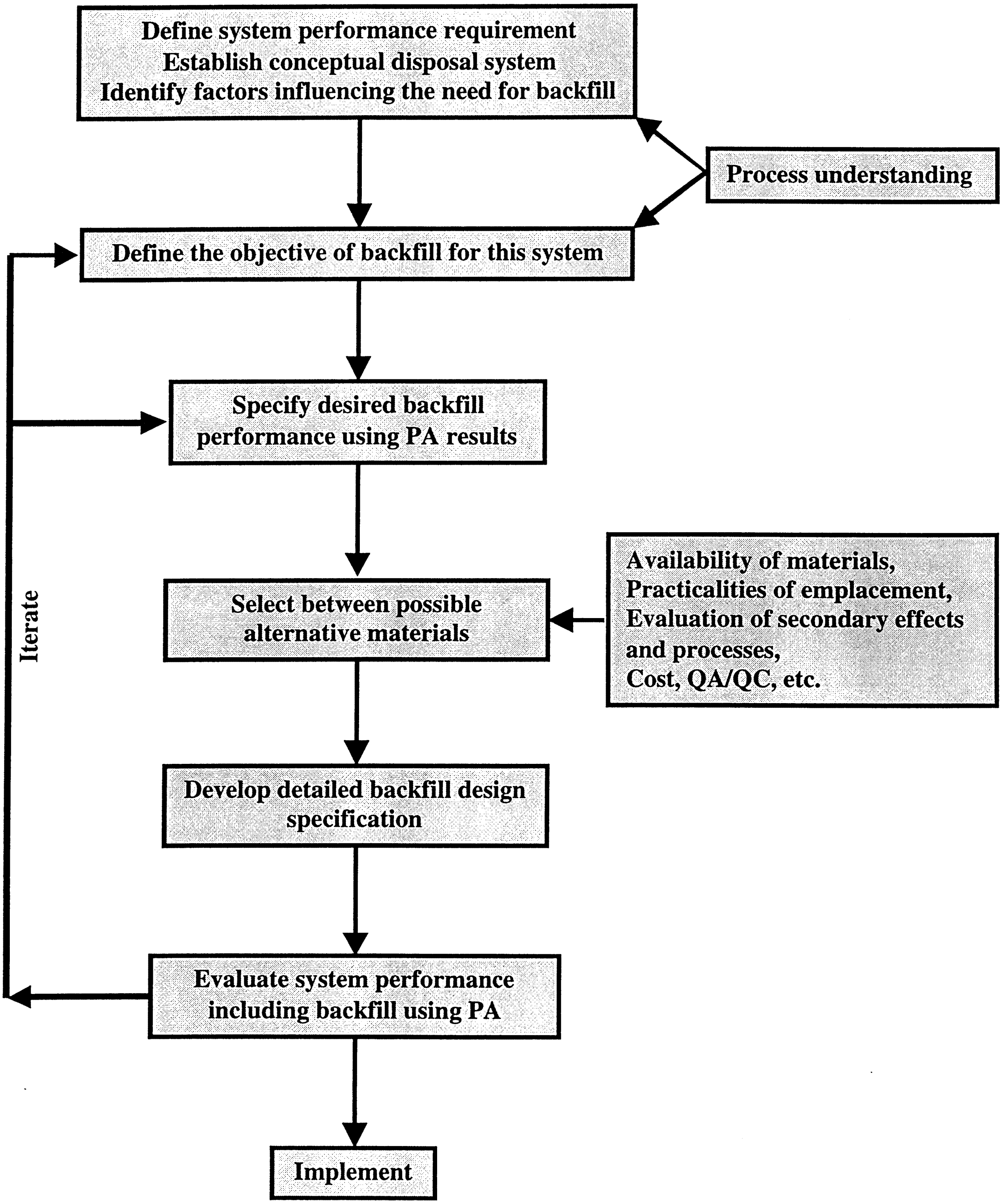

Figure 5. A reference methodology for backfill selection and optimization.

Hydrological/Physical Backfills

- The behaviour of clays is relatively well understood at small scales and at low temperatures.
- The thermal and mechanical behaviour of salt, and its radiolytic stability are well understood and adequate models exist to describe the long-term behaviour of salt.
- The short-term (<100 years) structural behaviour of cementitious materials and the radiolytic stability of cement are relatively well understood.

Remaining uncertainties and potential future research requirements identified by the groups are summarized in Table 2. The content of Table 2 reflects the experience and expertise of the working group members. The number of issues identified in Table 2 for each backfill type partly reflects the degree to which each material has been researched. For example, because a large amount of research has been conducted into the behaviour of cement, the working groups were able to define in more detail the limits of existing knowledge, which led to the identification of a larger number of uncertainties. A number of the issues identified for cements may also apply to some of the other materials. **The relevance and potential significance of each uncertainty must be considered in the context of the particular disposal system under consideration. Any conclusions regarding future research requirements need to be drawn on a programmatic basis.**

3.3 Representation of Backfill in Performance Assessment

The presentations of national disposal concepts included details of how backfills have been represented in performance assessment studies. In addition, a review of the treatment of backfills in performance assessment studies was presented to the workshop on the second day. Topics raised during discussion of this review are included in Table 2.

A key factor determining which flow pathways are evaluated in PA is the permeability contrast between the backfill or buffer and the host rock. For those disposal systems in crystalline rocks that use clay as a backfill, the pathway evaluated is generally the shortest route through the clay from the canister to the host rock. For disposal systems where clay backfill is emplaced in repositories in clay host rocks or where salt is used to backfill repositories in salt formations, the backfills are likely to have greater permeabilities than the host formations, at least over the short term, potentially resulting in preferential flow through the repository excavations.

The chemical properties of backfills are generally represented in PAs through just two parameters: radionuclide solubility and distribution coefficient (K_d). A number of recent PA studies have attempted to reflect the expected chemical evolution of the repository near-field by selecting radionuclide solubilities and distribution coefficients appropriate to different stages in repository history.

The basic hydrogeological properties of backfills (porosity, permeability, hydraulic conductivity) are used in PA calculations, and it is often assumed that these properties will remain constant over time, even though long-term durability is not well constrained.

PA calculations often exclude explicit representation of the physical properties of structural cementitious engineered barriers and repository components. For clay backfills, physical properties such as density and swelling pressure are indirectly accounted for in PA by use of appropriate permeability and diffusivity values. For salt-based disposal systems and salt backfills, PA simulations have included explicit modelling of salt creep.

Table 2. Uncertainties identified in recent performance assessment (PA) studies and during workshop discussions. The relevance and potential significance of each uncertainty must be considered in the context of the particular disposal system under consideration. Any conclusions regarding future research requirements need to be drawn on a programmatic basis.

Influence	Backfill Material			
	Cement	Clay	Salt	MgO
Chemical	The effects of elevated temperatures on the phase chemistry of cementitious materials has been studied to some extent, but thermodynamic data with which to predict the long-term behavior of crystalline cement phases is sparse above ~85°C. The effects of waste and backfill degradation products and other potential complexants (e.g., organics and CO_2, CO_3^{2-}) on radionuclide mobilization have not been studied extensively. The speciation and phase chemistry of certain radionuclides (e.g., +IV actinides) in high-pH, cement-conditioned waters is not fully understood, even though radionuclide solubility measurements may be available for some of these systems. The representation in PA models of radionuclide processes that may occur in cementitious materials by sorption, precipitation, co-precipitation, and/or solid solution processes is often simplistic and not well justified.	The chemical stability of clays under hypersaline and hyperalkaline conditions is not well constrained. Understanding of coupled, temperature-dependent processes in clays is limited.		The effects of chemical buffering by MgO and other possibly stable magnesium-hydroxy-carbonate minerals on actinide solubility have been evaluated using thermodynamic models but have not been quantified by experiment. The effects of spatial heterogeneity in the repository on the chemical control of actinide solubility by MgO may need further investigation. Passivation of MgO by reaction products is the focus of on-going research.

Table 2 continued. Uncertainties identified in recent performance assessment (PA) studies and during workshop discussions. The relevance and potential significance of each uncertainty must be considered in the context of the particular disposal system under consideration. Any conclusions regarding future research requirements need to be drawn on a programmatic basis.

Influence	Backfill Material			
	Cement	Clay	Salt	MgO
	The effects of microbial action on cementitious materials are not well understood.			The effects of interactions between the MgO backfill and other major element ions (e.g., Fe^{2+}, Ca^{2+}, etc) have not been fully assessed.
Hydrological	The evolution of the hydrogeological properties of cementitious materials is not well constrained. Spatial heterogeneity in the near-field and the processes leading to the cracking and re-healing of cracks in cementitious materials are uncertain. The compatibility of cementitious materials with other materials (e.g., clay, some host rocks) is poorly constrained. The potential effects of an alkaline plume migrating from a cement-conditioned repository into the surrounding host-rock have only recently been identified.	The degradation of clay materials over time (e.g., by hydrothermal alteration, the transformation of smectite clays to illite or micas, or silicification) may decrease swelling capacities and increase hydraulic conductivities of seals and backfills. Degraded barriers are sometimes analyzed during PA studies in "poor sealing" scenarios but the properties of degraded materials are not well known. The mechanisms of gas transport through clays are uncertain. The compatibility of clay with other materials in the repository, such as steel, is poorly understood.	PA results may be sensitive to the timing of brine inflow to the repository. Understanding of the temporal evolution of salt backfill physical properties (e.g., porosity and permeability) is limited.	The effects of microbial action on MgO are not well understood. The hydrological properties of waste cemented by MgO and the evolution of these properties are not well understood.

Table 2 continued. Uncertainties identified in recent performance assessment (PA) studies and during workshop discussions. The relevance and potential significance of each uncertainty must be considered in the context of the particular disposal system under consideration. Any conclusions regarding future research requirements need to be drawn on a programmatic basis.

Influence	Backfill Material			
	Cement	Clay	Salt	MgO
Structural	The evolution of the physical properties of cementitious materials is not well constrained. For example, there is a lack of information on the long-term compressive strength of cementitious materials, and only limited analogue information exists for the long-term structural behavior of cementitious materials. PA results may be sensitive to the length of time for which credit can be taken for the structural properties of cementitious barriers. In some cases, assumptions made in PA studies about the durability of certain engineered barriers are constrained by prescriptive regulations. The structural behavior of cementitious materials in hypersaline systems is not well constrained. The strength of cement-grouted waste and its influence on the consequences of human intrusion by drilling are uncertain.		The effects of small amounts of water on the properties of salt are not well understood. The effects of host-rock heterogeneity on backfill host-rock interaction are poorly constrained.	The strength of MgO conditioned waste and its influence on the consequences of human intrusion by drilling are uncertain.

Results from research studies into quantifying backfill degradation and dissolution rates have generally not been transferred to PA in a quantitative sense. Such studies contribute to safety assessment mainly through developing fundamental process understanding and building confidence in disposal concepts. PAs generally exclude explicit modelling of radiolysis, volume changes, colloidal processes, biological activity and physical and chemical heterogeneity within the repository. Such features and processes are often eliminated from PA calculations during the development of PA conceptual models, using reasoned arguments concerning their potential consequences to the performance of the disposal system.

3.4 Promotion of International Collaboration

The workshop itself was seen as an important first step in achieving the objectives of international collaboration between organizations considering the use and assessment of backfill in radioactive waste disposal systems. The range of backfill concepts under consideration is documented in Appendix 2 and has been summarized in Section 2 of this paper. Key results of the discussions during the workshop have been summarized in Section 3.

The workshop participants identified a need for an on-going forum to facilitate continuing discussion and collaboration. A number of suggestions were made as to what form this should take, what technical areas should be considered, and how this need could be fulfilled. Specific recommendations arising from the workshop discussions are presented in Section 4.

4 CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

The following general conclusions have been drawn from the workshop:

- **A relatively small number of concepts exist for the use of backfill, and there is therefore some overlap between the research efforts of the various national programs. Synergistic benefit would arise from greater communication and collaboration between national disposal programs.** For example, greater integration of research results could lead to the construction of common databases and/or assessment models.

- **Consensus exists as to the reasons why particular backfill materials may be selected, in terms of their desirable physico-chemical properties** for specific waste inventories and disposal concepts.

- **Research into "new", potentially beneficial materials / backfill additives** (e.g., phosphates, MgO) is on-going in a number of countries, but the status of research into these materials **is less advanced than for the common materials being proposed for use as backfill for radioactive waste (i.e., clay, cement and salt).**

- **The radioactive waste disposal community has a good understanding of the technical aspects that need to be evaluated** with regard to the use and assessment of backfill materials, **and has a clear picture of the remaining technical uncertainties.**

- **Continued effort is necessary to investigate some of the remaining technical uncertainties and to improve the interface between research on backfill materials and performance assessment.** The aim of such effort would be to improve and/or better justify the representation of backfills in PA models. Increasing the degree of realism in PA models by eliminating overly conservative assumptions would allow potential performance benefits to be realized, would increase confidence in performance assessment results, and would enhance optimization of disposal system and backfill design.

- **Considerable similarities exist in the methods used by regulators** of radioactive waste disposal **in different countries** to assess the safety of repositories. Emphasis is placed on evaluation of performance assessment results and the more qualitative arguments that necessarily form part of a safety case or compliance application. **However, differences exist in the degree to which regulators rely on independent performance assessment in decision making, and in the extent of regulatory guidance provided to disposers.**

- **The development, testing and use of an internationally agreed reference methodology for backfill selection and optimization would build confidence in the repository development and optimization process. A start on the development of such a methodology was made during the workshop; however, further work remains to be done to develop, refine and test the methodology at international level.** Optimization requires consideration of a number of factors beyond backfill material performance, such as repository siting and design, the nature of the waste, the nature of the repository host rock, practicalities and operational safety constraints on backfill emplacement, waste retrievability, and the availabilities of component materials for the backfill. The workshop participants rejected the idea that a "generic" backfill could be developed, that would be applicable in many different disposal concepts.

- **A need exists for a continuing forum to facilitate discussion, international collaboration and data exchange on near-field repository engineering and design issues.** Such a forum could be designed to allow discussion on backfill-related topics that were beyond the scope of this workshop, and to ensure that prioritization of future research work is based on assessments of the safety of disposal.

4.2 Recommendations

Work on backfill and the near-field environment will inevitably continue in a number of national programs with the aim of building confidence in radioactive waste disposal. The results of the workshop suggest that collaboration between national radioactive waste disposal programs in this area would be beneficial for a number of reasons. A general recommendation of the workshop is, therefore, that an on-going international forum for discussion of repository design, optimization and near-field issues be established, aimed at:

- enhancing collaboration and eliminating unnecessary duplication of effort between national disposal programs;
- promoting focussed discussion between technical specialists;
- promoting information and data exchange between national programs. This could involve managing a matrix of on-going research and development activities in the participating countries, with periodic circulation of a summary of R&D results;
- providing a credible route for publication of research and development results;
- providing a recognized forum for the development of reference near-field assessment and optimization methodologies;
- organizing future technical workshops; and
- providing a forum for model benchmarking exercises.

A consensus was reached among the workshop participants that discussions should be initiated with the Nuclear Energy Agency of the Organization for Economic Cooperation and Development (OECD/NEA) regarding a future international collaborative project[1].

The Reference Methodology for Backfill Selection and Optimization outlined at the workshop should be applied for a range of backfill material types and disposal concepts. An assessment of the methodology should be made to consider its usefulness in decision making, its role in helping to develop effective repository designs, and its benefit in terms of building regulatory and stakeholder confidence. The workshop also identified a need to consider and develop methods of cost-benefit analysis appropriate for application in the optimization process for radioactive waste disposal systems.

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[1] The Site Evaluation and Design of Experiments for Radioactive Waste Disposal Co-ordinating Group (SEDE) of the OECD-NEA Radioactive Waste Management Committee agreed at its meeting in Paris on 23-25 September 1998, to take this initiative forward and, as a first step, to elaborate the proposal for approval by national delegations in early 1999.

The workshop noted the increasing level of discussion among the national disposal programs over the issue of waste retrievability. It is recommended that the implications of waste retrievability be evaluated by the international community in terms of the implications for disposal system design, including backfill selection and the practicalities of backfilling in general, as well as for performance assessment, regulation, and public acceptability.[2]

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[2] The French Radioactive Waste Management Organization, ANDRA, has recently offered to sponsor an international meeting to consider engineering aspects of waste retrievability.

5 REFERENCES

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CEC. (1994) *Managing Radioactive Waste in the European Community.* Commission of the European Communities (CEC), Brussels, Belgium.

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ENRESA. (1998) *FEBEX, Full Scale Engineered Barriers Experiment in Crystalline Host Rock, Pre-Operational Stage Summary Report.* Technical Publication Number 01/98. Empresa Nacional de Residuos Radiactivos, S.A. (ENRESA), Madrid, Spain.

APPENDIX 1 WORKSHOP AGENDA

Workshop Schedule

Tuesday 5 May

Workshop Aims and Objectives

8.00	Welcome and introduction	**G. Dials**
8.30	Workshop aims and objectives	**S. Duerden**
8.45	Workshop organization and participant involvement	**D. Galson**
9.00	Participant introductions - round table	**All**

National Disposal Concepts Including the use of Backfill

9.45	Belgium	Backfilling Waste Disposal Galleries in Belgian Boom Clay	**L. van Cauteren**
10.10	Canada	Clay and Cement-based Backfill and Sealing Materials Designed for Use in a Canadian Nuclear Fuel Waste Disposal	**S. Stroes-Gascoyne**
10.35	China	The Sorption Behavior of Inorganic Material of Diatomaceous Earth and Cement	**B. Chen**
11.00	**Tea/coffee**		
11.25	France	Backfill Materials in France - Investigation and Research Programs	**F. Plas/E. Giffaut**
11.50	Germany	Backfilling and Sealing of Radioactive Waste Repositories in Rock Salt Formations	**W. Brewitz**
12.15	Japan	To Be Announced	**M. Shibata**
12.40	**Lunch**		
2.00	Korea	Development Status of Backfill Materials for Radwaste Disposal in Korea	**K. Chun**
2.25	Sweden	Clay Isolation of Radioactive Waste in Sweden	**R. Pusch**
2.50	Switzerland	Cementitious Backfill: The Swiss View	**U. Berner**
3.15	**Tea/coffee**		

3.45	Ukraine	Stability of Concrete inside Chernobyl Unite 4 Shelter	**V. Sinitsyn**
4.10	U.K.	Radioactive Waste Disposal in the UK: Use and Application of Cements and Backfill Materials	**S. Duerden/** **A. Hooper/** **D. Trivedi**
4.35	U.S.	Engineered Barriers and Backfill in LLW Disposal Facilities	**V. Rogers**
5.00	**Close**		

Wednesday 6 May

Introduction to Technical Sessions

8.00 Opening remarks **M. Matthews**

8.10 Round-table discussion led by **D. Galson/M. Chu** to allow elicitation of the participant's desires from the rest of the meeting in light of the first day's presentations. **All**

8.55 Introduction to the following sessions. **D. Galson/H. Papenguth**

A structured approach to achieving the aims of the following Workshop sessions will be described. This approach will include completing a multi-dimensional matrix that documents for each of the backfill materials, the principle reasons for material selection, the status of research, areas where claims for the performance of backfill are considered to be well supported, and priorities for further studies on the basis of PA needs.

Rationale for the Uses of Backfill and Backfill Material Selection

This session will be aimed at addressing questions such as: How and why do we choose between the different possible backfill materials? What are the aims of using the materials selected by each program? How can we show that the optimum backfill has been selected?

9.00 **V. Bynum** will present a summary review focused on identifying and contrasting the principle reasons for the use of backfill and the choice of backfill materials, and methodologies for optimizing this selection process.

9.25 Discussion led by **H. Papenguth** drawing on information on the rationale for the use of backfill contained in the national overview papers. The results of the discussion will be used to complete part of the matrix described above by documenting the principle reasons for backfill material selection and use.

9.50 Tea/coffee

Status of Research into Backfill Materials

This session will cover a range of experimental and modeling studies and will be aimed at making an assessment of how well research performed to date allows us to understand the various properties of backfill materials, the processes that will affect the backfill, and the influences of the backfill on other components of the disposal system. A technical oversight role will be played by **U. Berner** who will chair the session, lead the discussions and report on the session after the meeting for the conference proceedings.

10.15 Introductory remarks **U. Berner**

10.20	Cement	The Performance of Backfills Based on $Ca(OH)_2$ and Cement	**F. Glasser**

10.40	Salt	Backfills as Geochemical Barriers in Repositories in Salt Formation	**B. Grambow**
11.00	Discussion		**All**
11.20	MgO	Status of Research on MgO Backfill for the WIPP	**H. Papenguth**
11.40	Phosphates	Phosphate Based Backfill to Minimize Radionuclide Migration	**W. Runde**
12.00	Discussion		**All**

The results of the discussions will be used to complete a further a dimension of the matrix described above identifying the status of research on the different backfill materials in a range of technical areas.

12.30 Lunch

Representation of Backfills in Performance Assessment

The inclusion of backfill can lead to a range of assumptions in performance assessment analyses, concerning the FEPs that are included, the scenarios that are simulated, and the conceptual models employed to represent the backfill.

1.30 **D. Bennett** will present a summary review of the approaches being taken in the different disposal programs to include the effects of backfill in performance assessment.

1.50 **D. Savage** will present a paper on the requirement for, and use of, data from natural analogues in PA. This paper will draw on recent experience from the Maqarin Project, and from other relevant analogue projects.

2.10 Discussion led by **D. Bennett**. The discussion will be structured so that a systematic walk-through is made of the different sources of uncertainty in PA (scenario uncertainty, conceptual model uncertainty, parameter uncertainty) related to the use of backfill. The results of the discussion will be used to complete a further a dimension of the matrix described above that will identify priorities for further studies on the basis of PA needs, rather than simply an analysis of generic understanding and gaps in research.

3.00 Tea/coffee

Approaches to Regulatory Evaluation of Backfills

In this relatively brief session, regulatory research and assessment of backfill will be addressed.

3.25 **A. Campbell** will present a paper on the transfer of backfill research and process modeling into regulatory approaches for the evaluation of backfill, and the application of these approaches.

3.45 **P. Baudoin** will present a paper on the the French Regulator's program and approach.

4.05 Discussion led by **S. Duerden**. Because a performance assessment forms only one aspect of a safety case or compliance application, the discussion will inevitably go beyond those aspects covered when considering backfill materials in performance assessment, to include other qualitative lines of reasoning and supporting arguments. The results of the discussion will be used to complete a further a dimension of the matrix described above that will identify, from the regulatory perspective, where claims for the performance of backfill areconsidered to be well supported, and where there remains a need for further research and development.

5.00 Close

Thursday 7 May

Discussion Topics Arising

8.00 Throughout the meeting, the Secretariat will maintain a record of issues that arise during the technical sessions. During the first two days of the meeting, the sessions will include all of the participants. On the third day, however, it is planned to subdivide the group and discuss, in further depth, several of the key issues raised during the earlier sessions.

Thursday morning will therefore begin with a brief résumé by the Secretariat of the issues raised, and a proposal for the topics to be taken forward.

8.45 Discussion sessions will be convened on selected topics. Each discussion session will be led by one of the participants.

10.00 Tea/coffee

10.25 Topical discussion sessions continued.

12.30 Lunch

General Discussion "Where do we go from here?"

1.30 Under this and the following final session of the meeting, all of the participants will re-convene for a group discussion. The session leaders will report the results of the topical discussion sessions to the full group.

3.00 Tea/coffee

Wrap-up Discussion

3.30 This session will comprise a summary by the Workshop Secretariat of the meeting conclusions, and a round-table evaluation of the meeting by the participants.

5.00 Close

APPENDIX 2 BACKFILL IN NATIONAL DISPOSAL CONCEPTS

CONTENTS

CHOOSING THE OPTIMAL MIXTURE FOR BACKFILLING A HLW-DISPOSAL GALLERY IN BOOM CLAY

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1. INTRODUCTION

Nuclear power generation in Belgium relies on the operation of seven reactors of the PWR type, representing a total installed capacity of 5.5 GW(e) that accounts for nearly two thirds of the country's annual electrical output. Spent fuel is sent to France for reprocessing. In 1974 the Belgian Research Centre for Nuclear Energy (SCK-CEN) at Mol initiated a research and development programme on deep geologic disposal of radioactive waste (Heremans *et al.* 1984). Since 1985, the Belgian National Radioactive Waste Agency (ONDRAF/NIRAS) has supplied the guidelines for research and development and demonstration programmes. An underground laboratory was built at a depth of 230 m in the Boom Clay interval underlying the research facilities at Mol. Because spent fuel has been sent to La Hague (France) for reprocessing, ONDRAF/NIRAS has focussed on a backfill material for vitrified waste. Recently, the Belgian government asked ONDRAF/NIRAS and the power plant operator whether direct disposal of spent fuel would be more effective. Studies were therefore started to adapt the backfill material to the disposal of spent fuel.

2. DISPOSAL CONCEPT AND RATIONALE FOR THE USE OF BACKFILL

Belgium at present plans to dispose of its high level radioactive waste underground in excavations of horizontal galleries. The Boom Clay layer, one of the possible host rocks, has a rather limited thickness of approximately 100 m. Because of the thermal output of the waste, only one vitrified canister or four spent-fuel assemblies can be axially placed in 2.0 or 2.2 m ID disposal galleries (Figures 1 and 2). All disposal galleries must be bored and then equipped with either one or four disposal tubes and backfill material. The backfill must be hydrated before the waste canisters or assemblies are emplaced in the disposal tubes. Because the backfill material is emplaced before the waste, the backfill can be emplaced in a non-nuclear, non-heating environment (Van Miegroet 1993).

In this disposal concept, the waste form (glass matrix or fuel assembly) is the first barrier. It can significantly delay the emission of radionuclides to the environment. This barrier is supplemented by a 1 to 3 cm thick overpack, which ensures physical isolation of the waste during the warm period (300 to 1000 years) because the corrosion rate of glass in contact with clay increases substantially above a temperature of 90°C (Kursten *et al.* 1997). Moreover, because the migration of radionuclides in a clay layer subjected to a thermal gradient is much more difficult to characterize, the fact that radionuclides cannot be released from the overpack during the warm period avoids having to study the consequences migration would have on the system safety.

The Boom Clay layer is the main barrier. This layer is characterised by a high cationic sorption capacity and a favourable chemical environment (fairly alkaline pH, very reducing conditions), which provide very favourable radionuclide retention properties. Because the Boom Clay has a low vertical hydraulic conductivity ($K = 2.10^{-12}$ m/s) and a very low natural hydraulic gradient (0.02 m H_2O/m), radionuclide migration is controlled by diffusion and advection is of minor importance. It should be noted that the self-healing properties of the Boom Clay (because of its plastic nature) prevent the formation of open faults in response to tectonic deformation. Such faults are potential release outlets for the radionuclides.

The backfill material has two functions in the present concept:

1. It will dissipate the heat in order to avoid a high temperature increase, which could jeopardize the waste form and hence increase its leaching rate. This implies that the heat transfer coefficient of the backfill material should be greater than that of the host rock and that the emplacement voids must be controlled.

2. It will minimize the geomechanical perturbations of the clay formation that will occur if the galleries are not backfilled. If they occurred, the geomechanical perturbations would affect the confining properties of the clay layer. This implies that there must be a backfill material swelling pressure; however, it must not exceed the lithostatic pressure (P_s <4 MPa).

The backfill material must be compatible with the host clay. Its chemical composition must not substantially affect the retention properties of the Boom Clay.

3. RESEARCH INTO THE BACKFILL MATERIAL

3.1 Research into the backfill material for vitrified waste

The European Commission has co-financed part of the research described here.

3.1.1 Preliminary studies - first pre-mockups

The studies carried out by the French Research Centre for Nuclear Energy (CEA) on behalf of ONDRAF/NIRAS, until 1994, aimed at (1) selecting a hydration system and a backfill material based on laboratory information and experiments on industrial uniaxial compaction of blocks and (2) defining the backfill layout, i.e., conducting mockup tests and refining the emplacement procedure and the hydration system.

It was decided to work with blocks made of a mix of FoCa clay (calcium clay) and sand that could be shaped to leave minimal voids in the gallery. Boom Clay was rejected as backfill material because of its heterogeneity and its rather low swelling capacity. The annular void between the gallery lining and the disposal tube was filled with three concentric rings of blocks (Dardaine and Lajudie 1993, Dardaine *et al.* 1994).

Hydration system

Two types of saturation systems were developed: (1) a simplified system with hydration pipes placed only at the periphery of the backfill material, against the gallery lining and (2) an extensive system with hydration pipes placed at the periphery and within the backfill material, between the blocks.

Backfill material

Two types of backfill material were developed to test the function of the hydration system. As the saturation of the backfill material could not be ensured with the simplified hydration system (hydration pipes only at the periphery), the heat conductivity was increased by adding graphite to the FoCa clay/sand mix. The backfill material therefore always has a better heat transfer coefficient than the host rock.

In the case of the extensive hydration system, which contained additional hydration tubes between the blocks, no graphite was added to the mix. The required heat conductivity was obtained by a higher percentage of sand and by hydration of the backfill material. This backfill material, however, did not meet the heat transfer requirement prior to its hydration. Note that in both cases, the Belgian reference concept entails placing the waste in the disposal tubes only after hydration and swelling of the backfill material. That process will ensure adequate heat transfer.

Block compaction trials were conducted in an industrial uniaxial press. Because the density does not significantly increase at compaction pressures above 60 MPa, it was decided to compact the blocks at a pressure of 60 MPa. The blocks weigh approximately 25 kg, which allows manual preparation and handling. A swelling of the blocks was observed just after demoulding. Because swelling reached ~2%, it must be taken into account in determining the mould dimensions.

Pre-mockup with simplified hydration system

This pre-mockup consisted of a 2-m ID concrete cylinder made of two shells (a lower and an upper), an inner 0.5-m OD steel cylinder representing the disposal tube, and two covers at each end. The backfilled length was 1.5 m.

Blocks were manufactured with a mix consisting of 75% FoCa clay, 20% sand, and 5% graphite, compacted at a pressure of 60 MPa. The choice of the mix composition was based on expert judgment by the CEA. There were three different types of blocks, corresponding to the three concentric rings of, respectively, 16, 12, and 6 blocks needed to fill the entire annular section.

After placing the blocks and closing the mockup, hydration was carried out by 16 tubes placed regularly and parallel to the mockup along the concrete cylinder. These tubes, consisting of sintered filters placed in pipes with diffusing holes of 4 mm diameter, were connected with sleeves and were fed by a pressurized tank (max 3 bar).

Soon after the beginning of hydration, the upper concrete shell was lifted because of the swelling pressure of the backfill material. It was suspected that if the lining had been undeformable, the swelling pressure would have been higher than 4 MPa, the lithostatic pressure at the repository depth. After more than one week, the pre-mockup was dismantled: The upper shell and both covers were removed. All the lateral, inner and outer radial voids were filled because of swelling of the backfill material. The joints were filled and the blocks were stuck together so that mine rods were necessary to separate them.

The pre-mockup with the simplified hydration system gave good results, as the rapid swelling filled all the voids at the lining.

Pre-mockup with extensive hydration system

This pre-mockup structure was the same as the simplified hydration system. However, because the backfill material must be hydrated to fulfill the heat transfer requirement, the hydration network was more complicated. In addition to the 16 pipes placed around the backfill material, pipes were placed between the blocks. For the mockup, only six inner hydration pipes were run normally, the others being simulated by normal steel pipes.

Wet backfill blocks were made of a mix consisting of 60% FoCa clay and 40% sand. The block form was similar to that of the blocks in the pre-mockup with the simplified hydration system, except that openings were left to allow placement of the hydration pipes between the blocks. Block surfaces and ridges were not as clear as with the backfill material used for the simplified hydration system mockup, for which the presence of graphite improved demoulding. This fact and the presence of hydration pipes between the blocks made the placement in this pre-mockup more difficult than in the previous pre-mockup (some blocks had to be readjusted).

The results of the pre-mockup with the extensive hydration system were good as well.

Comparison of simplified and extensive hydration systems

Both pre-mockups gave good results. However, the simplified hydration system appears to be more useful for the following reasons: The placement is easier (better shaped blocks, no inner hydration pipes) and the wet backfill material for the extensive system must be hydrated to fulfill the heat transfer requirement, which cannot be accurately controlled. Therefore, it was decided to choose the simplified hydration system.

3.1.2 Backfill material optimization

After a successful hydration system was found and tested, the backfill material had to be optimized, taking into account the following requirements:

- good cohesion of the blocks to ensure easy handling and placement;
- residual swelling pressure between 1 and 4 MPa after hydration and filling of the emplacement voids; and
- high thermal conductivity (already studied at a previous stage).

The first requirement demands a high clay content. The second requirement, in contrast, calls for a limited clay content.

The optimization was conducted in three stages (Dardaine *et al.* 1996):

1. study of the swelling pressure at saturation of several clay-sand and clay-sand-graphite mixes;

2. validation of a procedure to measure the strength of the blocks; and

3. block manufacturing and strength measurements.

Study of the swelling pressure at saturation of different mixes

Clay/sand mixes (60 to 50% clay; 40 to 50% sand) and clay/sand/graphite mixes (45 to 75% clay; 50 to 20% sand; 5% graphite) were studied at saturation.

To this end, the mix was compacted in a cell between two mobile jacks fitted with pressure transducers. The mix was hydrated at atmospheric pressure and at room temperature. When a pressure reached a plateau, the sample was considered saturated. By successive relaxing of the mobile jack and maintaining hydration, the sample went through a succession of steady states.

Figure 3 shows the relation between the swelling pressure at saturation and the dry density in the mix. After modeling, the theoretical curves shown in Figure 4 were obtained. These curves enabled assessment of the swelling pressure at saturation as a function of the mix composition and its dry density.

Validation of a procedure to measure the strength of the blocks

Two kinds of tests were studied: the tensile test by splitting (Brazilian test) and the uniaxial compression test. The tensile test by splitting was chosen for characterizing the block strength because this test is easy to conduct and does not require any sample preparation.

Block manufacturing and strength measurement

The mixes were prepared and blocks were commercially manufactured at five compaction pressures ranging from 20 to 61 MPa.

Strength measurements carried out on the manufactured blocks showed that in order to obtain good strength, the compaction pressure must be higher than 35 MPa. For this pressure a maximum strength is obtained for the mix consisting of 60% clay, 35% sand, and 5% graphite. Therefore, it was decided to work with blocks made of a mix consisting of 60% FoCa clay, 35% sand, and 5% graphite, compacted at a pressure of 61 MPa. These blocks have a dry density of 2.09 kg/dm^3.

To obtain a residual swelling pressure lower than 4 MPa, the dry density (taking into account the placement voids) must be lower than 1.94 kg/m^3. This means that the initial placement void ratio must be higher than 7%, which remains acceptable.

3.1.3 Second pre-mockup

Before adapting the moulds and manufacturing high quantities of backfill blocks for a large mockup (the PRACLAY mockup), it was deemed wise to run a small mockup (called the second pre-mockup) to verify whether the swelling of the chosen backfill material is sufficient to fill an important peripheral void and whether the backfill material keeps its symmetry around the central tube after hydration (Dardaine and Gatabin 1996). For the PRACLAY mockup, it was decided to put all the placement voids at the periphery, which leads to an important peripheral gap (±35 mm) that needs to be filled properly by the swelling of the blocks.

Block manufacturing

Backfill blocks were manufactured with a mix consisting of 60% FoCa clay, 35% sand, and 5% graphite compacted at 61 MPa. The post-swelling of blocks and of rings was accurately measured to adapt the moulds for the PRACLAY mockup. Brazilian splitting tests were conducted on a percentage of the production, with satisfactory results.

Second pre-mockup structure

The structure was a light watertight steel structure simulating a gallery and a disposal tube. The ID was sufficient to leave a 34 mm peripheral void between the backfill material and the mockup lining. Hydration was carried out from the bottom by two square tubes bored with holes and fitted with a sintered filter. An overflow pipe at the top made it possible to verify the flooding.

Filling and flooding

The blocks were placed symmetrically around the central tube. Therefore, small steel blocks were placed under the backfill blocks in the lower part of the mockup to maintain the peripheral void constant around 360°. Five rings of sufficient length were accurately placed, and the mockup cover was then placed and welded to ensure that the structure was watertight.

Flooding was conducted at a pressure of 0.35 MPa. It required 1.5 hours to flood all the placement voids.

Dismantling

One month after flooding, four 50×150 mm openings were cut in the mockup jacket to access the backfill. The peripheral void had been completely filled because the backfill material was in direct contact with the lining. The four openings were subsequently closed to prevent drying of the backfill material.

Two months after flooding, the mockup was dismantled. Samples were taken radially at different distances from the centre, the water content and density of which were assessed. Sampling showed that only the outer 20 cm of the backfill had swollen to fill the peripheral void, while the backfill material located closer to the centre had kept its initial state. The axial symmetry of the backfill after hydration remained unchanged.

Conclusion

The second pre-mockup showed that the layout chosen for the PRACLAY mockup (large peripheral void) could be successfully hydrated: The voids were completely filled and the backfill kept its axial symmetry. The accurate study of the block post-swelling allowed the experimenters to fix the final dimensions of the block moulds for the PRACLAY mockup.

3.2 Adaptation of the backfill material for the disposal of spent fuel

Because of its long half-life, ^{129}I is one of the most critical radionuclides with regard to the deep disposal of spent fuel. Under *in situ* Boom Clay reducing conditions, the stable chemical form of iodine would be iodide. This anionic species is not sorbed on the negatively charged Boom Clay minerals at the slightly alkaline *in situ* pH and will be released without retardation from the host geological formation. If the geological barrier cannot efficiently retard the ^{129}I, and if the dilution in the aquifers is not sufficient to reduce the ^{129}I concentration, the confinement must then depend on the retention properties of the near field.

The first stage of an exploratory research programme has been performed to assess the efficiency of microporous active carbon (batch sorption tests and percolation experiments on reconsolidated backfill material plugs). The results of the sorption tests reveal that active carbon is effective for the sorption of iodine, especially if the getter is impregnated with silver. However, active carbon is not an ultimate sink for ^{129}I because the sorption is reversible. Because of the long half-life of iodine, the strong retardation seems to be insufficient to meet the long-term safety requirements. Moreover, as AgI is not thermodynamically stable under Boom Clay *in situ* conditions, this getter would be mainly suitable only during the oxidation phase after closure of the repository. It can be concluded that other materials have to be investigated. A possible candidate is apatite.

4. REPRESENTATION OF BACKFILL IN PERFORMANCE ASSESSMENT

In the most recent performance assessment studies for the disposal of vitrified waste (Marivoet *et al.* 1997), the backfill is given conservative values for its hydraulic conductivity and retention and dispersion coefficients. Because the influence of these parameters is negligible, the existence of the backfill could be ignored in the performance assessment studies, if desired. For the iodine present in the spent fuel, this viewpoint may not be realistic. Because the exact composition of the backfill around the spent fuel is not yet known, no detailed modeling has yet been conducted for this case.

5. CONFIDENCE BUILDING : THE PRACLAY DEMONSTRATION TEST

5.1 PRACLAY *in situ* demonstration test

This test will be conducted in a 30-m long, 2-m ID gallery that will be bored into the Boom Clay layer from an extension of the existing Underground Research Laboratory (Neerdael and Boyazis 1997).

The demonstration test will be equipped like a disposal gallery, with a disposal tube, backfill material, and a hydration system. Electrical heaters will be placed to simulate the vitrified waste. Instruments will be placed in and around the gallery to study the behavior of the clay host rock, the gallery, and the backfill material. Because of the construction time required to build the extension works, the demonstration test should begin around 2002. This 1:1 scale demonstration should prove the soundness of the disposal concept in clay.

5.2 PRACLAY mockup

To prepare for the *in situ* PRACLAY experiment, it was decided to run a mockup on the surface so that the filling stages could be verified and the hydration and heating stages could be tuned. Furthermore, this mockup will be the first opportunity to study at actual scale the thermal-hydrologic-mechanical (THM) behavior of the backfill material under conditions close to those that are actually expected to occur in disposal galleries (ONDRAF/NIRAS 1998).

The mockup represents a 5-m long section of a high-level waste (HLW) disposal gallery at a 1:1 scale. It is equipped with a disposal tube with electrical heaters to simulate the waste, and backfilled with the material that was refined during the second pre-mockup test. The THM behavior of the backfill material is monitored with instruments placed in and on the mockup (Figure 5).

In December 1997, the PRACLAY mockup was successfully hydrated. To date, the backfill material has behaved normally. Theem placement radial voids filled as a result of swelling, thus enhancing the global thermal conductivity of the backfill material to more than 3.5 W/(mK). The waste-simulating heaters will be activated in the near future.

6. METHODS OF EVALUATION

ONDRAF/NIRAS is preparing a Safety Assessment and Feasibility Interim Report (SAFIR). This report, SAFIR-2, will contain a synthesis of the information acquired in the multiple research programmes and studies on the disposal of high-level radioactive waste in the Boom Clay during the period 1988-1997. SAFIR-2 supplements the first SAFIR report (ONDRAF/NIRAS 1989).

ONDRAF/NIRAS will submit this report to the Belgian Government, which will then decide on the appropriate actions to be taken. At the time of the first SAFIR report, a scientific advisory committee was created, and its conclusions guide the expansion of the research programme after 1989. The SAFIR-2 report will also be submitted to the NEA for peer review.

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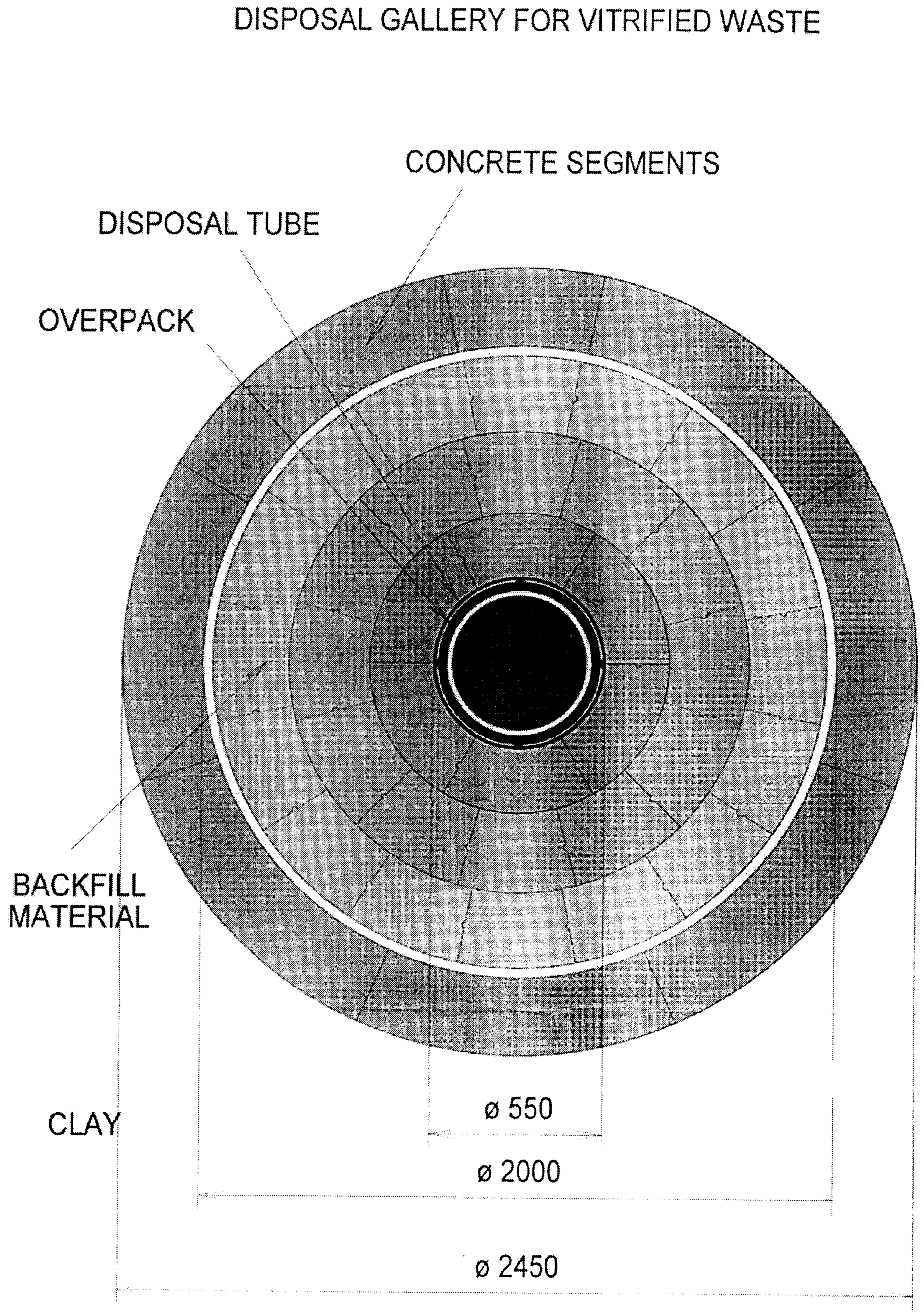


Figure 1. Disposal gallery for vitrified waste.

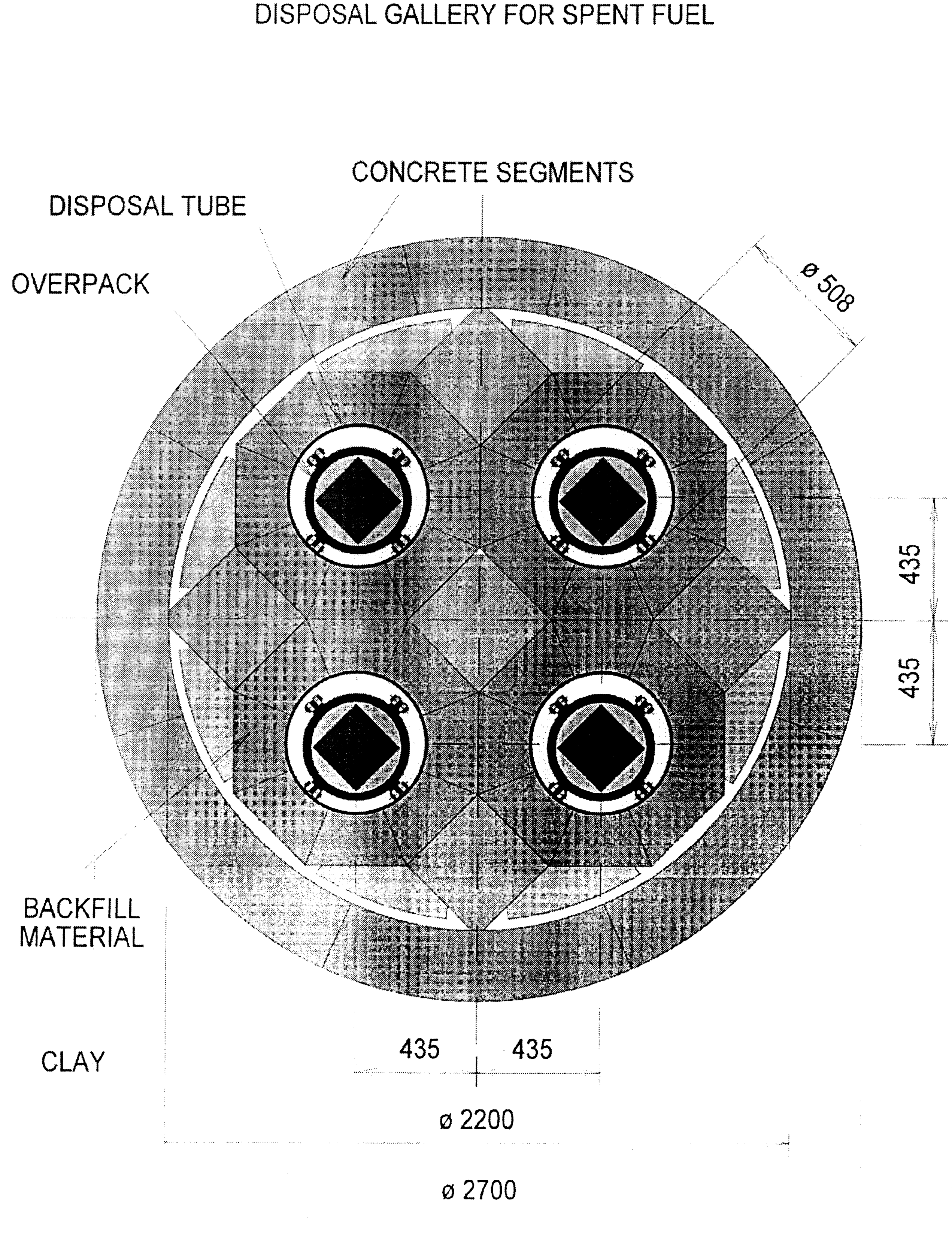


Figure 2. Disposal gallery for spent fuel.

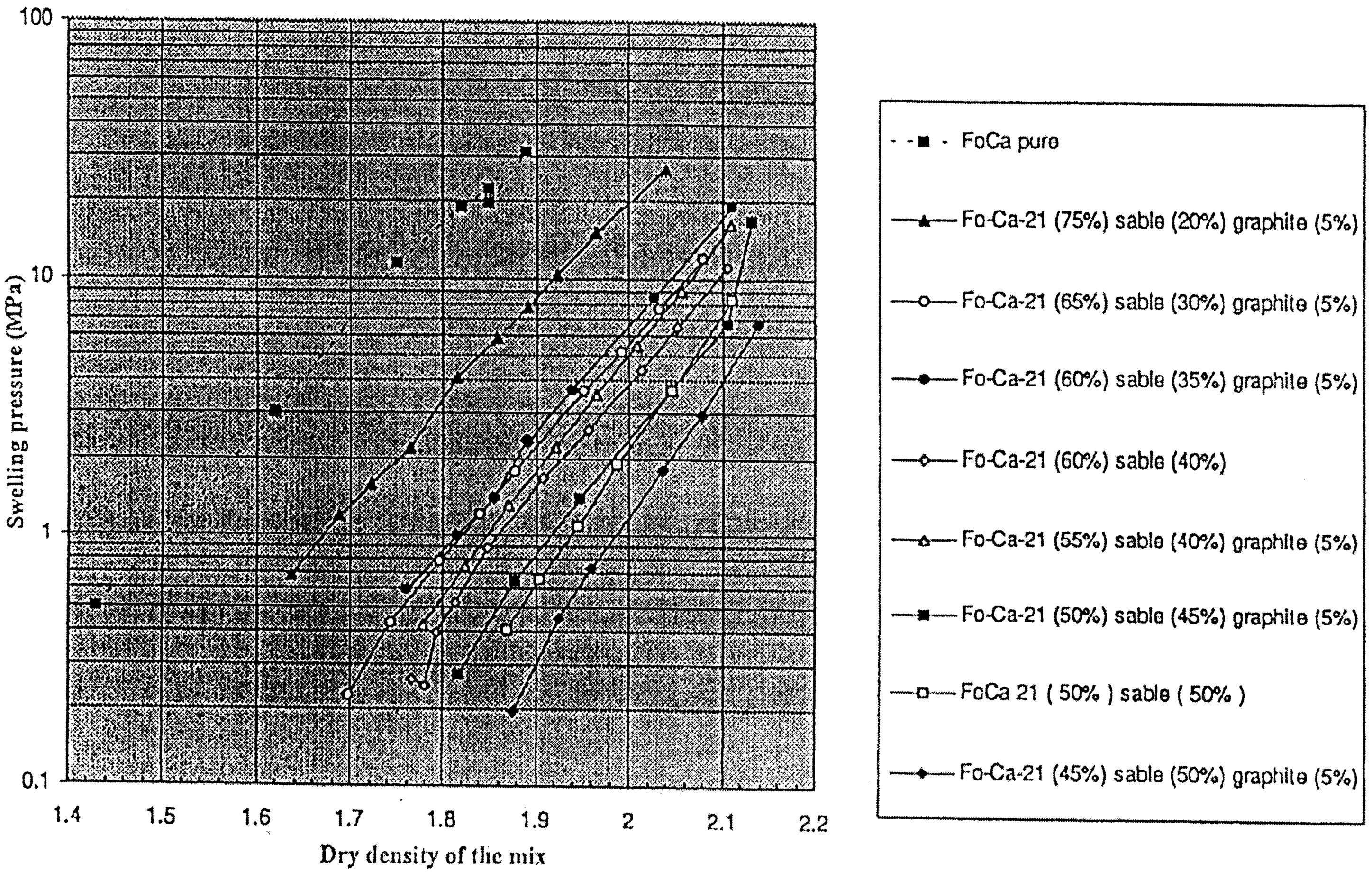


Figure 3. **Swelling pressure at saturation of clay-sand and clay-sand-graphite mixes as a function of the dry density of the mix.**

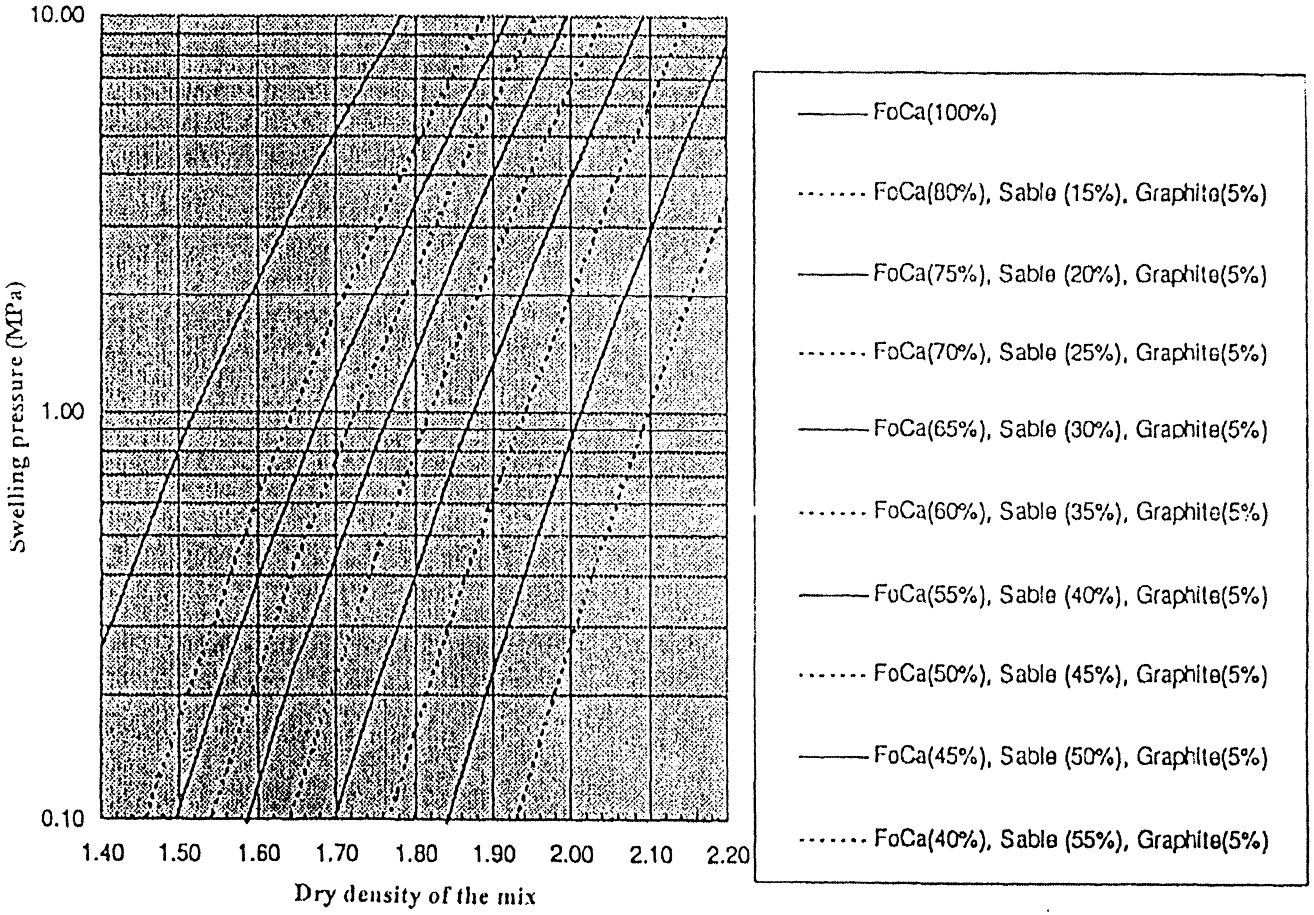
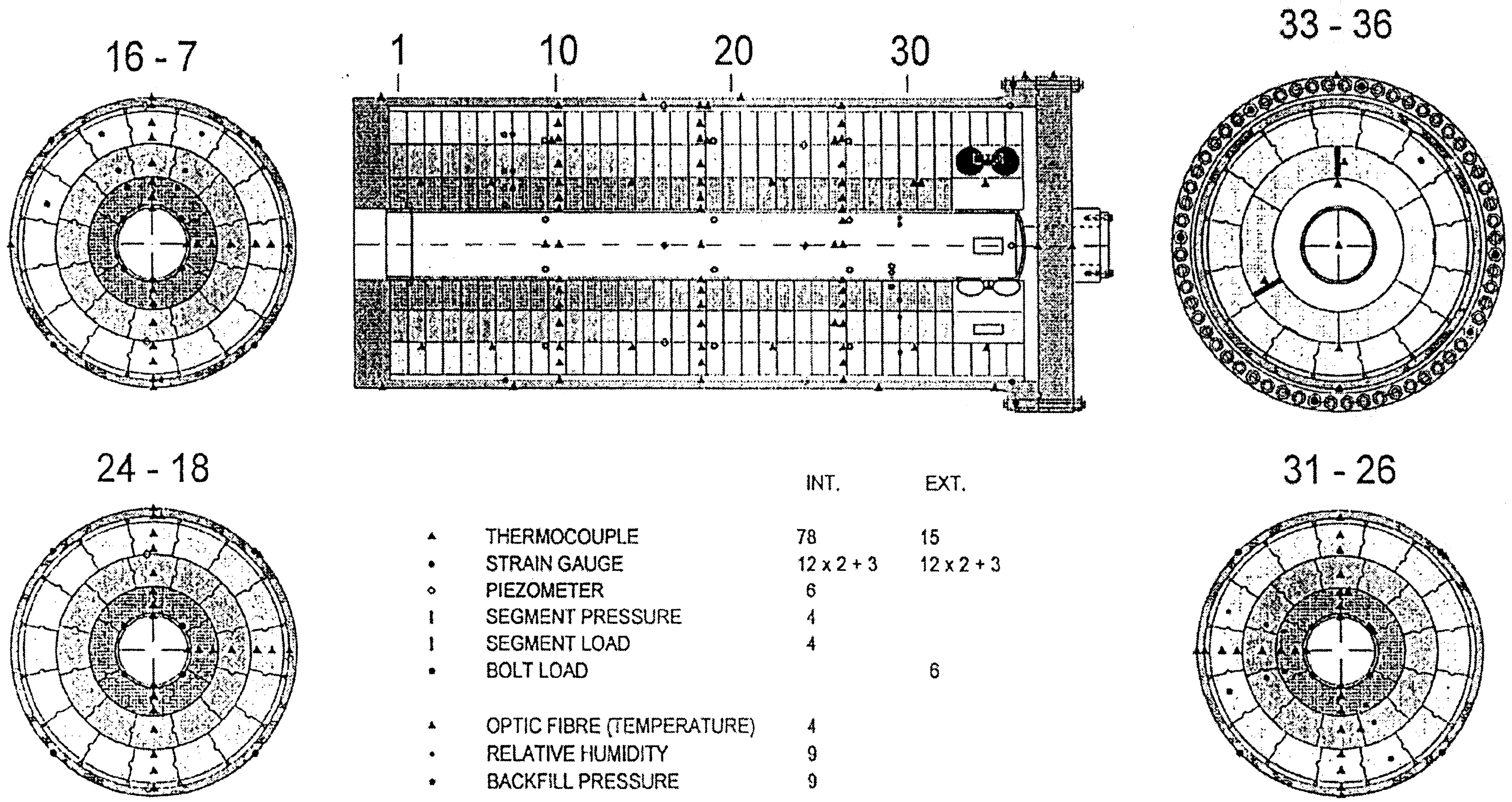


Figure 4. **Theoretical curves giving the swelling pressure at saturation of clay-sand and clay-sand-graphite mixes as a function of the dry density of the mix.**



		INT.	EXT.
▲	THERMOCOUPLE	78	15
•	STRAIN GAUGE	12 x 2 + 3	12 x 2 + 3
○	PIEZOMETER	6	
I	SEGMENT PRESSURE	4	
I	SEGMENT LOAD	4	
▪	BOLT LOAD		6
▲	OPTIC FIBRE (TEMPERATURE)	4	
•	RELATIVE HUMIDITY	9	
•	BACKFILL PRESSURE	9	

Figure 5. PRACLAY mockup instrumentation.

CLAY- AND CEMENT-BASED BACKFILL AND SEALING MATERIALS DESIGNED FOR USE IN A CANADIAN NUCLEAR FUEL WASTE DISPOSAL VAULT

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ABSTRACT

Canada's concept for nuclear fuel waste disposal is based on a multiple barrier system. The concept was developed by Atomic Energy of Canada Limited (AECL) and involves the disposal of nuclear fuel waste in an engineered excavation at a depth of 500 to 1000 m in the granite of the Canadian Shield. Used reactor fuel waste would be isolated in corrosion-resistant metal containers and emplaced in disposal rooms or in boreholes in the floor of disposal rooms, surrounded by a compacted clay-based buffer. The rooms, tunnels, and shafts would be backfilled with a clay-based backfill and sealed with cement-based high-performance sealing materials. This paper gives a summary of the sealing strategies and materials proposed in this conceptual study. In addition, a nuclear fuel waste disposal vault would not be a sterile environment, and microbial activity may therefore affect the performance of backfill and sealing materials. A program to study microbial effects in a disposal vault has been in progress since the early 1990s at AECL. Work from this program pertinent to backfill and sealing materials is also briefly summarized.

1. INTRODUCTON

A concept for permanent deep geological disposal of Canada's nuclear fuel waste has been proposed by Atomic Energy of Canada Limited (AECL) (AECL 1994). The concept is generic in that it was not developed for a specific site. The Environmental Impact Statement (EIS) on this concept includes a conceptual engineering study for a used fuel disposal center, which produced a reference design for a disposal vault, and a performance assessment case study (AECL 1994). Both are based on borehole emplacement and the use of Ti containers. An alternative case study, based on in-room emplacement and Cu containers, was prepared separately (Wikjord *et al.* 1996, Johnson *et al.* 1996). The concept is based on a multiple barrier system and would involve the disposal of nuclear fuel waste in an engineered excavation at a depth of 500 to 1000 m in the granite of the Canadian Shield. Used reactor fuel waste would be isolated in corrosion-resistant metal containers and emplaced in disposal rooms or in boreholes in the floor of disposal rooms, surrounded by a compacted clay-based buffer. The rooms, tunnels, and shafts would be backfilled with a clay-based backfill and sealed with cement-based sealing materials. This paper gives a summary of the sealing strategies and materials proposed in this conceptual study. A detailed description of vault backfilling and sealing is given by Johnson *et al.* (1994b). In addition, a nuclear fuel waste disposal vault would not be a sterile environment, and microbial activity may therefore affect the performance of backfill and sealing materials. A program to study microbial effects in a disposal vault has been in progress since the early 1990s at AECL (Stroes-Gascoyne and West 1996, 1997). Results from these studies that pertain to clay-based buffer and backfill and cement-based sealing materials are also summarized.

2. RATIONALE FOR USE OF BACKFILL AND BACKFILL MATERIAL SELECTION

Deep geological disposal of nuclear fuel waste in granitic rock implies eventual contact of the waste form with groundwater. The main rationale for, and purpose of, using engineered backfills and seals would be to control and minimize the water flux in and around the waste containers and the entire vault in order to retard contaminant release from the waste form into the surrounding rock and ultimately the biosphere.

Factors that affect the selection of backfill and sealing materials include the waste form characteristics, the size and type of waste containers, and the range of possible site characteristics. For instance, waste characteristics (age of used fuel or vitrified waste) will affect the temperature in a vault and therefore the temperature range in which backfill and seals have to function. The size of waste containers will affect emplacement strategies (e.g., in-room versus borehole emplacement; thin-walled containers may require remote handling) and hence the composition of backfill, and quantities needed. The type of container will affect the geochemistry of the near field (e.g., carbon steel corrosion produces H_2; concrete containers may affect pH) and therefore the chemical conditions to which the backfill will be subjected. The range of possible site characteristics that will affect backfill and sealing material selection include heat transfer properties of the rock, *in situ* stresses and strains in the rock (excavation damage and the need to seal this), and the potential occurrence of transient events (glaciation, seismic disturbances).

A variety of vault designs has been studied in Canada (Johnson *et al.* 1994b), resulting in the reference disposal vault design (Simmons and Baumgartner 1994), which is based on the so-called room and pillar method of vault construction. Figure 1 is a schematic representation of a nuclear fuel waste disposal facility, showing both borehole emplacement (used in the performance assessment case study) and in-room emplacement (used in the alternative case study). The reference vault is essentially square, with an area of 4 km^2. The vault is designed to receive about 140,000 containers, each holding 72 used fuel bundles, with a total mass of about 191,000 Mg U. Each disposal room is 8 m wide, 5 m high, and 230 m long and contains 282 vertical emplacement boreholes, drilled into the floor, each with a diameter of 1.24 m and a depth of 5 m.

In contrast to excavations in media such as salt or clay, which can be expected to close as the surrounding rock creeps into the openings, excavations in granite would be stable and would need to be appropriately filled and sealed. For the reference vault design, the following four basic backfill and sealing strategies were employed to limit radionuclide release from a vault (Johnson *et al.* 1994b):

- minimize water flow around the container to limit corrosion and waste-form dissolution;
- decrease the hydraulic conductivity such that water in contact with waste containers is stagnant and radionuclide transport is diffusion-controlled;
- provide enhanced seals at hydraulically critical points in a vault, such as intersections between excavations (tunnels and shafts) and faults and in regions of intense natural fracturing; and

- retard radionuclide release and migration by incorporating materials that inhibit water movement and have the potential to entrap radionuclides and /or chemically condition the groundwater (to minimize the solubility of radionuclides).

These strategies were applied to backfill and seals located directly around the waste, in and around rooms and tunnels (near field), and to those farther away from the waste, in and around access shafts, ramps, and exploration boreholes (far-field).

A number of screening studies (e.g., Cameron 1982, Coons 1987, Mott *et al.* 1984) identified clay-, cement- and bitumen-based materials as having the highest likelihood of meeting the vault backfill and sealing requirements. Because bituminous materials would introduce relatively large amounts of organics into the vault, which might in turn affect radionuclide transport and enhance microbial activity, the studies in Canada have focused on clay- and cement-based materials. Practical considerations included the fact that millions of cubic meters will be needed to fill the excavations, the material must be workable (i.e., capable of being placed to the design specifications) using available technology, and its performance over very long time periods needs to be reasonably predictable.

3. STATUS OF RESEARCH INTO BACKFILL MATERIALS

3.1 Clay-based sealing materials

Their small particle size and surface charge make clay minerals highly surface-active, which is reflected in their ability to sorb cations. Montmorillonite, a member of a group of clay minerals termed smectites and the predominant clay mineral in bentonite clay, is one of the more highly surface-active clay minerals. Other properties that make smectite (and therefore bentonite) particularly attractive as a sealant are its very low hydraulic conductivity and its swelling capacity.

Studies at AECL have determined the relationship between effective clay dry density and hydraulic conductivity (e.g., Dixon *et al.* 1987) and between effective clay dry density and swelling pressure (e.g., Gray *et al.* 1985). To obtain the lowest possible hydraulic conductivity, clays should be used at high density. The emplaced density would depend on the location in the vault where the clay would be used as a sealant and on the methods used for its emplacement (e.g., clays to be used as grouts need to behave as a liquid during injection; clays to be used for backfilling large excavations could be placed as pre-compacted blocks). Particulate aggregates can be mixed with clays to produce materials with improved characteristics for particular backfill or sealing applications. The density to which clay and aggregate mixtures can be compacted (using a given technique) tends to increase with increasing aggregate content. Provided the aggregate content does not exceed 80% of total dry mass, hydraulic conductivities of clay-aggregate mixtures remain very low (Yong *et al.* 1986, Dixon *et al.* 1985). In addition, mixing with aggregate increases the thermal conductivity of clays, which would reduce the thermal gradient and maintain a lower temperature at the surface of waste containers in a disposal vault. The measured hydraulic conductivity of compacted bentonite material ranges from 10^{-13} to 5×10^{-11} m/s, and it is far lower than what is required to ensure that advective transport in clay is negligible (i.e., $<10^{-9}$ to 10^{-10} m/s). Even the hydraulic conductivity of bentonite-based grouts can be as low as 10^{-9} m/s at water contents of about 1.2 times the liquid limit (Pusch *et al.* 1988) whereas it would be higher for other clay types. (The liquid limit of a soil drying from a liquid state is that point at which it ceases to behave as a liquid and begins to acquire the properties of a plastic).

Clay-based sealing materials in a Canadian nuclear waste vault would be subjected to elevated temperatures that may cause drying, shrinking, and cracking. These changes could lower the hydraulic conductivity of the material. Studies were conducted at AECL to examine the permeability and diffusivity of compacted bentonite plugs (dry density from 0.9 to 1.3 Mg/m^3). The plugs were either slotted (to mimic fractures) parallel to the direction of mass flow, or heated at 150°C and 250°C for several weeks at various moisture contents before testing. Results showed that the saturated hydraulic conductivity and diffusivity (for I^- and Cs^+) of the treated or defected bentonite plugs were essentially the same as those of untreated plugs at similar densities (Oscarson *et al.* 1996a, Dixon *et al.* 1993).

3.2 Cement-based sealing materials

Cement-based sealing materials have been considered largely for applications such as bulkheads, shaft seals, and grouting. Screening studies at AECL (e.g., Hooton and Mukherjee 1982) have indicated that sulphate-resisting cement (Canadian Standards Association Type 50) is probably the most suitable for use in vault sealing because some granitic groundwaters contain enough sulphate to be considered aggressive to cementitious materials. Unhydrated cement is composed of six major compounds: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium ferroaluminate (C_4AF),gypsum and alkali sulphates ($C=CaO$, $S=SiO_2$, $A=Al_2O_3$, $F=Fe_2O_3$). When hydrated and exposed to sulphate, the aluminate can react to form ettringite (calcium sulpho-aluminate hydrate), and the resulting solid-volume increase can cause the cement to crack. Type 50 cement has a limited proportion of C_3A, which restricts the formation of ettringite.

The exothermic hydration reaction of cements liberates lime ($Ca(OH)_2$) in ordinary Portland cement and low-replacement cement blends. Lime has low strength and is very water soluble. Admixing pozzolans (e.g., fly ash and pulverized fuel ash from coal-burning power stations) limits the presence of lime in the hardened material and tends to increase strength and decrease porosity. When included in significant proportions (>20 wt.%), these materials also significantly reduce the evolution of heat during hydration. Pozzolanic condensed silica fume (amorphous silica, a by-product of the ferro-silicon industry) is becoming increasingly used as an additive to cements, and it minimizes the amount of readily soluble residual lime in the hardened product (Onofrei *et al.* 1992a, 1992b); as a result it is possible to greatly reduce the high pH effect normally associated with concretes, mortars, and cements. A high-performance concrete formulation (containing both silica fume and superplasticizer), Low-Heat, High-Performance Concrete (LHHPC), developed as part of the Canadian nuclear waste management program, was leached for >100 d at different temperatures in various groundwater compositions to evaluate pH values. Results showed pH values ranging from 10.5 in distilled deionized water at 10°C to as low as 8.6 in WN-1 groundwater at 100°C (Oscarson *et al.* 1996b).

The effects of silica fume addition (10 wt.%) and the water-to-cement (W/CM) ratio on the 50-d unconfined compressive strength have been studied at AECL (Al-Masaneer and Keil 1990). There was considerable increase in the compressive strength by addition of silica fume.

However, the addition of silica fume, with its very high specific area, requires an increase in the W/CM ratio for better 'workability', and an increase in W/CM ratio reduces strength. This can be offset by the use of additives called superplasticizers, which have been studied at AECL for use in cementitious materials for vault sealing purposes. The effects of a naphthalene-based superplasticizer (Na-sulphonated naphthalene formaldehyde condensate, Na-SNFC) on the flow properties of Type 50 Portland cement with 10 wt.% silica fume showed that 0.75 wt.% Na-SNFC is sufficient to turn a mixture with a W/CM ratio of 0.4 from a stiff viscous paste into a flowing pumpable fluid for the first few hours after mixing. Experiments at AECL's Underground Research Laboratory (URL) (Onofrei *et al.* 1989, Gray and Keil 1989) have shown that this material can be used to grout fissures in granite rock with apertures as narrow as 20 μm.

Superplasticizers principally affect the rheology of cement/water mixtures for the first few hours after mixing, and this effect results from the fact that they interfere primarily with the fastest hydration reactions. Onofrei *et al.* (1992c) have confirmed the adsorption of Na-SNFC on, and its incorporation in, the two fastest hydrating components of Portland cement (C_3A and C_3S). The Na-SNFC in hardened cement is retained within the structure of the C-A-H and calcium-rich C-S-H phases. The silica-rich phases (i.e., unreacted silica fume particles) appear not to be the place of residence of the Na-SNFC (Onofrei *et al.* 1992c). In combinaton with silica fume, superplasticizers have led to the development of high-performance cements and concretes that have lower heat of hydration, lower pH, higher strength and durability, and much lower hydraulic conductivity ($<10^{-15}$ m/s) than traditional cement-based materials. Even under very high hydraulic gradients, hardened high-performance grouts have been shown to totally resist any measurable throughflow of water (Onofrei *et al.* 1989, 1992c).

The porosity, pore-size distribution, and hydraulic conductivity of cements and concretes all change with time. These changes are the result of crystallization of amorphous phases, changes in crystalline phases, reactions of hydration products with internal and external ions diffusing through the material, dissolution of soluble compounds (such as $Ca(OH)_2$) and progressive hydration reactions (even in materials produced at very high W/CM ratios, some unhydrated material remains). The structure of the hydration products formed on the surfaces of cement grains appears to control the rate of hydration of the grains' inner cores (Johnson *et al.* 1994b). Calcium carbonate, the result of carbonation of lime, is invariably found in both ancient and historic concretes. Some fractured cement-based materials have shown self-sealing behaviour, likely caused by a combination of hydration, carbonation, and dissolution-reprecipitation reactions. Cements and concretes in structures exposed to the elements (freezing, thawing, wetting, drying) degrade, but in an underground vault these effects would not be present. It is therefore expected that high-performance cementitious materials can persist for hundreds of thousands of years in rock masses where hydraulic gradients are small and groundwater flow is low. Calculations to that extent have been performed by a number of researchers (e.g., Alcorn *et al.* 1992). Cracking and fracturing of cement-based vault seals could realistically arise only from stresses generated by excessive physical forces (loads), from shrinkage and expansion occurring autogenously, from temperature variations in the vault, and from degradation reactions such as dissolution of the cement or the formation of ettringite.

Loss of water can cause shrinkage and subsequent cracking in cements and concretes. However, much of the shrinkage can be reversed if the material is subsequently exposed to water (Al-Masaneer and Keil 1990). Therefore, in a vault that would eventually become water-saturated it is expected that the effects of shrinkage would be minimal. Differential thermal expansion and contraction between cement-based sealing material and the host rock could cause cracking and compromise the hydraulic efficiency of the seal. However, the use of low-heat cements, pozzolans, and established concrete placement techniques (i.e., the use of cooled materials in concrete production) could minimize these effects. Thin films of cement grouts are not as subject to heat of hydration effects as large structures and have been shown to self-seal when disrupted. The processes giving rise to self-sealing could also ameliorate the effects of thermally induced cracking in massive concrete structures in a vault (Johnson *et al.* 1994b).

3.3 Near-field seals

In the absence of a specific site, the backfill and sealing material choice for the performance assessment case study was based on the conceptual vault design by Simmons and Baumgartner (1994). Waste disposal would be confined to 'intrablock' regions (i.e., volumes of rock that do not contain hydraulically active features). Near-field seals are those materials used to separate the waste containers from the rock and to fill the excavations in the 'intrablock' regions. In addition, specially designed plugs and associated treatments such as grouting of the excavation damage zone (EDZ) would be needed. The near-field seals include the clay-based buffer, the clay-based room- and tunnel-backfills, the cement-based plugs for rooms and tunnels, and grouts used at plug/rock interfaces and within the rock mass. It is also likely that any investigation boreholes drilled at the waste emplacement horizon would be plugged and grouted to ensure the integrity of the near field. Special plugs and seals would be located where excavations intersected hydraulically active features, to maintain very low hydraulic gradients and water flows in the zones of rock where waste was deposited.

Clay-based materials would be used next to the containers and to fill the rooms above the waste packages. Studies at AECL (discussed by Johnson *et al.* 1994b) have led to the selection of a reference buffer material (RBM). The RBM is composed of bentonite and silica sand mixed in equal proportions by dry mass; it would be compacted *in situ* to a minimum effective clay dry density of 1.21 Mg/m^3. Compared with highly compacted 100% bentonite at the same density, the RBM has a higher thermal conductivity, similar hydraulic properties, and would exert a significantly lower swelling pressure. A reference backfill material, composed of crushed granite and glacial lake clay mixed at a ratio of 3:1 in dry mass proportions, has also been developed (lower backfill) and would also be compacted *in situ*. A swelling clay-based material similar to the buffer (upper backfill) would be pneumatically placed to complete the filling of the rooms above the lower backfill. Table 1 gives the composition and selected physical properties of the reference buffer and backfill materials selected for the used-fuel disposal center conceptual design study.

The entrances of waste emplacement rooms would be plugged with bulkheads consisting of high-performance concrete, and similar materials would be used to plug access tunnels where these tunnels pass through hydraulically active fracture zones. The concrete bulkheads and plugs could be enhanced with highly compacted bentonite gaskets which would virtually eliminate flow at the interface between the plug and the rock. The remainder of the access tunnels would be backfilled similar to the emplacement rooms.

The EDZ around the concrete bulkheads and plugs would, where possible, be grouted with cement-based grout or sealed with cutoff walls extending from the plugs into the rock. The EDZ around the backfilled excavations would remain ungrouted.

3.4 Far-field seals

Far-field seals are those materials used to plug or otherwise seal shafts, tunnels, ramps and exploration boreholes that connect the near field to the ground surface. The materials developed for near-field seals are also suitable for far-field seals. Because access shafts, tunnels, and ramps would be open for a minimum of 40 years, normal contamination arising from vault operations (grease, oils, vehicle fumes, dust, etc.) would accumulate on the rock surfaces, and some weathering and degradation of the rock surfaces of shafts, tunnels, and ramps would likely occur and might require cleaning and scaling before seal installation. Similarly, temporarily emplaced materials (rock bolts, wire mesh, concrete roadways, etc.) would be removed and underlying surfaces cleaned before seal installation to minimize the effects of vault operation. Composite seals, consisting of concrete bulkheads that support clay-based backfills, which are then sealed with highly compacted bentonite gaskets, appear to offer the best possibility for minimizing flow in the excavations and the EDZ. The need to plug and seal investigation boreholes would depend on the hydrogeological conditions at the vault site and their location in relation to both the waste and hydraulically active features. It is likely that all boreholes would be sealed with highly compacted bentonite and high-performance cement plugs and grouts. Unlike shaft and tunnel sealing, borehole sealing is a remote process that may require further development of methods that would need to be tested and verified in future experimental work and at the actual disposal site.

4. REPRESENTATION OF BACKFILL IN PERFORMANCE ASSESSMENT

The total system performance model that has been used to carry out the performance assessment case study divides the disposal system into three major subsystems—the vault, the geosphere, and the biosphere—and links these subsystems to assess the total system performance.

For the reference vault (which is based on borehole emplacement, Ti containers, and a geosphere of low-permeability rock), the buffer and backfill materials are incorporated into the vault model (Johnson *et al.* 1994a). Failure of all containers occurs between 1000 and 5000 years after disposal, and container failure is represented as instant complete disappearance of the container. Radionuclide release from the used fuel is partially by instant release (gap plus grain-boundary inventory) and partially by congruent release (controlled by fuel matrix dissolution). Transport in buffer and backfill materials is represented using 1-dimensional diffusion equations with radionuclide decay. Diffusion coefficients, both transient and steady-state, have been measured for a variety of radionuclides in buffer (e.g., Oscarson *et al.* 1984). Ranges in the values of the diffusion coefficients have been defined to include the possible changes that could occur in the properties of the backfill materials as the vault system evolves (e.g., the ranges of radionuclide diffusion coefficients used in the model include the laboratory-measured effects of salinity and temperature changes).

For the alternative vault (which is based on in-room emplacement, long-lived Cu containers [only a very small fraction will defect], and a poor geosphere), buffer and backfill materials are also incorporated into the vault model (Johnson *et al.* 1996). Transport of radionuclides is modeled by diffusion of dissolved contaminants through a small pin-hole sized defect in the container into the surrounding buffer. Transport through the buffer is by diffusion, and through the backfill and EDZ into the surrounding host rock by a combination of diffusion and some advection.

The geosphere model (Davison *et al.* 1994) indirectly incorporates the performance of sealed shafts and boreholes by assuming that these do not act as preferred pathways for radionuclide migration. Sensitivity analyses using modified geosphere models (Davison *et al.* 1994, Johnson *et al.* 1994a) have been carried out to test the implications of this assumption. The site-specific conditions encountered during excavation of a vault would ultimately determine the layout of the vault and thus the locations and dimensions of concrete plugs and bulkheads as well as the extent of grouting activities. Grouting would be used for construction expediency and to increase confidence on the long-term performance of seals. The effects of these grouting activities are not included in the vault and geosphere models used in the post-closure assessment case study.

5. CONFIDENCE IN BACKFILL AND SEALING MATERIALS PERFORMANCE

Both clay- and cement-based materials have been extensively used in civil engineering practice, and a wealth of information on their properties and performance is available that provides confidence in the choice of these materials. The laboratory experiments with clay-based materials performed at AECL (see section 3) have confirmed the desired properties of low-permeability and self-sealing of clay-based materials. One of the objectives of AECL's natural analog study on the Cigar Lake uranium deposit (Cramer and Smellie 1994) was the evaluation of generic transport models for potential radionuclide migration through clay-based sealants (near-field analogy). Conclusions from this study were that clay (in this case illite) can provide effective, long-term sealing. Illite is stable under suitable conditions over geological time, and clay is an efficient barrier to radionuclide and colloid migration (Cramer and Smellie 1994). In addition, clay seals have been used for a number of years in a variety of near-surface waste disposal applications (see for instance the many examples in Johnson *et al.* 1985).

In recent years, significant advances have been made in cement and concrete technology through the invention and use of special additives such as superplasticizers and silica fume in concrete mixtures. These advances are likely to continue at a rapid pace into the next century, and conventional concretes are unlikely to be used for vault sealing. Some ancient and historic concrete structures can be considered analogs that testify to the longevity of materials resembling conventional concretes. For instance, the Acquarossa aquaduct in Italy (700-600 BC) can be considered an analog for conventional concretes used in the construction of a repository in tuff (De Putter and Charlet 1994). The continued use of high-performance concretes, which are an improvement over the conventional materials, should build confidence in the suitability and longevity of these materials.

In addition, AECL has conducted a number of large- and full-scale experiments at its Underground Research Laboratory (URL) in which backfill and sealing materials and emplacement methods were tested. An example is the buffer/container experiment in which the *in situ* performance of compacted RBM in a full-size single emplacement borehole under vault-relevant conditions was determined, over a period of 2.5 years, using a heater as a heat source (Dixon *et al.* 1998). Another example is the internationally sponsored tunnel sealing experiment currently taking place at the URL, in which a full-size tunnel is sealed with composite seals consisting of concrete, pre-formed compacted bentonite-based bricks, and backfill. These large experiments are vital to building solid confidence in materials performance and emplacement methods.

7. QUALITY ASSURANCE REQUIREMENTS AND REGULATORY EVALUATION SPECIFICALLY FOR BACKFILL MATERIALS

The total system performance assessment for the reference disposal system (which included bentonite-based buffer material, backfilling of excavations with materials possessing hydraulic conductivities $<10^{-10}$ m/s, and a vault located in sparsely fractured rock with at least a 50-m distance between waste containers and the nearest major fracture zone in the rock) has shown that regulatory criteria with respect to radionuclide release can be met (Goodwin *et al.* 1994). However, performance assessment relies on reliable input data for a number of parameters, including those for sealing materials. To ensure that these parameter values can be met *in situ* for sealing materials, quality assurance procedures are necessary. Vault sealing operations would be carried out under an appropriate quality assurance program and would be subject to the general requirements for planning, reviewing, controlling, and documenting work that this program prescribed. Details of possible quality assurance strategies are discussed by Johnson *et al.* (1994b).

Clays would need to be processed prior to their use in vault backfill and sealing, which includes excavation, drying, and milling. To ensure the quality of vault seals, these processing operations would require careful control because the properties of bentonite clay products can be particularly sensitive to the processing procedures. Based on the use of bentonite materials at AECL over a period of >8 years, specifications have been developed for bentonite products for use in the reference vault design. During emplacement of bentonite-based materials in a vault, testing procedures for a number of specific parameters would need to be in place to guarantee adherence to the end-product specifications developed for the clay-based sealing materials.

Existing civil engineering practice and standards provide considerable guidance for the methodologies and tests that would be used for the construction and the quality assurance of cement-based vault seals. The performance of concrete seals would very largely depend on high-quality workmanship. The need for a highly qualified work force would demand special consideration when establishing the vault operating infrastructure.

In a vault it might not be possible to monitor some of the engineered barrier system components without compromising the integrity of the disposal room or near-field seals. It might therefore be necessary to construct a component test area to obtain the data necessary to give confidence in vault performance. For the reference vault, a test area location near the service shaft complex was suggested (Simmons and Baumgartner 1994) . Testing would begin during the underground evaluation of the site and would continue during the construction and operation lifetime of the vault. Examples of such component test activities relevant to backfill and seals are given by Johnson *et al.* (1994b).

8. POTENTIAL MICROBIAL EFFECTS IN BUFFER AND BACKFILL MATERIALS

AECL initiated studies to address the potential of microbial effects on the integrity of the multiple barrier system for nuclear fuel waste disposal as early as 1982 (Stroes-Gascoyne and West 1996). An accelerated research program was initiated in 1991 to respond to the specific issues raised in the guidelines for the preparation of the EIS on the geological disposal concept (Federal Environmental Assessment Review Panel 1992). These guidelines indicated the expectation that microbial effects would be addressed specifically in the EIS. Over the past five years, many applied microbial studies have been conducted at AECL and the URL to quantify the potential for microbial presence, activity, and effects in various parts of a Canadian-design nuclear fuel waste disposal vault and the surrounding geosphere (Stroes-Gascoyne and West 1997). A number of these studies were conducted specifically to determine if microbial activity could directly or indirectly affect the integrity and effectiveness of sealing materials.

The radiation effects on microbes naturally present in clay-based sealing materials were studied (in the dark) to determine if radiation may deactivate or kill microbes and as such reduce or inhibit microbial activity in sealing materials. Results showed that radiation at the dose rates expected in a Canadian vault is detrimental to the activity and survival of the natural microbial population in buffer material, but that this effect is dependent on container design and age of the used fuel, and is limited to a narrow band (<50 cm) around the waste containers (Stroes-Gascoyne *et al.* 1995, King and Stroes-Gascoyne 1995, 1997).

The effect of relevant temperature and moisture conditions on the survival of microbes in clay-based sealing materials to determine survivability under adverse conditions of low moisture and high temperatures has been studied during the Buffer/Container Experiment (BCE) at the URL. This experiment determined the *in situ* performance of compacted RBM in a full-size single emplacement borehole under vault-relevant conditions, over a period of 2.5 years, using a heater as a heat source (Dixon *et al.* 1998). Buffer cores for microbial analysis were taken from many locations throughout the 6-m deep borehole. Results showed an almost universal disappearance of viable microorganisms in samples with low moisture (<15%) and higher temperature (50 to 60°C). A statistical evaluation of all culture data demonstrated clearly that the moisture content (or water activity, a_w) was the variable that had the largest influence on the culturability of microorganisms in buffer (Stroes-Gascoyne *et al*, 1996 1997c).

The mobility of microbes in highly compacted buffer material was studied in relation to their potential role in radionuclide migration in and through this barrier. The experiments involved the use of radiation-sterilized 5-cm long compacted buffer plugs of three dry densities (1.20, 1.68, and 1.80 g/cm^3) in contact with a solution containing a pure culture of *Pseudomonas stutzeri*. Results showed that *P. stutzeri* did not appear to migrate into compacted buffer over a 20-week period but that the interface between buffer and the confining structure (rock) may be a preferred pathway for microbial migration (Stroes-Gascoyne *et al.* 1997b).

The introduction of bacterial nutrients into a vault as a result of backfill and sealing material emplacement in relation to potentially enhanced microbial activity in these materials has also been studied. An inventory of total nutrients suggested that nitrogen and phosphorus may be limiting microbial activity in buffer and backfill materials (Stroes-Gascoyne 1989). Backfill may contain up to 75 wt.% crushed rock spoil. A recent study (Stroes-Gascoyne and Gascoyne 1998) showed that explosives residues associated with fresh rock spoil could potentially introduce large amounts of microbial nutrients (nitrates and organic carbon) into a vault. A scoping study was conducted to determine degradation of superplasticizer by groundwater bacteria in relation to potential enhancement of microbial activity through the presence of superplasticizer in cement-based sealing materials. Results showed that the presence of Na-SNFC stimulated bacterial cell numbers by an order of magnitude in groundwater when incubated under nitrate-reducing conditions (anaerobic, in the presence of nitrate) and low temperature (10°C) (Haveman *et al.* 1996).

The potential for increased availability of organic material as a result of heat and radiation effects on organic material naturally present in clay-based sealing materials was investigated. Experiments were carried out at AECL in which RBM was heated at 60°C and 90°C for periods of 2, 4, and 6 weeks, in some cases followed by γ-radiation to 25 kGy. The RBM was subsequently leached in distilled water for 24 hr. The leachates contained considerably higher dissolved organic matter than a leachate from an untreated RBM (Vilks *et al.* 1997). When incubated with equal volumes of URL groundwater, these leachates were able to stimulate bacterial cell numbers by 2.5 orders of magnitude (Stroes-Gascoyne *et al.* 1997a).

The potential for methane production in, and hence potential physical disturbance of, backfill was investigated by incubating slurries of backfill components and groundwater anaerobically. Results suggested that the sulphate concentration in backfill clay (from gypsum) may inhibit methane production and that, in a vault, methane production would proceed only when sulphate concentrations were drastically lowered through the activities of sulphate-reducing bacteria (Sheppard *et al.* 1997).

These studies have shown clearly that microbial activity may influence, either directly or indirectly, the performance of backfill materials. Assessment of potential microbial effects should be an integral part of any backfill or sealing strategy applied to material selection.

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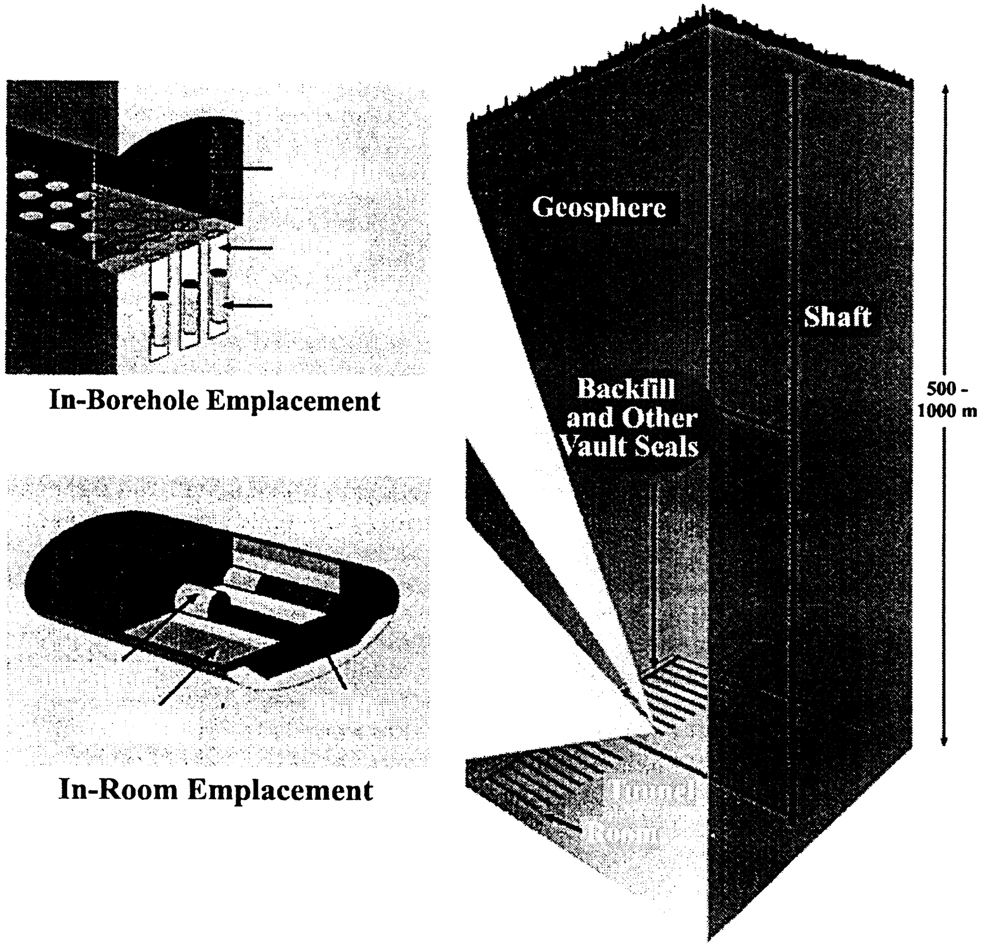

Figure 1. Schematic representation of a Canadian nuclear fuel waste disposal vault.

THE SORPTION BEHAVIOR OF DIATOMACEOUS EARTH AND CEMENT

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ABSTRACT

To identify materials suitable for retarding the migration of ^{99}Tc, ^{36}Cl, ^{90}Sr, and ^{137}Cs, sorption and leachability studies were performed with several different types of diatomaceous earth and cements. Results show that three types of diatomaceous earth have good sorption properties for ^{90}Sr and ^{137}Cs and two Chinese blast-furnace cements, "Hoz 35" and "Hoz 45", have good sorption properties for ^{99}Tc.

1. INTRODUCTION

In the Chinese concept of nuclear waste disposal, safely isolating wastes in a geologic repository requires a series of barriers to restrict the release of specific radionuclides to the biosphere. Backfill and sealing materials, the waste canisters, and the waste form itself are considered engineered barriers which augment the natural barrier provided by geological formations. Some materials, typically inorganic in nature, are utilized as engineered barriers because of their strong sorption ability for specific radionuclides. These materials, which also must be durable and resistant to degradation, can be used as the backfilling material, or as additives in the conditioned waste form to enhance the role of the engineered barrier.

In this paper, attention is directed toward the sorption behavior of some selected inorganic materials. Several types of diatomaceous earth and cements were evaluated for sorption behavior with four important fission products: ^{99}Tc, ^{36}Cl, ^{90}Sr, and ^{137}Cs.

2. EXPERIMENTAL APPROACH

2.1 Sorption behavior

2.1.1. Sorptive Materials

Three types of diatomaceous earth were selected for evaluation:

1. Merck diatomaceous earth (average particle size of 0.2 mm in diameter);
2. VDK diatomaceous earth (average particle size of 0.8 mm in diameter); and
3. Tremonis diatomaceous earth (average particle size of 0.2 mm in diameter).

The microstructures of these three kinds of diatomaceous earths appear to be similar (Figure 1).

Two kinds of blast-furnace cements were also used, “Hoz 35” and “Hoz 45.”

2.1.2 Radioactive Tracers

The following radionuclides were used:

- ^{99}Tc, obtained as NH_4TcO_4 solid (0.334 MBq/mg NH_4TcO_4);
- ^{36}Cl, obtained as NaCl solution (137 Ci/ml);
- ^{90}Sr, in solution form (13.3 MBq/ml); and
- ^{137}Cs, obtained as CsC_{l2} in 1M HCl (4.95 mCi/ml).

For ^{99}Tc, the NH_4TcO_4 was first dissolved in double-distilled water. Various concentrations of all radionuclides were obtained by diluting with double-distilled water.

2.1.3 Sorption Experiments

Batch sorption experiments were conducted using 100 to 900 mg sorbent with 20 ml of solutions with a range of sorbate concentrations. Containers were shaken (160 times per minute) for a 24-hour period to allow sufficient contact time for equilibration. Plastic vials were used rather than glass to avoid adsorption of radionuclides on test containers. Following the batch reaction, the aqueous phase was separated by centrifuging at 3000 revolutions-per-minute. Activities were then measured from an aliquot of supernatant.

2.1.4 Measurement of Radioactivity

A liquid scintillation analyzer (2000 CA Tri-Carb, Packard) was used to measure the radioactivity of ^{99}Tc, ^{36}Cl, ^{90}Sr, and ^{137}Cs. For each measurement, 100 µL of the liquid phase was used. The standard 29-ml glass vial (Packard) was used as a sample holder and 19-ml of scintillation cocktail (Packard) was added to each sample.

2.1.5 Data Reduction

The sorption ratio, R_S, was used in this work to express the sorption behaviors of diatomaceous earths and cement:

$$R_S = (N_0 - N_1)/N_1 * (V/W),$$

where:

N_0 = initial activity per ml of the radionculde in the liquid phase;
N_1 = activity per ml in the supernatant solution after contact with the sorbent;
W = weight of the sorbent in g; and
V = volume of the supernatant in ml.

2.1.6 Results and Discussion

2.1.6.1 Sorption of ^{99}Tc and ^{36}Cl

Results indicate that the three diatomaceous earths tested do not sorb ^{99}Tc and ^{36}Cl (Figures 2a and 2b). In contrast, the Hoz cements did sorb ^{99}Tc and ^{36}Cl, although sorption of ^{99}Tc was about ten times greater than that of ^{36}Cl. The sorption ratio increased as the ratio of solid-to-liquid increased (Figure 2c).

2.1.6.2 Sorption of ^{137}Cs

As shown in Figure 3a, Hoz cement had a small sorption capacity for ^{137}Cs. As shown in Figure 3b, however, ^{137}Cs was strongly sorbed by diatomaceous earths, yielding sorption ratios of about 1000 to 4000 ml/g. The order of sorption ability was Merck > Tremonis > VDK > Hoz 35 > Hoz 45. The sorption ratio decreased as the ratio of solid to liquid (weight/volume) increased. The initial activity of the liquid phase slightly affected the sorption ratio (R_S) as shown in Figure 3c. Higher activities in the liquid phase resulted in higher sorption ratios.

2.1.6.3 Sorption of ^{90}Sr

As shown in Figure 4, ^{90}Sr was sorbed by diatomaceous earths, but to lesser extents than was ^{137}Cs. Regarding sorption characteristics, the sorbents tested behaved nearly the same for ^{90}Sr as they did for ^{137}Cs.

2.2 Leachability behavior

In these experiments, simulated cemented waste forms were tested for retention of the radionuclides ^{99}Tc, ^{35}Cl, ^{90}Sr, and ^{137}Cs. Cement, as an inorganic material, is particularly attractive for use in disposal because the solidified waste forms are not combustible, physically strong, radiation resistant, and have reasonable chemical and thermal stability.

2.2.1 Experimental Methods

The same materials described above were used in these experiments. To test the effect of cement additives, the three types of diatomaceous earths were used as additives in the two blast-furnace cements.

2.2.2 Waste Form Preparation

Radionuclide tracers were added to distilled water, which was then mixed with cements to be tested. Diatomaceous earth was added to some samples. A liquid to cement weight ratio of 0.5 was used. The cement slurries were cured in plastic beakers at room temperature. Cement specimens (about 60 g each) were then removed from the beakers and placed in polyethylene bottles. Distilled water (about 500 ml for each sample) was used as the leachant.

2.2.3 *Results and Discussion*

Leaching behaviors are illustrated in Figures 5 to 8. Each curve represents a leaching characteristic of one speciment (the legend indicates the additive type and weight and the type of cement).

2.2.3.1 *^{99}Tc Leach Behavior*

Both types of blast furnace cements tested showed good retention of ^{99}Tc (Figure 5). In all cases, the leached fraction of ^{99}Tc was less than 0.2 percent.

2.2.3.2 *^{36}Cl Leach Behavior*

The leached fraction of ^{36}Cl was about 25 to 30 percent in the simulated waste experiments (Figure 6). Hoz 35 consistently performed better than Hoz 45. Increasing the quantity of VDK and Tremonis types of diatomaceous earth could help improve the leaching behavior of the cements.

2.2.3.3 *^{137}Cs Leach Behavior*

The leached fraction of ^{137}Cs was about 20 to 40 percent, making it the most readily leached element tested (Figure 7). However, the increasing the quantity of diatomaceous earth additives in the cement samples could improve waste form performances. In all cases, Hoz 35 performed better than Hoz 45.

2.2.3.4 *^{90}Sr Leach Behavior*

The leached fraction of ^{90}Sr was about 2 to 3 percent (Figure 8). Increasing the amount of diatomaceous earth additives slightly improved ^{90}Sr leaching resistance. Again, Hoz 35 showed better leaching resistance than Hoz 45.

3. CONCLUSIONS

Results show that the anions ^{99}Tc and ^{36}Cl were not sorbed by diatomaceous earths, but that the cations ^{90}Sr and ^{137}Cs were sorbed. The sorption ratios of ^{90}Sr and ^{137}Cs were about 200 to 500 ml/g and 1000 to 4000 ml/g, respectively. The leached fraction of ^{90}Sr and ^{137}Cs were about 2 to 3 percent and 20 to 40 percent, respectively. These results indicate that diatomaceous earth has useful properties as a component of an engineered barrier to retard cationic forms of fission products. They should be considered as an additive to backfill and sealing materials, waste canister structural materials, and waste forms.

Results also show that the blast furnace cements Hoz 35 and Hoz 45 have good sorptive properties for ^{99}Tc. The cement waste form also had good leaching resistance with respect to ^{99}Tc, with a leached fraction of only about 0.2 percent.

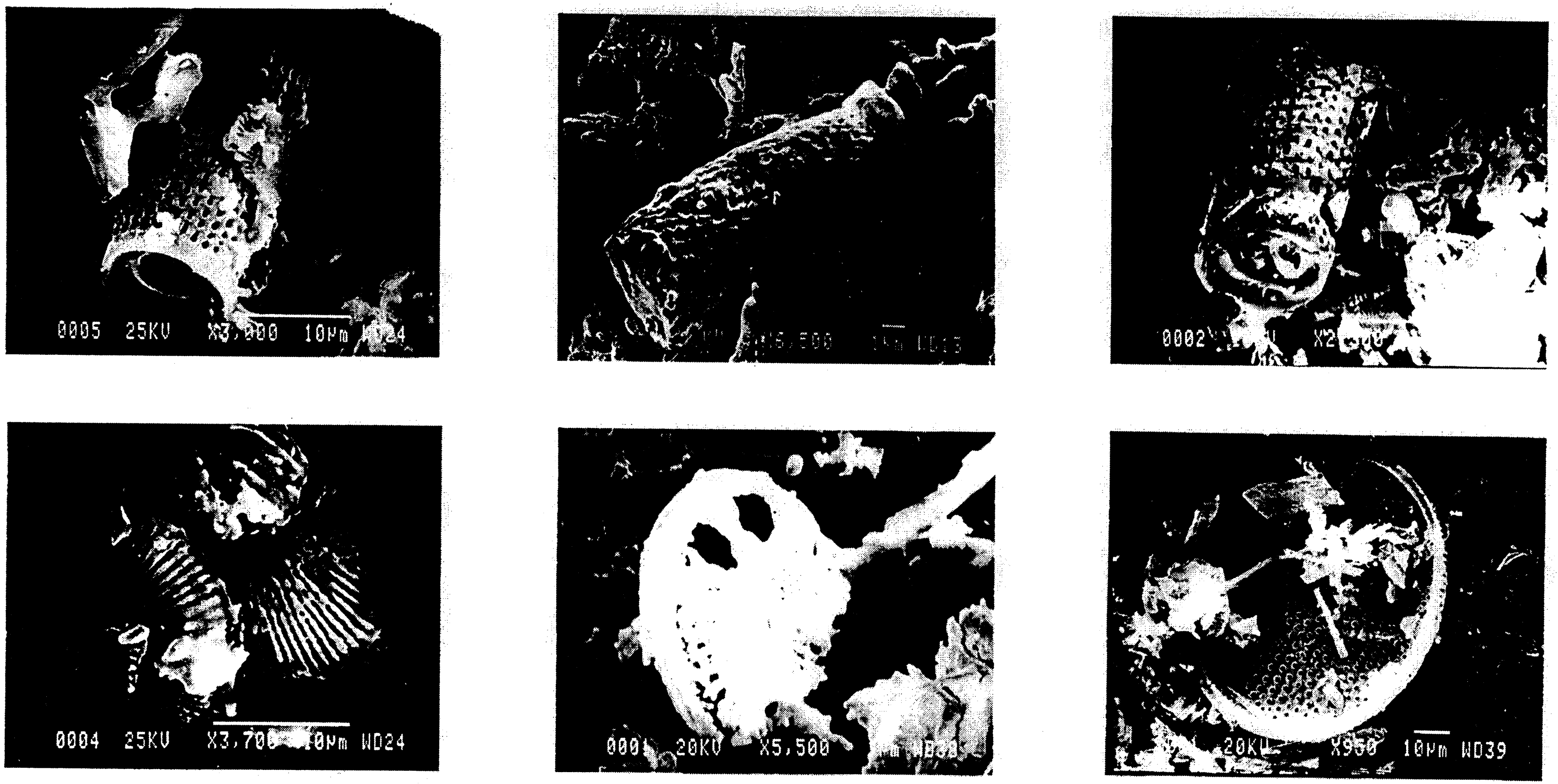

Figure 1. Microstructure of Merck (left), Tremonis (centre) and VDK (right) diatomaceous earth.

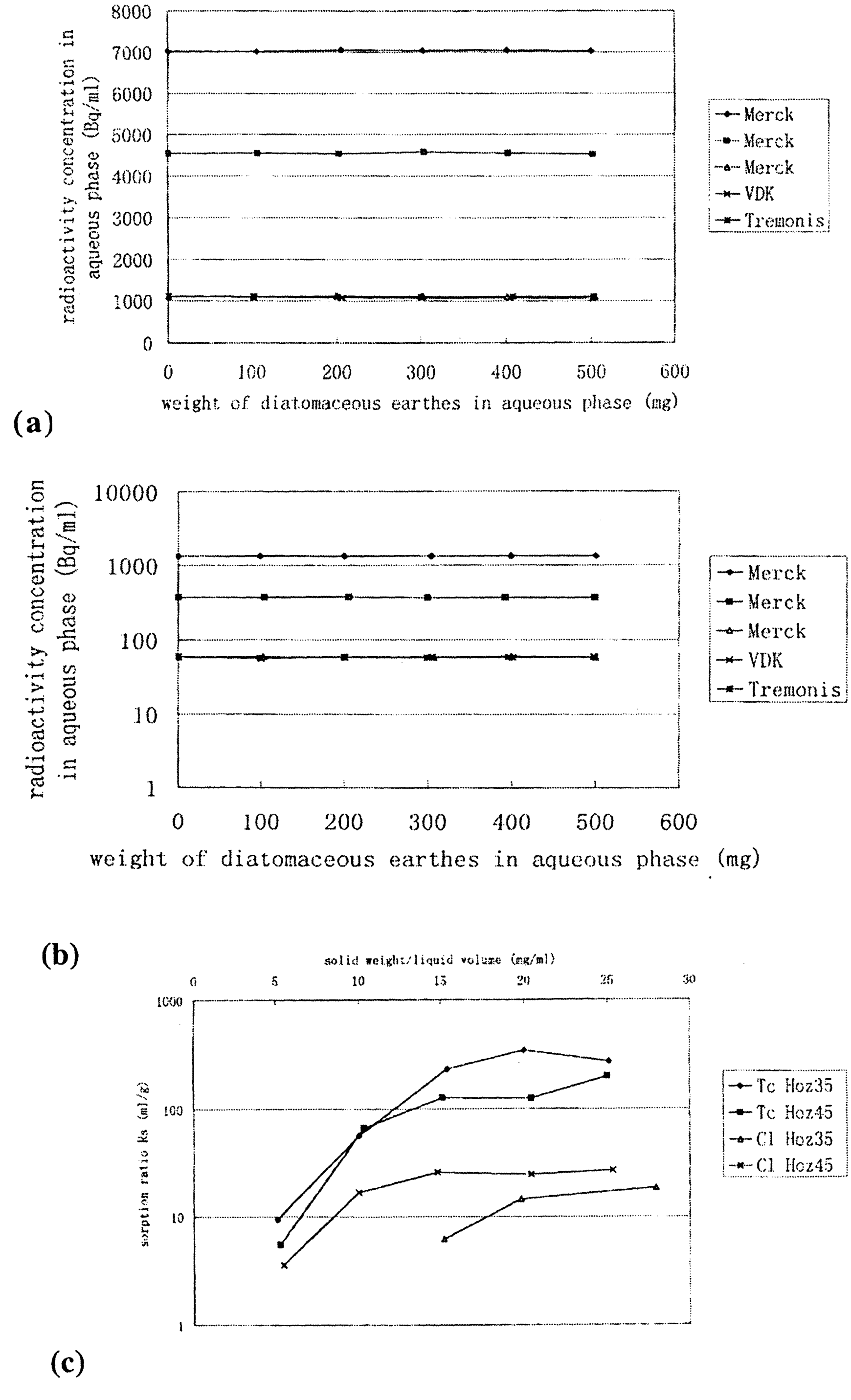

Figure 2. Sorption of Tc and Cl. (a) Tc sorption on diatomaceous earth; (b) Cl sorption on diatomaceous earth; and (c) Tc and Cl sorption on cement, including the effect of the solid-to-liquid ratio.

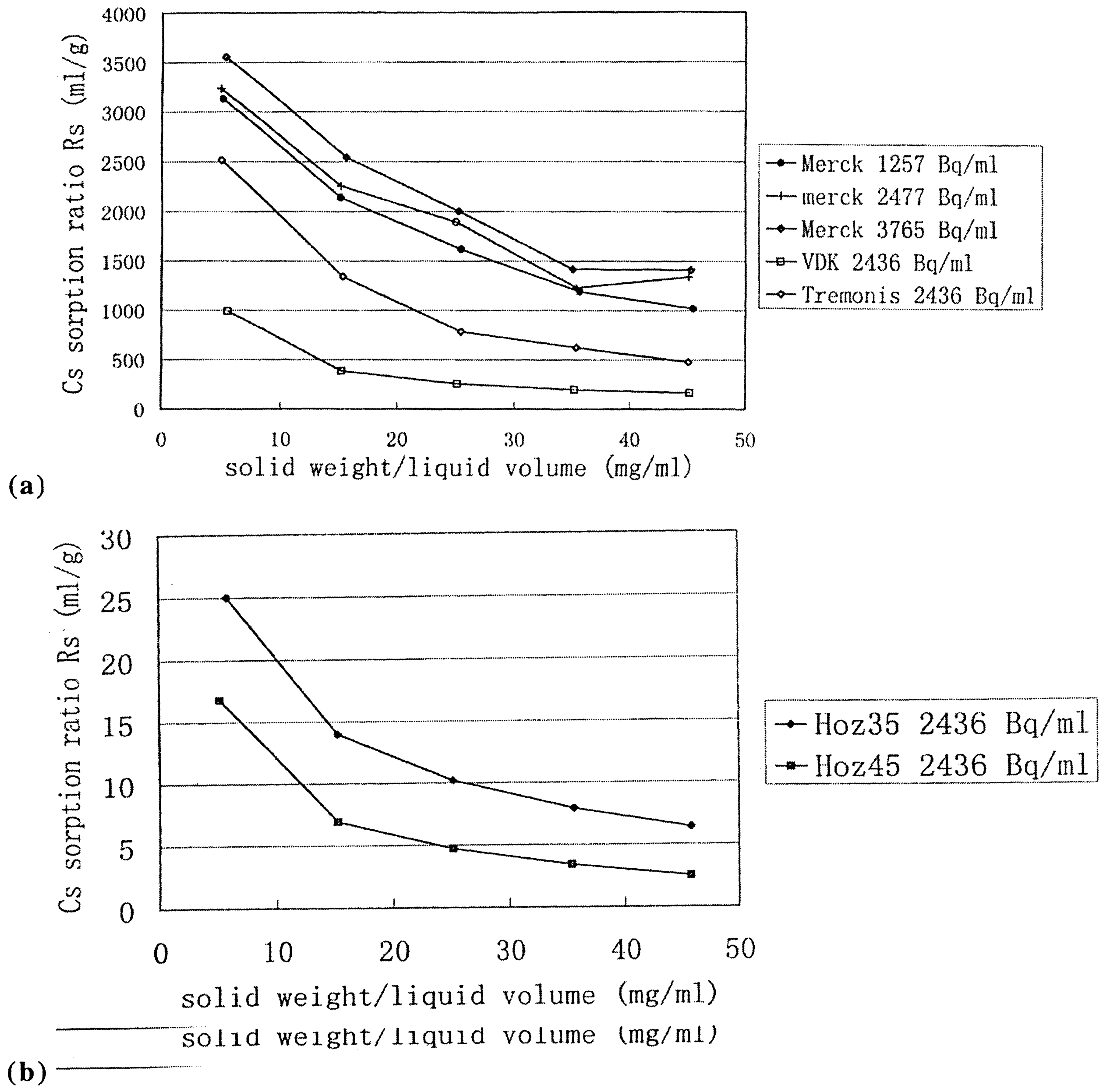

Figure 3. Sorption of Cs. (a) Cs sorption on diatomaceous earth, including the effect of the solid-to-liquid ratio and initial radionuclide concentration and (b) Cs sorption on cement, including the effect of the solid-to-liquid ratio.

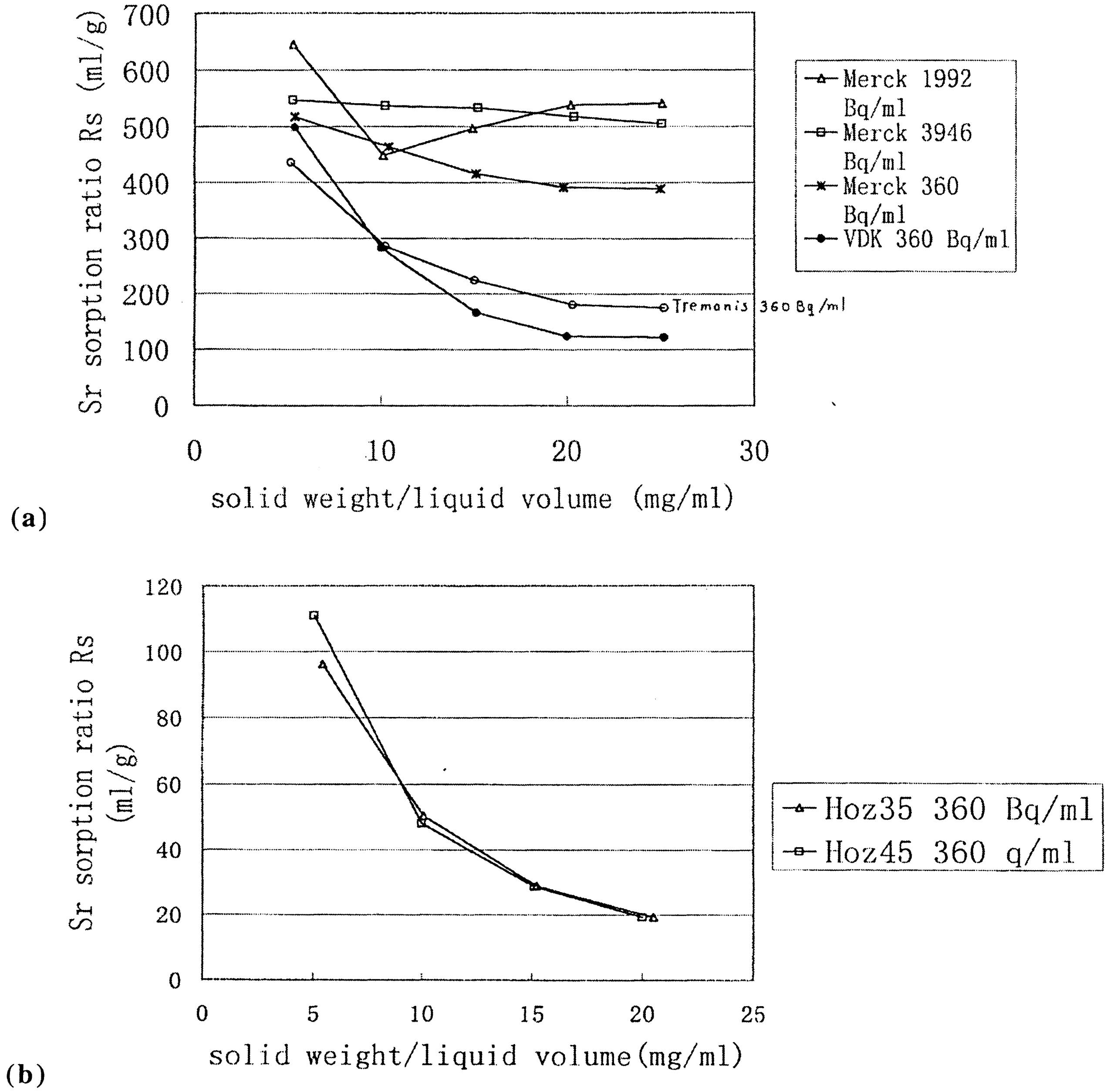

Figure 4. Sorption of Sr. (a) Sr sorption on diatomaceous earth, including the effect of solid-to-liquid ratio and initial radionuclide concentration; and (b) Sr sorption on cement, including the effect of the solid-to-liquid ratio.

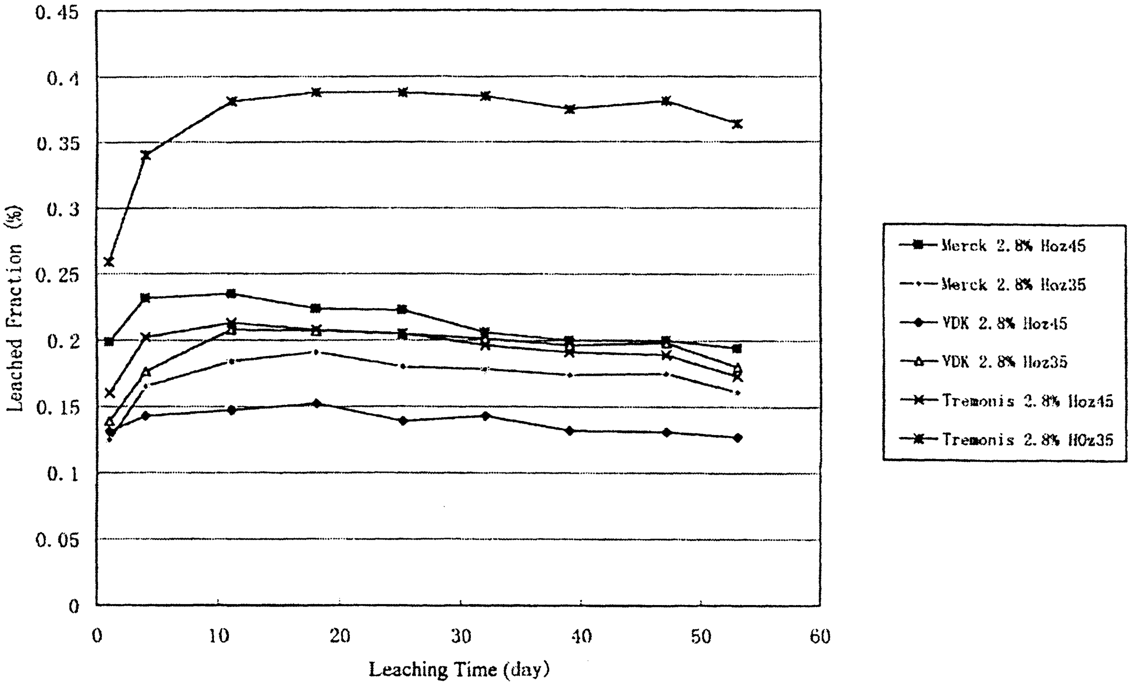

Figure 5. Leachability of Tc from cements with diatomaceous-earth additives.

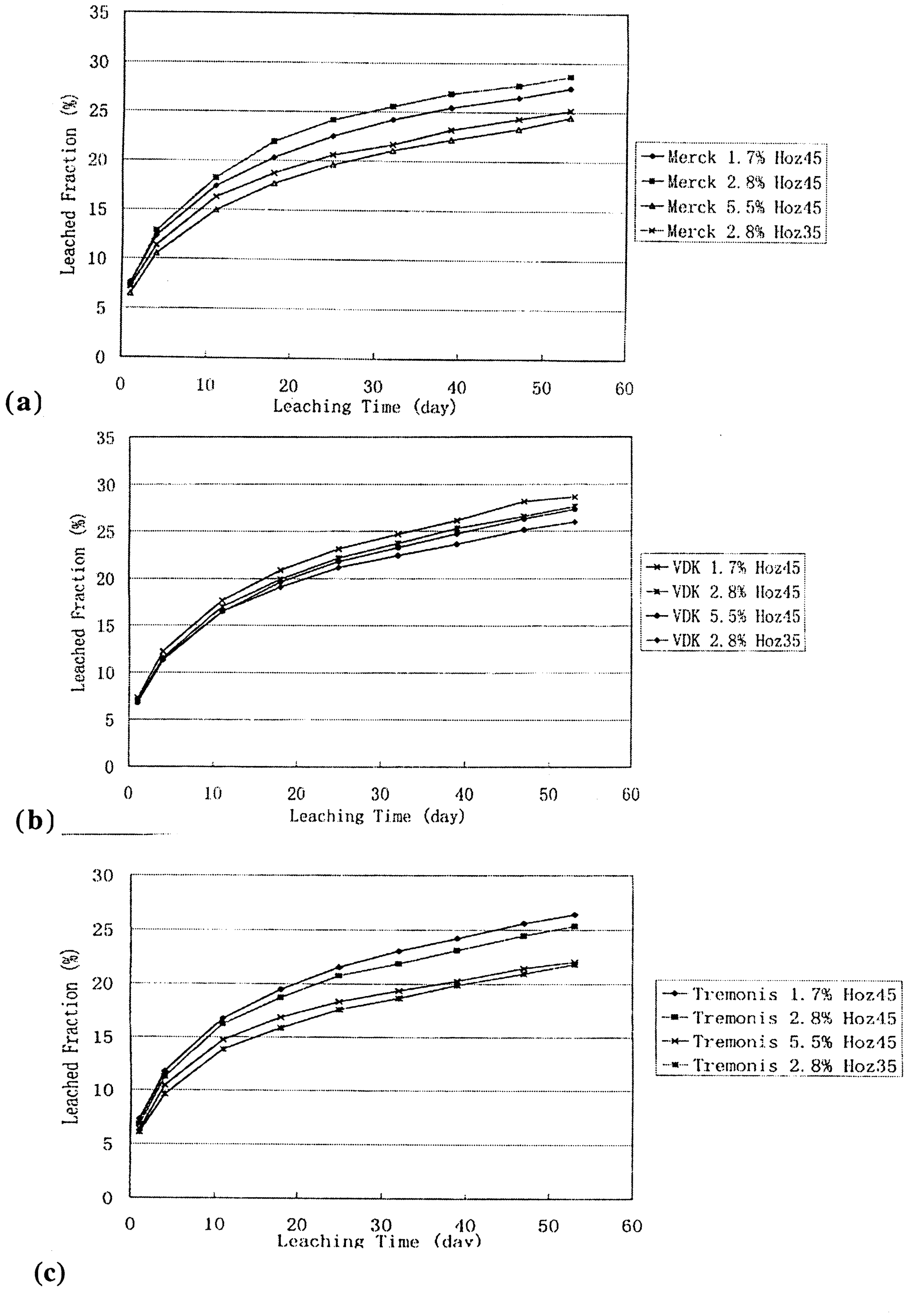

Figure 6. Leachability of Cl from cements with diatomaceous-earth additives. (a) Merck diatomaceous earth; (b) VDK diatomaceous earth; and (c) Tremonis diatomaceous earth.

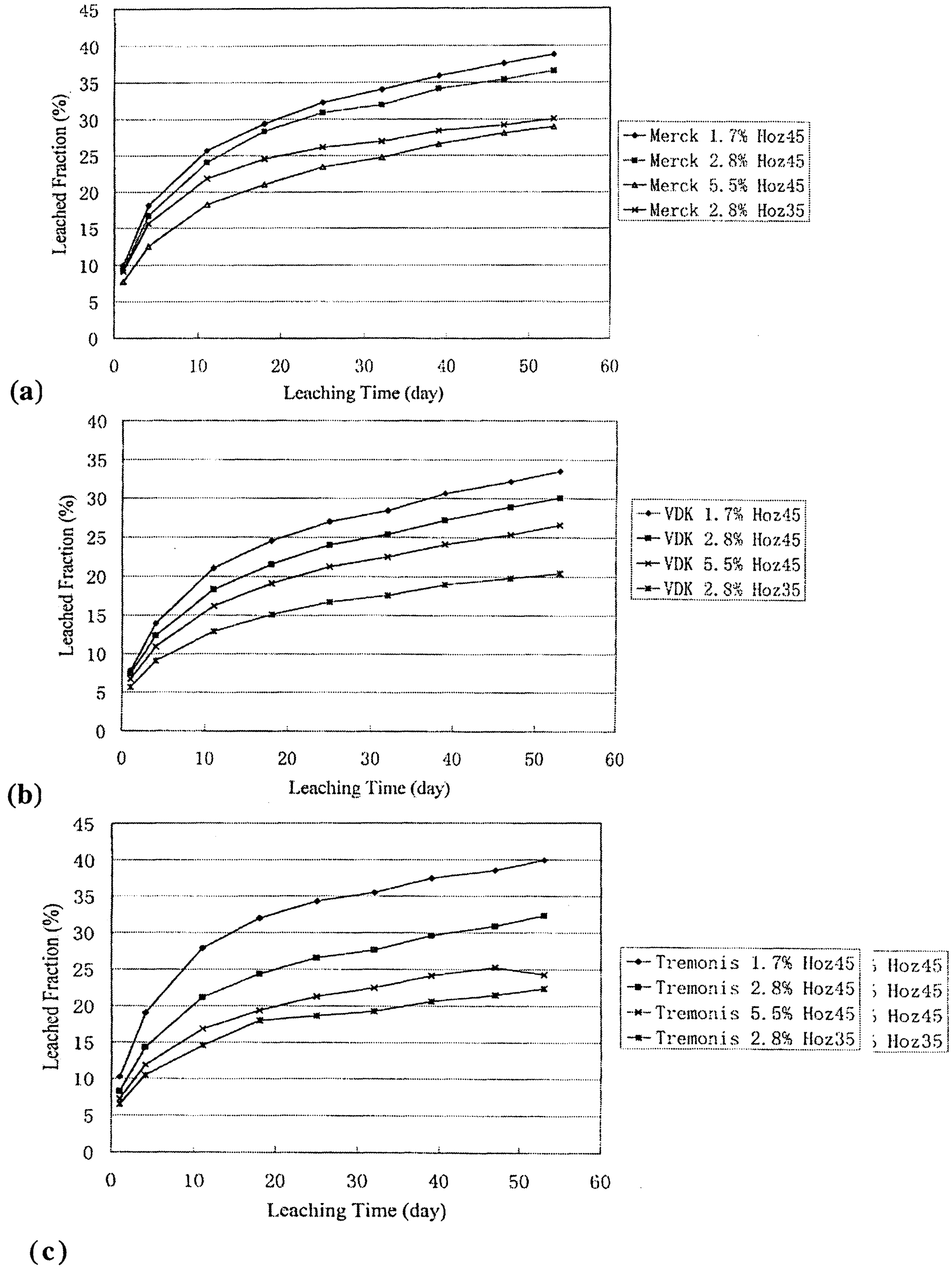

Figure 7. Leachability of Cs from cements with diatomaceous-earth additives. (a) Merck diatomaceous earth; (b) VDK diatomaceous earth; and (c) Tremonis diatomaceous earth.

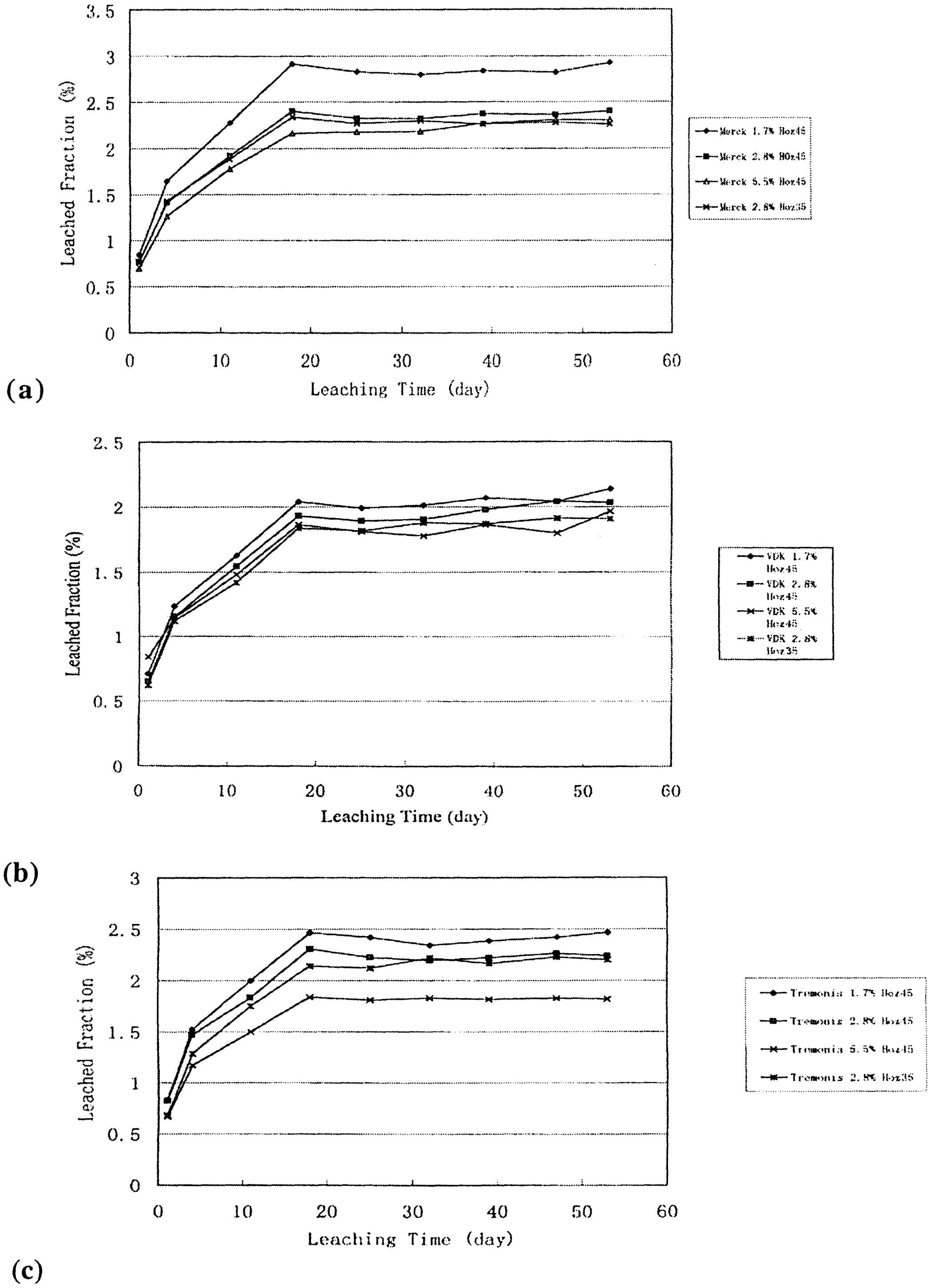

Figure 8. Leachability of Sr from cements with diatomaceous-earth additives. (a) Merck diatomaceous earth; (b) VDK diatomaceous earth; and (c) Tremonis diatomaceous earth.

FRENCH BACKFILL CONCEPTS FOR LLW AND HLW

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ABSTRACT

Since the passing of the French Waste Act in December 1991, the French National Radioactive Waste Management Agency (ANDRA) has been engaged in a program of research concerning the deep geologic disposal of high-level, long-lived radioactive waste. Three geologic sites are being investigated, a granitic formation and two clay formations. Initial design options were proposed for vitrified waste and transuranic (TRU) waste. Clay-based materials and concrete have been chosen as the respective backfill materials. Concrete is also the backfill for low-level, short-lived waste, and the near-surface disposal of this waste type is now being carried out. The physico-chemical properties of clay-based materials and concrete considered for safety assessment are discussed according to current scientific knowledge and the robustness of the concepts. In particular, the properties of the concrete proposed for the near-surface disposal and the deep geological disposal projects are summarized.

1. INTRODUCTION

Industrial procedures for processing low-level and short-lived radioactive wastes have been implemented in France for many years. These wastes are sent to near-surface disposal facilities, first the Manche center and, since 1992, the Aube center, at the border of the Aube and Haute-Marne Departments, about 250 km east of Paris. Since passage of the French Waste Act of 1991, the management of high-level, long-lived radioactive wastes has been the subject of research in three areas:

- partition and transmutation;
- reversible or irreversible disposal in a deep geological repository; and
- waste conditioning and long-term interim storage.

The French National Radioactive Waste Management Agency (ANDRA) is responsible for researching the reversible or irreversible disposal of high-level, long-lived waste in deep geologic formations. By law, three different sites, combining favorable geologic conditions as well as conditions acceptable to nearby communities, were selected for this research:

1. A clay formation in the south of the Meus Department, 'the East site'. The target formation is the 130-m thick Callovo-Oxfordian interval at about 450 m depth. This clay formation has a very low water content (about 5 to 7%, very strongly bound to the rock matrix) and a high clay mineral content that gives it high radionuclide retention capacity.

2. A clay formation in the Gard Department, located close to the Marcoule COGEMA reprocessing plant and the CEA research center, 'the Gard site'. The formation being investigated lies at a depth of 500 m and is up to 400 m thick. Its water content is lower than the East site (4 to 5%, indicating the absence of free water). The site also possesses high radionuclide retention capacity.

3. A granitic site in the south of the Vienne Department, 'the Vienne site'. At this site, the granite underlies a 150-m thick sedimentary cover. The granite occurs in the form of very low permeability blocks bounded by fracture zones, most of them sealed by secondary minerals.

After licence applications for the construction and operation of at least two underground laboratories, the research program will run until 2005. At the end of 2005, ANDRA will submit a report on the progress of its research to the Commission Nationale d'Evaluation, which will then report to the French parliament on the status of the three options. On the basis of an overall assessment report, the parliament will decide on which direction to follow for waste management. If the disposal option is chosen, a new law will have to be passed to authorize the construction and operation of a facility. The task of ANDRA's program is to assess the safety of a deep repository and the ability of the geologic formations proposed to accommodate the waste. This will require:

- the proposal of a disposal concept, with a description of the means required to build and operate it;
- the assessment of the containment performance of the barriers and their robustness;
- the verification of the feasibility of installing the disposal structures in the geologic formations; and
- the evaluation of retrievability in a repository including practicable levels of retrievability and technological means for retrieving the packages.

The time schedule of ANDRA's program is structured around three main phases:

- First phase: Research and concept selection (1997). In this phase, different foreseeable concepts were compiled and compared on the basis of various criteria, such as feasibility, safety, robustness, complexity, flexibility, retrievability, and cost.
- Second phase: Design phase (1998 to 2001). This phase involves the design of a preliminary disposal project that will indicate structure dimensions, materials specifications, and the design of handling facilities.
- Third phase: Qualification phase for the 2005 horizon. This phase will include safety evaluation, concept optimization, and qualification of geologic sites, particularly by underground laboratories that should be operational in 2000-2001.

2. DESCRIPTION OF THE FRENCH DISPOSAL CONCEPTS

The disposal concepts are different for different types of radioactive wastes. The French classification of radioactive wastes is described in the following sections.

2.1 Low-level and intermediate short-lived radioactive waste

Short-lived wastes of low or intermediate activity essentially contain beta and gamma-emitting radionuclides with half-lives of less than 30 years and, in certain cases, long-lived radionuclides present in trace amounts. Most of these wastes are produced by nuclear power stations and spent fuel reprocessing plants. The remainder arise from the operation and maintenance of plants at the front end of the fuel cycle, from major research centres, and from a large number of small users in industry, universities, and hospitals. This category accounts for 95% of the total quantity of wastes produced, but it contains only 1% of the total radioactivity.

2.2 High-level, long-lived radioactive waste

High-level, long-lived radioactive waste from the nuclear power generation cycle in France is stabilized by reprocessing. However, the direct disposal of a part of this spent fuel must also be considered. After the uranium and plutonium present in the spent fuel are separated, the minor actinides and fission products are stabilized in a silica glass matrix. The hulls (Zircaloy with an oxidized layer, zircon) and endpieces (stainless steel, Inconel), which were immobilized in cement grout until 1995, are now compacted. In some cases, chemical (coprecipitation) sludges ($BaSO_4$, ferrocyanide, CoS, $NaNO_3$, K_2SO_4), with or without the addition of heavy solvents (deriving mainly from the liquid effluents of the reprocessing plants at La Hague and Marcoule), were bitumized. All these wastes may be considered as transuranic (TRU) wastes or intermediate-level wastes (ILW). Considering current levels of production, both in quantity and grade, until 2040, the typical volumes will be:

- about 7600 m^3 of vitrified waste;
- about 80,000 m^3 of intermediate level waste; and
- about 25,000 m^3 of unreprocessed spent UOx and MOx fuel.

However, different alternatives, such as no reprocessing after 2010 or total reprocessing, are also being investigated, along with proposals for modular concepts offering relative simplicity of design as well as architectural flexibility.

The studies of the relevant geologic disposal concepts cannot be conducted in generic terms. They demand characterization of the geologic sites and detailed understanding of site-specific characteristics such as hydrogeology and geochemistry.

2.3 French disposal concept for low-level and intermediate short-lived radioactive waste

The French disposal concept for these radwastes is surface land disposal using the principle of multiple barriers. This principle applies as long as the necessary duration of the institutional control period is regarded as acceptable by society, for example, a few hundred years (in France, 300 years).

Most of these wastes are stabilized in a concrete matrix and are deposited in concrete bins filled with concrete or gravel. The disposal site is covered by a clay layer, mainly to reduce water inflow.

2.4 French initial option for high-level, long-lived radioactive waste

The deep geologic environment is thought to remain stable long enough for the activity of the radionuclides contained in the waste to decrease to levels that are considered safe. The disposal facility must be designed with multiple barriers that will confine the radionuclides and prevent them from returning to the biosphere, or will limit the effects of their eventual return to an acceptable level of impact on human beings. The barriers are:

- the geologic formation;
- the access seals, whose purpose is to repair the openings made in the geologic surroundings (galleries, shafts); and
- the engineered barriers consisting of the waste packages and the buffer/backfill placed between the packages and the geologic surroundings.

Disposal design is specific to the geologic site and the type of radwastes involved. The respective contributions of the different barriers to the global safety of the repository are meaningful only when considered as a part of the whole, each of them for the minimum time periods fixed by the safety requirements. Also, the functions that each barrier are expected to provide over time with regard to the safety scenarios are related to specific groups of radionuclides. However, the philosophy on which the principle of disposal in deep geologic formations is based requires that the geologic barrier ensure long-term confinement on its own. This is why the materials used to seal the accesses to the disposal areas are included with the geologic barrier when evaluating safety.

In addition, a specific component of the French project is the study of the technical conditions of the retrievability option. In particular, this option means that the conditions for retrieving and confining the packages during the retrievability phase must be specified. Also, the safety of the repository for the irreversible phase must not be degraded by the technical options for the retrievability phase.

The major initial reference design options that were selected in 1997 for each French geologic site considered include:

- the safety-related functions of the waste packages and, in some cases, potential requirements for overpackaging;
- the safety-related functions of the engineered barriers, which are associated with the types of materials selected and the approximate dimensions of the barriers;

- the beneficial aspects of the isolation capability of the geologic formations;
- a very preliminary design of the underground excavations; and
- waste package handling principles.

However, uncertainties associated with the reference options may lead to the consideration of other alternatives.

2.4.1 Argilite layer in the east of France

The major characteristics of this layer are its large horizontal extent, 130-m thickness, and moderate mechanical strength. The reference option consists of depositing the waste in horizontal tunnels. For TRU wastes with a low thermal impact, each tunnel (with a diameter of 4.5 to 6 m) will hold several hundred packages. The capacity of the tunnels dedicated to high-level vitrified waste will be limited to eight packages so that the temperature in the engineered barrier can be kept below the range 100°C to 150°C (see Figure 1).

To provide robustness of the concept in altered scenarios, the initial options of engineered barriers for high-level vitrified waste are:

- a carbon steel overpack with a lifetime of 500 to 1000 years; and
- a clay-based backfill material (involving bentonite) with zeolite as an additive.

The initial option of a buffer/backfill defined for TRU waste is made of concrete and will function as a chemical trap for radionuclides, mainly actinides.

Uncertainties about the feasibility of the horizontal handling of waste packages on the one hand, and the extent of the alkaline disturbance due to the use of significant amounts of concrete for TRU wastes on the other, may lead to the consideration of alternative options.

2.4.2 Siltstone layer in the Gard Department

The Marcoule layer provides a large thickness and high mechanical strength. Along with reference options similar to those described for the East site, concepts based on much larger openings are also being considered.

2.4.3 Granodiorite formation in the Vienne Department

Adequate flexibility in the design is required in order to emplace disposal modules in low-permeability granodiorite blocks away from meso- and macroscopic faults that might be potential pathways for radionuclides. The very high strength of the rock mass and its vertical extent make it possible to dispose of TRU wastes in very large silos (see Figure 2). Packages would be stacked in a concrete structure providing favorable chemical conditions for long-term isolation. High-level vitrified wastes would be stacked in vertical boreholes drilled from handling drifts, with a limited number of packages in each borehole. Carbon steel overpacks and a clay-based buffer/backfill with zeolite are also being considered.

3. THE KEY ATTRIBUTES OF CLAY-BASED MATERIALS

The use of clay-based materials involving bentonite as buffer/backfill for vitrified waste or spent fuel has been studied for many years. Their advantageous properties are quite well known and have been widely discussed (Greenfield *et al.* 1997). These properties include:

- very low hydraulic conductivity that retards transport of solutes by diffusion;
- high sorption capacity;
- high swelling capacity and plasticity, which support the stability of the canister and the hydraulic performance of the buffer/backfill;
- natural and simple material, which supports confidence in long-term stability;
- extremely small porosity that prevents transport of colloids;
- capability for screening specific minerals; and
- adaptability to different manufacturing technologies (e.g., highly compacted blocks, pellets).

A characteristic of the French initial design concept is the use of zeolite to ensure high and long-term sorption of caesium. The mass ratios of zeolite are maintained at concentrations between 20% and 30% in the clay mixture in order to control caesium behaviour with this particular backfill additive.

All the properties of the clay-based materials have to be compatible with the properties of the other engineered barriers:

- the corrosion of the glass matrix is very slow; the time scale of the radionuclide releases is $>10^5$ years: a conservative corrosion rate of 10^{-5} per year with a congruent radionuclide release is considered in the French initial design options; and
- the corrosion rate of carbon steel could support an overpack lifetime minimum of 500 to 1000 years.

The performance of the clay-based engineering barrier is then assessed using a mixture of initial material (clay + zeolite) with several degradation products from the waste package (e.g., silica oxides, magnetite, siderite, goethite, iron silica).

To increase the chemical retention of the engineered barrier, some other additives are being studied. The main option for TRU waste is apatite. A review of apatite solids has led to the selection of francolite[2]. Considering the favorable hydrodynamic properties of the host rock, the rather high solubility of such a solid is not of great importance. Francolite's availability and stability in radioactive environments are favorable characteristics. Moreover, it is well known that apatites, especially francolite, have a high affinity for alkaline earth and actinide elements. Retention mechanisms such as adsorption, substitution, precipitation, and solid-solution formation are considered in modeling because of their large capacity to retain heavy radionuclides. Francolite is being studied in alkaline media too, on the assumption that it may be added to concrete formulas. However, apatites are not selected as reference backfill materials.

4. THE KEY ATTRIBUTES OF CONCRETE

The favorable properties of the concretes are:

- availability;
- low cost;
- good handling capacity;
- good mechanical properties;
- rather good hydraulic properties for the short term; and
- chemical conditions producing low solubility of actinides.

However, the key attributes of concrete are different for each radwaste type because the stability of properties over time is uncertain. For low-level, short-lived waste, hydrodynamic properties (hydraulic conductivity, coefficient of diffusion, porosity) and chemical properties (solubility and sorption) are considered with respect to the radionuclide inventories and the time scale of the repository (a few hundred years). For high-level, long-lived radwastes, only water chemistry (solubility) is considered, with respect to radionuclide inventory, the lifetime of the repository (a few ten thousand years at least), and the favorable hydrodynamic properties of the geologic formations that should not interfere with the alkaline chemical buffering properties within the TRU waste cavities.

5. BACKFILL PERFORMANCE ASSESSMENT AND ROBUSTNESS

The design and acceptability of the repository require scientific and technical knowledge at a level that will support the demonstration. The physico-chemical representation and the design of the backfill must be consistent with the safety requirements, the description of the phenomena that contribute directly or indirectly to its performance, and all the uncertainties about the phenomena or the parameters related to them. The demonstration of engineerer barrier system (EBS)

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[2] Natural fluorocarbonate apatite.

performance, in particular for the medium and long term, may be supported by the search for a reasonable balance between the safety requirements and the available scientific and technical knowledge. The coupled analyses of the backfill's (i.e., EBS's) robustness and its performance are of great importance for the confidence of the demonstration. Confidence can be improved by utilizing two approaches:

- increase scientific and technical knowledge; or

- increase the robustness of the EBS by design.

5.1 Clay-based materials

The physico-chemical processes that could directly or indirectly degrade the properties supporting the performance of a clay-based material (mainly hydrodynamic properties) have been the subject of longstanding debate. The most important phenomena are probably the alteration of the clay-based materials (e.g., a decrease of bentonite/smectite content or cementation that degrades the hydrodynamic, mechanical, and sorption properties) and the production of H_2 gas caused by the corrosion of the carbon steel overpack (which could induce irreversible fracturing of the clay core and thus decrease the hydrodynamic properties). The first phenomenon (alteration of clay-based material) concerns physico-chemical processes caused by the degradation products of the overpack (Fe phases) and the glass matrix (silicon); the second (production of H_2 gas) concerns geochemical interactions with the geological formation. To improve understanding of these processes, and our confidence in the use of clay-based materials, they are the focus of much scientific research.

Also, buffer/backfill design modifications could be proposed to limit or eliminate the effects of the interaction processes or their uncertainties, thus increasing the robustness of the buffer/backfill demonstration. In this way Nagra (McKinley 1997) developed the idea of a second-generation EBS concept (Greenfield *et al.* 1997). An interesting example is given with the use of specific (ferrous iron) sand around the waste package and in the interface with the bentonite. This design maintains the concept of clay-based materials as a hydrodynamic barrier around the waste package while the ferrous iron sand acts as a physico-chemical buffer between the waste package and the bentonite. The corrosion gas problem or uncertainties about oxidation-reduction characteristics of pore water may be eliminated.

5.2 Concrete

As already noted, the use of concrete in backfill, sealing, or lining materials is supported by its availability, its low cost, its good handling capacity, and its mechanical properties. However, hydrodynamic and chemical performances are not so clear because of limited long-term predictability. Accurate modelling of concrete degradation depends on experimental feedback. Such data are available for standard cements, but high alkalinity and chemical reactivity are not represented in the data. On the other hand, the chemical and hydrodynamic properties of the engineered 'high-performance concretes' are usually not well known, nor even investigated, so that the prediction of their long-term stability is not guaranteed.

The distinction among different concretes appears somewhat open to criticism. The goal here is to present two considerations for selecting concrete backfills and improving their design:

- there is a poor correlation between the engineering development of 'high-performance concretes' and the understanding of their chemical and hydrodynamic mechanisms; and
- there is a compromise between chemical reactivity and durability of mechanical and hydrodynamic performance. Priorities have to be established.

The first consideration suggests that one should select a well-known concrete. ANDRA has now collected a large dataset from LLW disposals, which are partly built with ordinary Portland cement (OPC) and CLC[3] concrete. On the other hand, measurements of solute diffusion confirm the difficulty of explaining and modelling solute transport through concretes with very low porosity. Another question is the presence of such porosity over time.

The second consideration suggests that one should select a simple and consistent approach. Performance assessment is based mainly on demonstration capability, so priorities among physico-chemical properties of concrete are closely linked to a demonstration of durability with respect to the lifetime assigned to a backfill system. Here it is necessary to repeat the two requirements for buffer/backfill:

- protect waste packages from corrosion processes; and
- limit radionuclide releases to the geosphere.

Both requirements are connected with water, suggesting that hydrodynamic and chemical performances are a clear priority. Given this, stability of the hydrodynamic properties seems to be most important, but long-term prediction is also highly uncertain; a coupling of the chemical and the hydrodynamic properties has been modelled for OPC and CLC, but the results concern only the pastes and mortars (see Figures 3 and 4). On the other hand, prediction of the chemical performance of OPC and CLC seems to be more confident, and concrete backfill concepts are based on it. Chemical performance is broken down into two parts: one is connected with sorption properties, the other with alkaline buffer capacity.

If there is a very low water content and a very low solute transfer in the geological formation, modelling a long-term alkaline buffer capacity becomes feasible. Important parameters are alkalinity and cement content of the concrete, the volume and mass of the concrete in cavities, and water flow through the cavities. The water inflow and outflow in the cavities are controlled mainly by the geologic formation because of its very low hydraulic conductivity ($>10^{-13}$ m/s) and its low hydraulic gradient (between 0.005 and 0.02); all other parameters are defined within the EBS design. Moreover, low water content is a common characteristic of the French geologic sites (water content between 4% and 11%).

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[3] French blended cement: 'Ciment de Laitier au Clinker'.

Given this point of view, backfill concrete can be considered as a buffer material. A performance assessment is then based on pore water composition. The most important parameter is pH value, rather than parameters that are difficult to evaluate because of their close relation to solid degradation. Water buffering and associated high pH are taken into account in order to limit the solubility of radionuclides to a low level. The main requirement is to keep the pH value >10, for 10^4 years. Figure 5 shows the evolution of a front into the concrete for pH values of 12.6 and 10, which is the range required.

These calculations are based on a conservative hypothesis, i.e, convective transport with high Darcy velocity. For example, more realistic values of Darcy velocity in caverns for the French sites should be between 4 and 8 orders of magnitude lower than those selected for the pH front evaluations. Nevertheless, initial evaluations have confirmed the high buffering capacity of OPC, with a consistency that meets our time scale requirement.

The minimum value of pH 10 has been defined according to the solubility limits of several radionuclides. In order to assume a meaningful decrease of radionuclide solubility, a sensitivity analysis was performed as a function of concrete formulation and degradation. Two parameters appear to be most important: pH value and calcium concentration, which are linked in degradation processes. The calcium concentration could control the stability of very low-solubility phases for many radionuclides. However, thermodynamic data are poorly defined for such equilibria. ANDRA has thus decided to support a specific experimental program to obtain a consistent thermodynamic dataset. For the initial specifications of backfill concrete, the only parameter today is the evolution of pH over time.

Of course, each radionuclide has a specific behaviour in alkaline media, and solubility limits do not always decrease as a function of pH. Such an approach is more efficient for actinides than for other fission and activation products. Concretes are then associated with specific wastes, where the actinide contribution is important. A solubility approach also seems convenient for several fission and activation products (Zr, Tc, Pd, Nb, Ni), although their solubility limits may be high in alkaline conditions. However, a few fission products have a high activity contribution and their behaviour is not controlled by solubility, for instance, caesium. To be consistent with the waste inventory, each concrete cavity is given a thick bentonite plug. Sorption is then introduced in the performance assessment calculations to determine the interaction between buffer and plug materials. There are two important points:

1. The sorption efficiency of a clay-based material plug has to be evaluated with respect to alkaline and alkaline earth releases from concrete. Near the interface with concrete, new mineralization could occur, causing important changes in sorption characteristics (which does not always mean lowering of the retention level). An alkaline plume, probably the main perturbation of the plug, could affect ionic exchange processes. A first hypothesis is to neglect remineralization effects and to consider the stability of sorption sites of clay. The competing effects of alkalinity then become the main adjustments to evaluating caesium behaviour in the plug. To take into account the hydrolysis of other elements, the effects of high pH on sorption reactions are studied because new processes could be occurring (e.g., surface precipitation). An ongoing experimental program is exploring these points.

2. A more established method is also being developed to evaluate solubility. Sorption is introduced in performance assessments of concrete engineering barriers, using K_d[4] values. Different studies are under way:

    - For each radionuclide, one K_d value and one solubility limit are combined, whatever the degradation state of concrete. This method is applied to LLW disposal, where constant conditions are assumed for 300 years.

    - For each radionuclide, three K_d values and solubility limits are combined for three degradation states of concrete: (a) alkaline controlled pH, greater than 13; (b) portlandite-controlled pH, about 12.4; and (c) CSH-controlled pH at a value of 10.

      The degradation processes over time are simplified. Different degradation steps are defined and their duration is specified after an evaluation of alkaline earth elements and hydroxide migration toward the host rock. The migration parameters consist mainly of the solubility of concrete hydroxides and the hydrodynamic properties of the host rock. Initial results show that caesium migration could be controlled in these conditions by a concrete barrier. Hence backfill and plug systems are redundant and increase the confidence for the EBS design with respect to caesium release.

    - For each radionuclide, the functions of K_d and solubility over time are combined. These functions have to be defined by mechanistic thermodynamic modelling of retention processes in concrete. Unfortunately, the state of the art is very poor. A program is being developed to try to apply this third realistic model in the near future.

This last point shows clearly the problems arising from the aqueous chemical degradation of concrete over time. This explains the confidence level of a solubility approach, if radionuclide releases remain less than safety requirements. At this stage, confidence is built on solubility calculations and measurements. Uncertainties surrounding such data are a function of thermodynamic data consistency and how accurately aqueous composition is represented.

Since 1996, ANDRA has developed a thermodynamic database, which is supported by an experimental program on actinides and some fission products (Ni, Se, Nb, Tc). Each reference datum with its uncertainties allows us to conduct parametric calculations to define direct uncertainties on solubility limits.

The problem of accurately representing aqueous conditions is more ambiguous. The main source of uncertainty is of course the change in the conditions over time. Although, solubility scales can be defined for nearly all ranges of conditions. The problem, however, is quite different if one important parameter is missing. Consider, for example, the organic content of additives in concrete. Unfortunately, the identity and concentration of these organic species are not well

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[4] Distribution coefficient.

known for most of the concretes. Moreover, experimental data are not consistent: organic additives are more or less dependent on solubility limits and whether sample measurements are made with or without cement solid phases. For aqueous media, much data in the literature show a significant increase in solubility limits, especially for actinides (see e.g., Greenfield *et al.* 1997). On the other hand, experimental results from batch experiments show low or negligible effects for the same radionuclides and conditions. It is quite clear that the sorption of additives explains this discrepancy, but the mechanisms are not yet understood. If additives effects are really negligible, the problem is to evaluate the effects of the desorption mechanisms of these organics, which could be linked to concrete degradation. To limit these uncertainties, concrete formulation (and initial water content) and handling requirements are two parameters that must be defined.

The same kind of problem exists with the complexation capacity of waste degradation products. Many papers have been published on cellulose degradation products (e.g., Holgesson *et al.* 1997). Without repeating information on the effects of isosaccharinic acid, this problem occurs in France only for LLW with low cellulose content. A few organic complexants introduced in waste, such as ethylenediamine tetraacetic acid (EDTA), are in the same category. These organic species are not very important for deep disposal. For ILW, radionuclide solubility could be clearly influenced by bitumen degradation products. Dissolution of salts introduced in bitumized radwaste packages is the origin of an important release of nitrate and sulfate ions. This should lead to the selection of a sulfate-resisting Portland (SRP) cement in order to limit the rate of alteration. When calculating radionuclide solubility, problems arise because of uncertainties in the thermodynamic data (e.g., complexation) and the determination of nitrate and sulfate concentrations in interstitial solutions. Bitumen degradation involves a release of organic species such as oxalates, monocarboxylate acids, and hydrocarbon and could increase radionuclide solubility. The problem is to select these organic species with respect to a complexation capacity, and to evaluate their concentration in interstitial water. It could then be possible to use the same approach as for concrete additives. The lack of knowledge about the behaviour of these organics in concrete is one important problem that needs to be solved to increase the confidence of a performance assessment based on solubility evaluations. Bitumized radwaste packages are quite unique among French radioactive waste packages because of their organic matrix and their content (PUREX organic residues). This is why both options, clay and concrete, are being studied concurrently as backfill systems for these wastes.

6. CONCLUSIONS

The disposal of LLW has been an industrial reality in France for many years. The use of well known concretes (Portland cement and French CLC) in backfill has been considered appropriate for meeting the safety requirements according to the chemistry of the waste packages, the radionuclide inventory, and the time scale of disposal. The performance assessment of the concrete is mainly based on its hydrodynamic and sorption properties.

For high-level, long-lived radwastes, ANDRA is still engaged in research. The base backfill properties used to build the design option for each radwaste type were defined with a conservative approach. Clay-based materials are usually proposed as a hydrodynamic buffer/backfill for vitrified wastes, and zeolites are proposed as additives for the sorption of caesium. This choice allows us to increase the robustness of the buffer/backfill. However, the state of knowledge of the physico-chemical processes among the clay-based materials, the glass matrix, and the carbon steel overpack appears to be insufficient for demonstrating long-term peformance. That is why a research program is moving in that direction. However, another method that consists of using a high-porosity medium between the waste package and the clay buffer could reduce or eliminate the effects of many interaction processess. The use of well known concretes (Portland cements, French CLC) for TRU wastes is proposed. Currently, the alkaline buffer property of concretes is the only aspect considered in performance assessment. A research program on the durability of concrete hydrodynamic and sorption properties will be undertaken in the future and could allow us to reduce the performance standards required for the clay plug of the TRU waste cavities. However, the degradation products of some TRU wastes may reduce the effectiveness of the alkaline buffer and it is therefore appropriate to maintain an option for the use of clay-based backfill.

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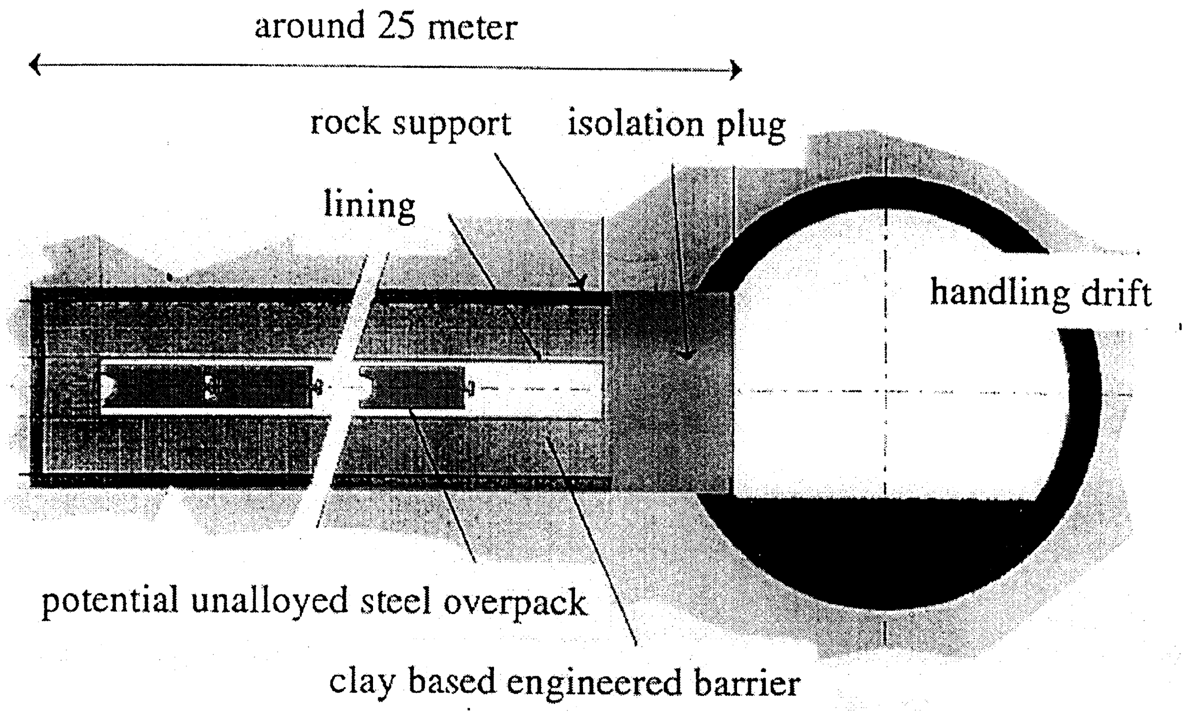

Figure 1. Initial design option for high-level waste in a clay layer.

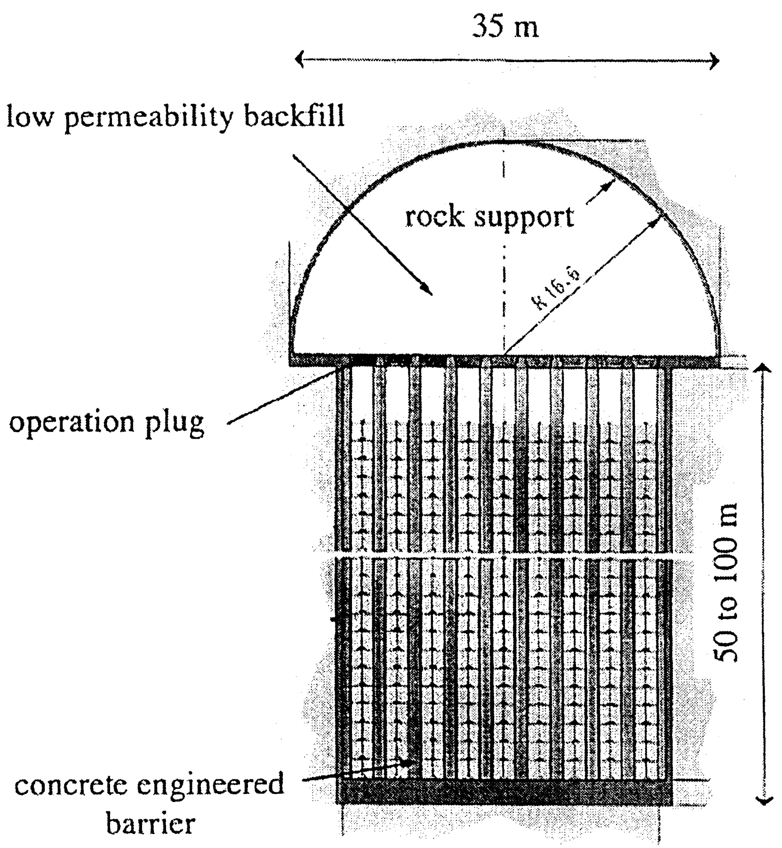

Figure 2. Initial design option for non-heat generating TRU wastes in granitic formation.

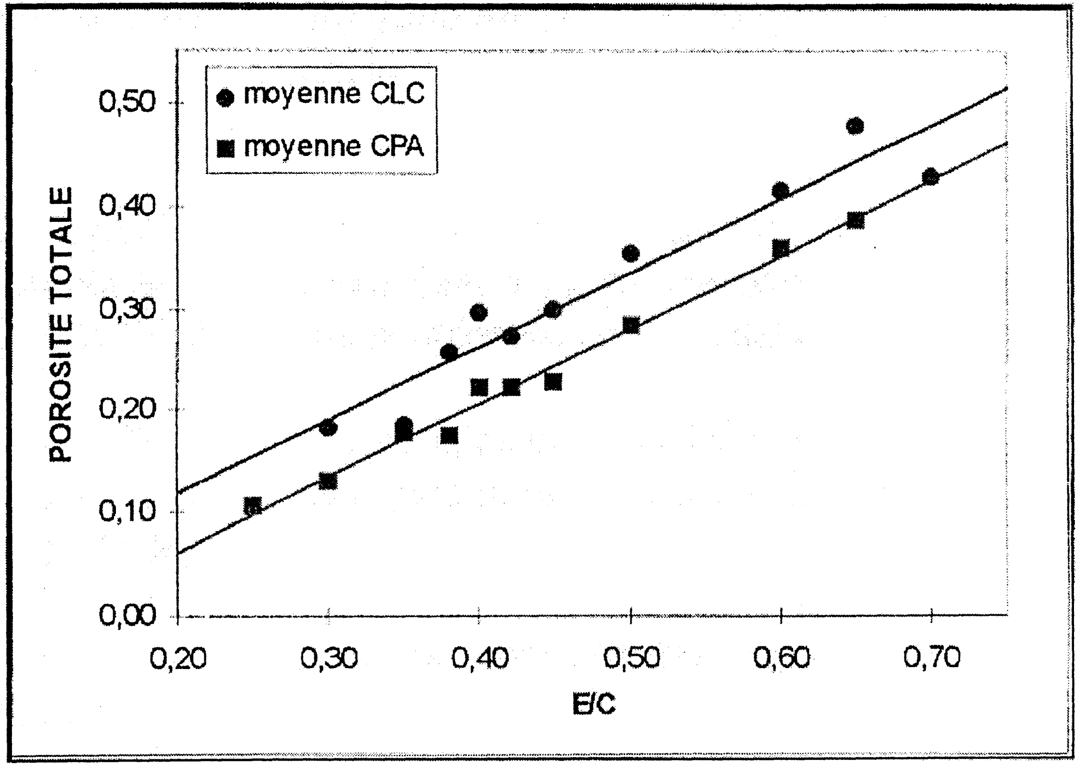

Figure 3. Evolution of the porosity of OPC (CPA) and CLC pastes with water-cement ratio E/C.

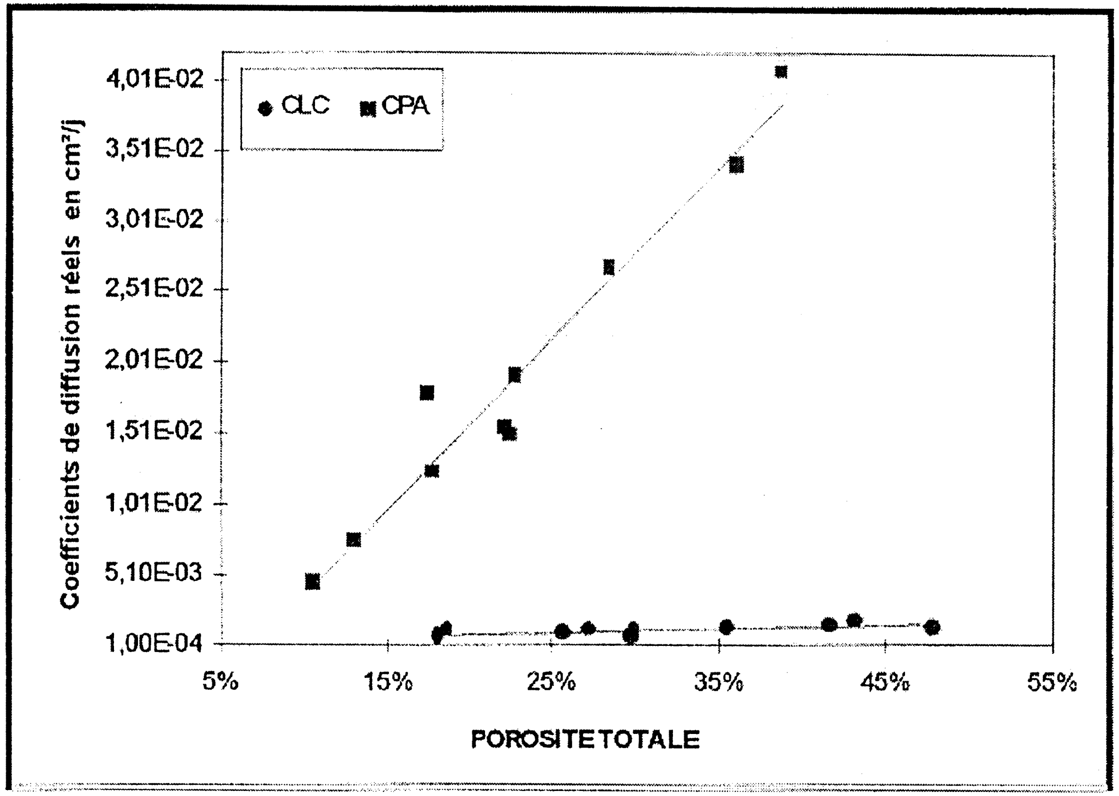

Figure 4. Evolution of the effective diffusion coefficient of OPC (CPA) and CLC pastes with porosity.

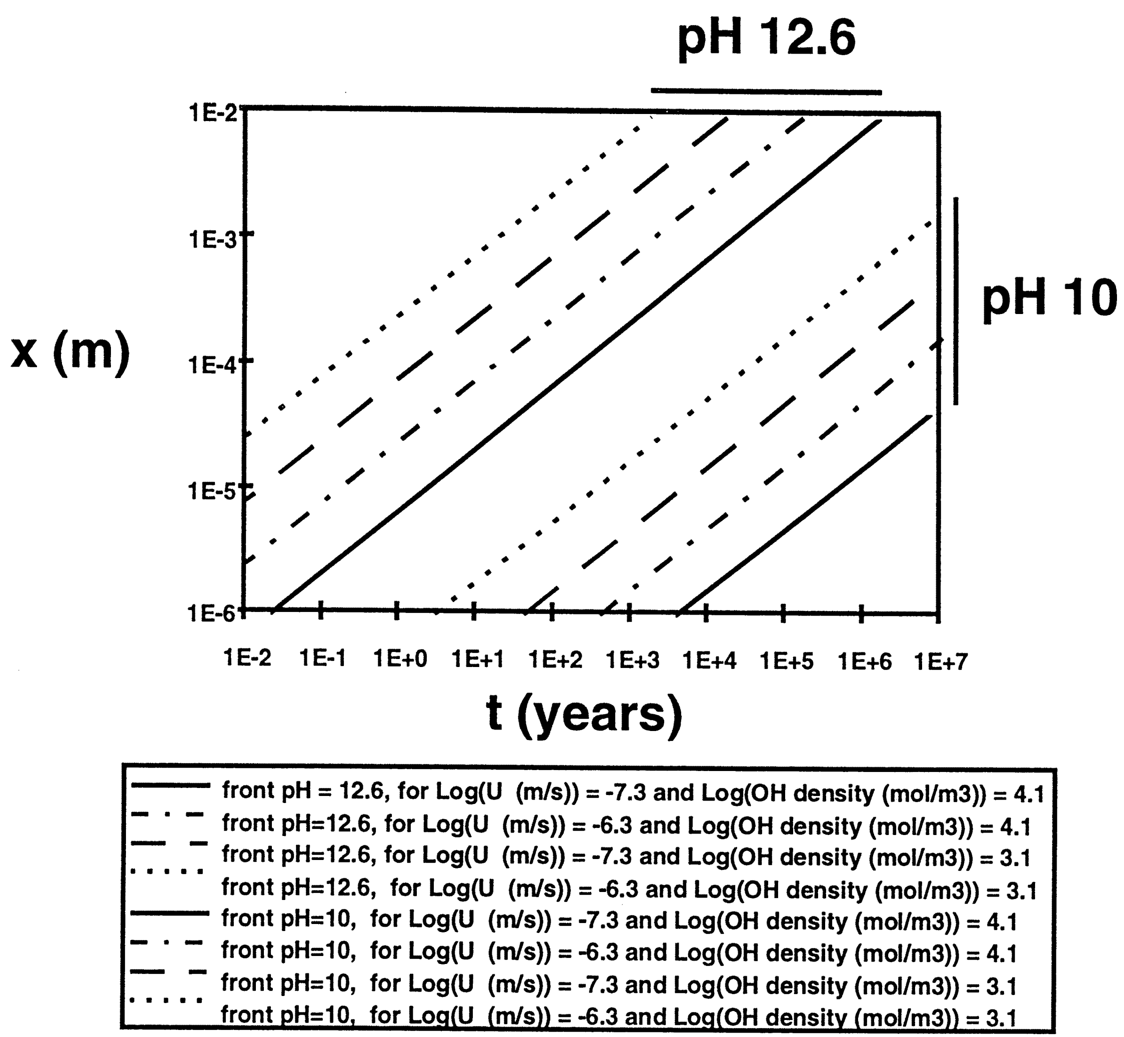

Figure 5. The pH fronts as a function of time for several Darcy velocities and several OPCs.

BACKFILLING AND SEALING OF RADIOACTIVE WASTE REPOSITORIES IN ROCK SALT FORMATIONS—TECHNICAL CONCEPTS AND R&D APPROACHES IN GERMANY

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ABSTRACT

In Germany, rock salt formations have been selected for the final disposal of both radioactive waste and hazardous chemically toxic waste. For low-level waste (LLW) the underground repository at Morsleben is in operation. For intermediate-level waste (ILW) and high-level waste (HLW) the salt dome at Gorleben is being investigated for its feasibility. In addition, there is also the research and development (R&D) facility at Asse, which has been used for LLW and ILW disposal and is now is being backfilled. For chemically toxic waste disposal, five salt and potash mines are in operation. Some others are in the licensing stage.

So far only one of these mines has started backfilling the old mine workings in order to prepare the entire mine for sealing and final termination. This is the Asse salt mine, which has been operated as a test facility for radioactive waste disposal since 1963. In addition to the backfilling operation, two R&D experiments are being performed to investigate the mechanical behaviour of salt gravel under heat load and as backfilling and sealing material for disposal boreholes. The main concern is the behaviour of backfill in close vicinity to the heat-generating waste.

For the Morsleben repository, various backfilling and sealing concepts are being examined to find adequate solutions for stabilizing the old mine workings and sealing the disposal sections. A wide range of lab tests accompanied by some *in situ* tests as well as performance assessment calculations are under way. Of specific interest are backfilling and sealing materials based on clay minerals.

An important component of the multibarrier concept for underground repositories is the backfilling and sealing system for access and ventilation shafts. Salt mines or salt formations have been selected as repositories because of their absence of groundwater. The main purpose of geotechnical barriers is to preserve this condition, the dryness of the repository, as long as possible. In particular, for repositories with large amounts of hazardous toxic waste, shaft seals must provide a substantial barrier against water intrusion from outside the rock salt formation. With this objective in mind, the Federal Minister for Education, Science, Research and Technology (BMBF) and the German potash mining company Kali & Salz mbH have started a shaft backfilling experiment at 1:1 scale.

With respect to the long term safety of a high-level waste repository, GRS (on behalf of BMBF) has performed several national and international performance assessment studies for various disposal concepts in rock salt. The convergence of underground voids and the permeability of underground sealing dams were identified as the primary and secondary features contributing to the possible release of radionuclides into the overlying strata and the biosphere. That is why

intensive R&D efforts are being made to characterize these parameters and to forecast long-term performance with great confidence.

However, experiments have demonstrated that, without a distinct convergence rate, specific techniques are needed for getting the required tightness of the geotechnical barriers in the repository. With respect to the mechanical and hydraulic properties of the various geotechnical barriers, several alternatives are being investigated. The final decision about which material to use (either in Morsleben or in a high-level waste repository) is still undetermined.

Additional R&D work is focused on the testing of backfilling materials with a high sorption capacity, such as hydroxylapatite. The idea is to use physical barriers also as geochemical barriers, which should substantially improve confidence in the long-term safety of repositories. In this paper, the geotechnical aspects of the various backfilling and sealing strategies are discussed, with specific emphasis on the ongoing R&D work.

1. BACKFILLING OF REPOSITORIES IN "LOW CONVERGING" ROCK SALT FORMATIONS

Unlike some other salt and potash mines in the northern part of Germany, the Morsleben repository is only 386 to 506 m deep. Because of this shallow depth and a specific internal structure with anhydrite formations providing rock mechanical support, the convergence of the underground cavitities is relatively small. The annual rate of volume convergence falls in the range of 10^{-4} to 10^{-5}. For the long-term performance of the backfill, this is quite important because compaction takes much longer than anticipated. For this reason, material other than crushed rock salt has been pre-selected for technical analysis.

The Morsleben repository will be closed for radioactive waste disposal after the year 2000. Presently an intensive research and development (R&D) program is being conducted to develop an appropriate backfilling and sealing concept. The mine has an open cavity volume of about 7.6 million m^3, which comprises a complex system of galleries, mining chambers, and boreholes. The disposal chambers are located on the fourth mining level. At the end of the disposal operation, the repository will host 40,000 m^3 of LLW. On behalf of the German office for radiation protection (BfS), GRS is conducting a performance assessment calculation for the entire mine system. A scenario analysis revealed that brine intrusions into the mine and the repository cannot be ruled out from the outset despite the mechanical stabilization of the mine cavities. A basic assumption is that brine fills the open voids shortly after closure. Only the disposal chambers remain free of brine as long as the sealing dams act as impermeable or low permeability barriers. Thus the physical and chemical properties of the materials to be used for the construction of the geotechnical barriers are of utmost importance.

So far three alternative concepts are being investigated. In concept 1, permanent isolation of the disposal area is assumed by using sealing dams made of highly compacted bentonite. In the heterogenous rock salt formation of the Morsleben site, the construction of such sealing dams is not everywhere feasible so that an alternative encapsulation (concept 2) is planned using mineral mixtures as low-permeability barriers. This concept is shown in Figure 1 for disposal areas in the southwest sections. Concept 3 focuses on long pathways in the repository where brines might travel. A combination of high- and low-permeability clay-based material has been pre-selected as backfill to provide sufficient mineral surfaces for radionuclide retardation. In addition, the old mine workings will be filled with a sand-gravel mixture or a pumpable backfilling.

Performance assessment calculations were performed for these concepts using provisional input data and model approaches. The calculated maximum dose rates remained below the applicable limiting values of the German Atomic Act. Comparison of these dose rates and the respective functions of time has shown that they differ by about a factor of three, assuming a dam permeability one order of magnitude higher than given. Because of the highly permeable sand-gravel mixture, the dose rate starts to rise earlier in concept 3 (after 10^4 ys) than in the two other concepts (after 10^5 ys). This finding reveals that backfilling is a key issue in the development of a long-term safety strategy for the Morsleben repository.

2. BACKFILLING OF REPOSITORIES IN "HIGH CONVERGING" ROCK SALT FORMATIONS

The German disposal concept for heat-generating high-level waste (HLW) is based on the use of a salt dome mined specifically for this purpose. From both safety and mining perspectives, a depth of about 800 m to 900 m is being investigated for waste disposal. At this depth, rock stress plays an important role not only in the mining operation but also in the post-operational safety of the repository. After backfilling of the underground voids, the resulting convergence will contribute substantially to material compaction and permeability reduction. When considering the geotechnical and performance assessment aspects, the mechanic and hydraulic parameters as a function of rock stress and time are of utmost importance. The same applies to salt mines that are being used as repositories for other kinds of hazardous waste. Here the problem is the backfilling of large mine workings and the performance of sealing construction under stress load.

2.1 Backfilling of mine workings

In the R&D facility for radioactive waste disposal, the Asse salt mine, old mine workings are being backfilled at a large scale. About 140 mine workings with a total volume of about 2.5 million m^3 resulted from salt mining between the 1920s and the 1960s. Underground cavities still open today are affected by increased rock pressure. To reduce convergence and stabilize the entire mine between the 490 m and 700 m depths, salt gravel from an old mine dump is being filled into the cavities. About 1,200 t/day are being dried and pneumatically conveyed from the surface into the mine workings. From August 1995 until December 1996, a total of 285,000 t was placed into the mine, backfilling all workings between the 700 m and the 679 m depths. This operation was accompanied by a quality assurance program consisting of weight and volume determination, sampling, and measurement of the backfilling density (presently 1200 to 1300 kg m^{-3}) and *in situ* rigidity. In addition, a comprehensive rock mechanics observation program is aimed not only at the deformation behaviour of pillars and foot/hanging walls but also at the stabilization processes taking place once the backfilling is pressurised.

2.2 Backfilling of access drifts and disposal rooms

Crushed rock salt has been identified as the most suitable backfill for heated sections within a HLW repository in salt formations (Rothfuchs *et al.* 1996). As a consequence of the thermally induced increased convergence rate, the crushed rock salt compacts rapidly. At the same time, the permeability decreases by several orders of magnitude, to a permeability similar to that of undisturbed rock salt. In disposal galleries and borehole seals, the backfill material consists of crushed rock salt taken from the excavation by continuous mining producing coarse grained material with a maximum grain size of 60 mm. The material to be used in the borehole annulus will be fine grained with a maximum grain size of 10 mm.

Two *in situ* experiments are being conducted at the 800-m level in the Asse salt mine. The Thermal Simulation of Drift Storage (TSS) experiment is designed to examine the compaction of crushed salt in disposal drifts, and the Development of Borehole Seals for High-Level Radioactive Waste (DEBORA) experiment is designed to investigate the crushed salt in HLW disposal boreholes.

2.2.1 R&D for backfilling of disposal galleries

The TSS test layout (Figure 2) consists of two parallel drifts separated by a 10-m wide pillar. Additionally, the test field includes several observation and access drifts on the 800-m and 750-m levels, from which a large number of boreholes extend into the vicinity of the test drifts. The boreholes are equipped with various measuring gauges to determine the thermomechanical reactions of the surrounding rock. Other devices are installed in the backfill and at the surface of the heater casks. Measurements are conducted in the heated area around the heater casks as well as in the non-heated rock mass farther away from the casks, where the impact of heating is less significant. Heating started on 25 September 1990. Since then each heater cask has been operated with a constant power output of 6.4 kW. The total power output in each drift is about 19.2 kW. Some electronic components had to be replaced in 1995.

Temperatures

Before heating, the ambient temperature in the test drifts on the 800-m level was about 36°C. Immediately after the heaters were activated, the temperatures in the surrounding area increased rapidly. At the surface of the casks, a maximum temperature of 210°C was reached after five months. Because of the increasing thermal conductivity of the backfill during its compaction, the temperature subsequently decreased to between 165 and 175°C.

Drift closure

Before heating, convergence rates averaged 0.25% per year in the horizontal direction and 0.3% per year in the vertical direction. Different values for different orientations are mainly a result of the local stress field. With the start of heating, a significant acceleration of the drift closure rate was observed. Within three months, the rates increased by a factor of 8 to 10 compared to the non-heated sections of the test drifts (Figure 3). Because of the increasing rigidity of the compacted backfill, the rates subsequently decreased again. Present rates in the vertical direction amount to 0.6% per year, whereas horizontal rates of 0.45% per year were recorded. These values are still twice as much as before heating. In the non-heated area, the drift closure increased gradually, currently reaching 0.5% and 0.3% per year in the vertical and horizontal directions, respectively.

Backfill Porosity

As a result of drift closure, the initial backfill porosity of about 35% has been reduced to between 25 and 26% in the heated area. The actual porosity in the non-heated sections ranges between 31% and 32.5% (Figure 4). Because of the slower drift closure rates in the heated area, the observed backfill compaction is also significantly lower than predicted.

Backfill Pressure

Increasing backfill compaction causes pressure to rise at the interface between the backfill and the surrounding rock. This pressure is recorded by hydraulic pressure cells at the floor, the roof, and at the walls of the test drifts. In the non-heated backfill, the pressure increased gradually and currently ranges between 0.125 and 0.25 MPa. In the heated area, the pressure at the walls increased immediately after the beginning of heating. Pressure increases at the roof and floor, however, started several months later. Generally, the maximum backfill pressure is measured at the roof, currently reaching up to 3.5 MPa.

2.2.2 R&D for backfilling of disposal boreholes

In terms of the German disposal concept, the DEBORA test is aimed at investigating the backfill compaction and permeability in HLW boreholes. Two single experiments have been designed in order to simulate the conditions in HLW disposal boreholes: the first because the temperature and thus the rock mass convergence is different in the borehole annulus and the seal section, and the second because the grain size of the backfill material is significantly different.

The DEBORA 1 experiment (Figure 5a) is focused on investigating the backfill behaviour in the annulus between the waste canisters and the borehole wall. The experiment is being conducted in a 600-mm diameter, 14-m deep borehole beneath a 8 to 10.5-m wide drift in the mine. A liner in the borehole represents the waste canisters in a disposal borehole. Electric heaters inside the liner produce 9 kW of power. In a 15-month testing period, the heat-induced compaction of the backfill between the liner and the borehole wall and the related decrease of porosity and permeability were investigated. The experiment has been in operation since February 1997.

In the DEBORA 2 experiment (Figure 5b), a backfill borehole seal is being investigated. The experiment is being conducted in a 600-mm diameter, 14-m deep borehole located 15 m away from the DEBORA 1 borehole. Crushed salt is emplaced in the lower 5.5 m of this borehole. This section simulates the seal of an HLW disposal borehole and is heated by four external peripheral heaters producing 3.5 kW each (14 kW total). Measurements are focused on the interaction among backfill compaction, temperature, pressure, convergence, and permeability. The experiment became operational in September 1997. In both DEBORA experiments, the temperature, the radial stress, and the borehole closure are measured at three different levels and three different directions (see Figures 5a and 5b). The backfill porosity is determined by volumetric measurement of the borehole convergence.

According to design calculations (Rothfuchs *et al.* 1996), both experiments will provide substantial data on crushed salt compaction and the resulting permeability over a comparably wide parameter range. Heating of the DEBORA 1 borehole led to a rapid increase of the backfill temperature to about 185°C. The temperature has risen only slightly higher as the experiment has continued. Surprisingly, the measured temperatures are considerably lower than predicted. The reason for this discrepancy will be investigated in the future. In the DEBORA 2 experiment, the agreement between the predicted and measured temperatures is much better. Also, compared to the DEBORA 1 experiment, the temperature increase is less rapid because the heaters are located outside the central borehole at a radial distance of 1.1 m.

In both DEBORA experiments, the heat-induced borehole convergence (closure) is being measured at three levels: 10.5, 12, and 13.5 m below the drift floor. The decrease in backfill porosity is determined on the basis of borehole convergence measurements. Figures 6 and 7 show the comparison of the development of the measured and predicted porosity for both experiments. The predictions were made with the code Supermaus (Breidenich 1993) under consideration of a constitutive equation describing the thermomechanical behaviour of crushed salt published by Hein (1991). In both experiments, the measured compaction rates are smaller than the predicted rates. In DEBORA 1, however, the porosity reaches values similar to those predicted, although the development is somewhat different.

To determine the permeability of the compacted backfill, nitrogen is injected into the deepest part of the boreholes, the gas-injection volume, causing a gas flow upwards. The gas is collected at the upper end of the backfill column in the gas-collection volume. Instruments were installed to measure inlet and outlet gas flow and the gas pressures in both the gas injection and collection volumes. Under stationary gas flow conditions, the permeability of the crushed salt can be calculated according to the generalized Darcy's law for compressible media. The permeability measurements are made periodically when a sufficient progress of crushed salt compaction is indicated by borehole convergence measurements. In DEBORA 1, the first reliable measurement was possible two months after start-up of heating when a backfill porosity of 0.25 had been reached. Correlating with the changing porosity, the backfill permeability reached a plateau value between 6.9×10^{-14} m^2 and 1×10^{-13} m^2 after six months of heating. The total permeability decrease covers a range of two orders of magnitude. In DEBORA 2, only one measurement has been made so far; it indicates an initial permeability of approximately 1.3×10^{-10} m^2 at a porosity of 0.35. The DEBORA experiments are scheduled to run until the end of 1998. After termination, it is planned that the boreholes will be uncovered through a new access drift and the spatial distribution of porosity and permeability in the compacted backfill will be analyzed.

3. CONCLUSIONS

A wide range of performance assessment studies has revealed that efficient backfilling and sealing measures are most important for the long-term safety of waste repositories located in rock salt. Using clay/bentonite-based materials, high impermeability can be achieved from the outset. Despite specific construction requirements, problems may exist with the contact zone at the rock face and with the proof of the system performance.

Salt gravel backfill is initially permeable. However, over time it develops into a material similar to the neighbouring rock mass, depending on the geomechanical conditions at the site. Important results have been achieved in specific experiments in the Asse mine.

In the TSS test, the backfill behaviour of crushed rock salt in emplacement drifts is being investigated. More than seven years of measurement results are available. In the DEBORA tests, the backfill behaviour in HLW disposal boreholes is being investigated. These tests were started in February and September of 1997.

In the TSS and DEBORA tests, the compaction of the crushed salt is somewhat slower than predicted. In the DEBORA 1 experiment, however, the backfill compaction finally reached values similar to those predicted, although the development is somewhat different than expected. Also, the stress build-up in the backfill is smaller than expected in both experiments. In the TSS test, for instance, the backfill pressure has reached only 24% of the initial vertical stress in the test field, which was determined to be about 12 Mpa.

Because of the deviations between predictions and measurements, it seems necessary to improve the models and the material laws used to describe the compaction behaviour of crushed salt backfill. Therefore, a benchmark exercise, including comparative calculations and simulations of suitable laboratory experiments, is currently being performed by the respective project partners. The free convergence measurements in the 500-m borehole were very useful in establishing the effective parameter values for the Norton-type law describing rock salt creep. Based on the measurements at the different depths, the mean rock pressure at the 800 m level was found to be in the range of 8 to 10 MPa.

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Table 1. Parameters of backfill material under investigation for the Morsleben repository.

Backfilling Material	**Porosity**	**Permeability**
clay-sand mineral mixture (Dywidag)	20 %	1.0×10^{-17} m^2
sand-gravel mixture	25 %	1.0×10^{-11} m^2
self solidifying pumpable backfill	30 %	1.0×10^{-11} m^2
sealing dams made of high compacted bentonite	20 %	1.0×10^{-19} m^2
excavation damage zone in rock salt (for comparison)	(0.4 %)	(1.0×10^{-17} m^2)

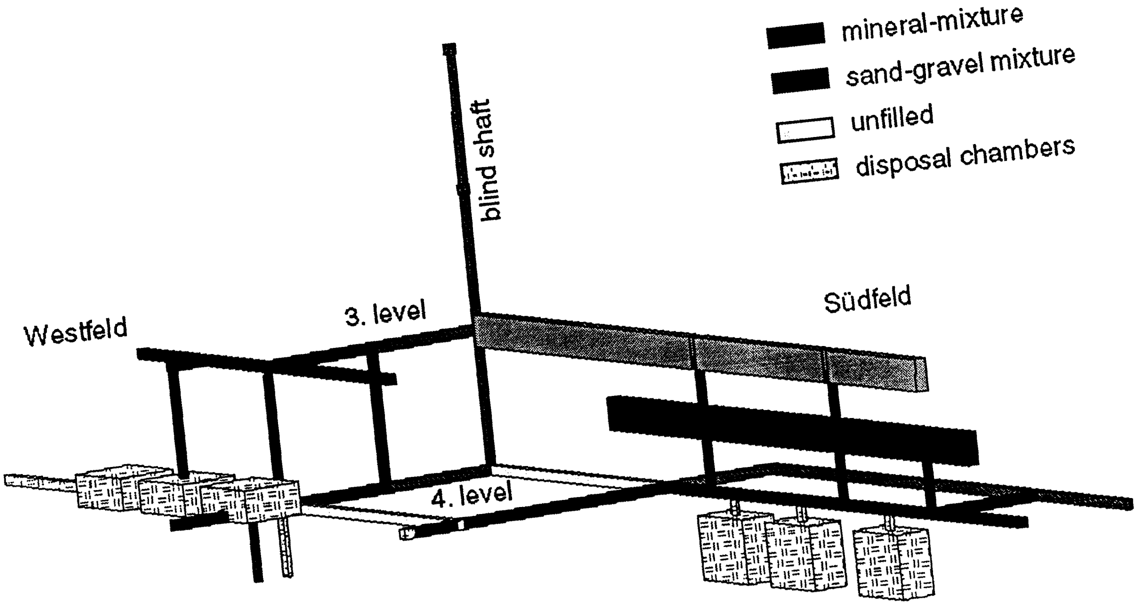

Figure 1. **Backfilling and encapsulation concept 2 for the Morsleben repository.**

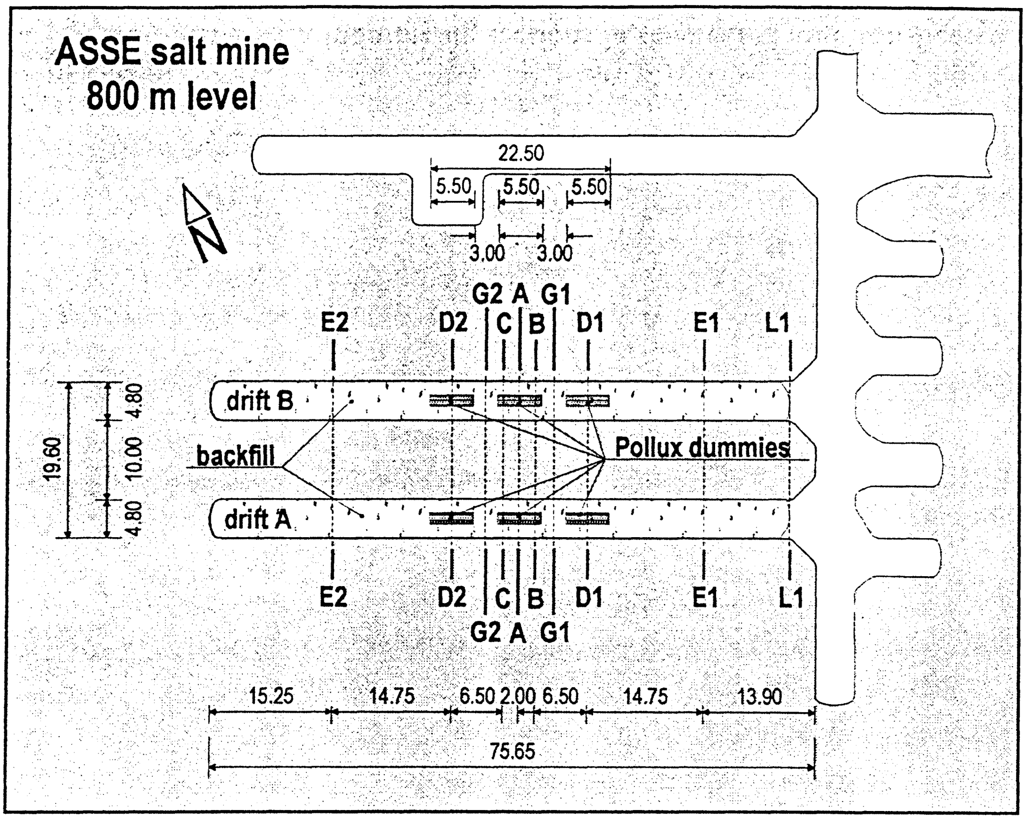

Figure 2. Test drifts with monitoring sections in the heated and non-heated areas.

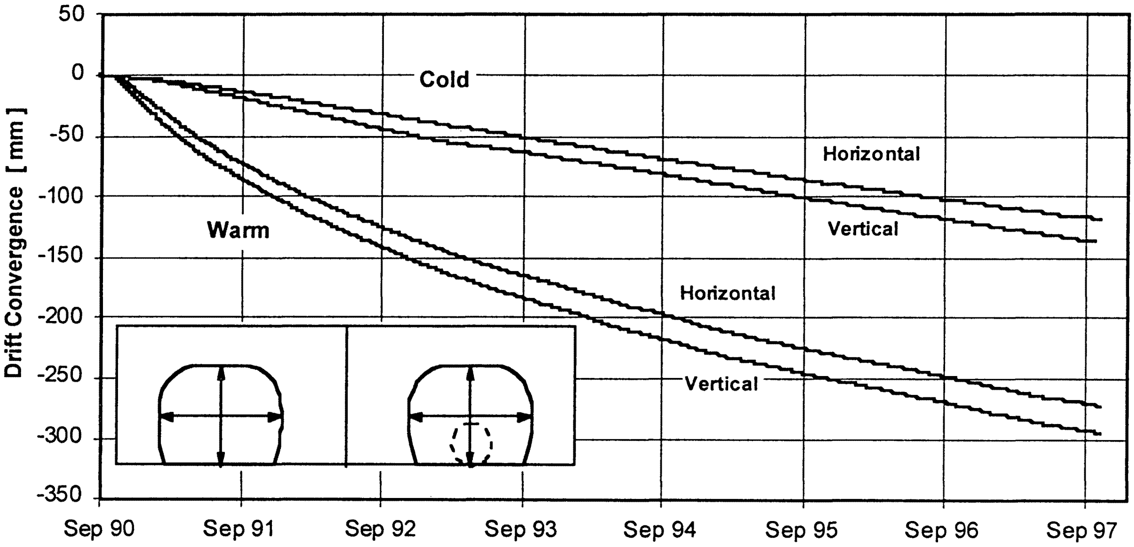

Figure 3. Horizontal and vertical drift closure in the heated and the non-heated areas.

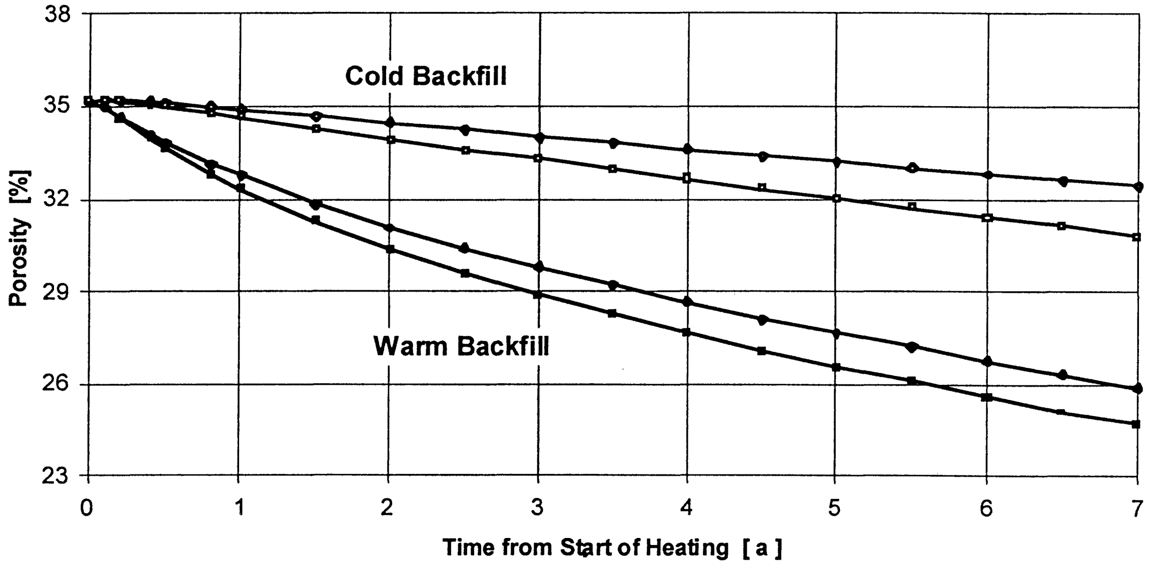

Figure 4. Range of measured backfill porosity in the heated and the non-heated area.

(a)

(b)

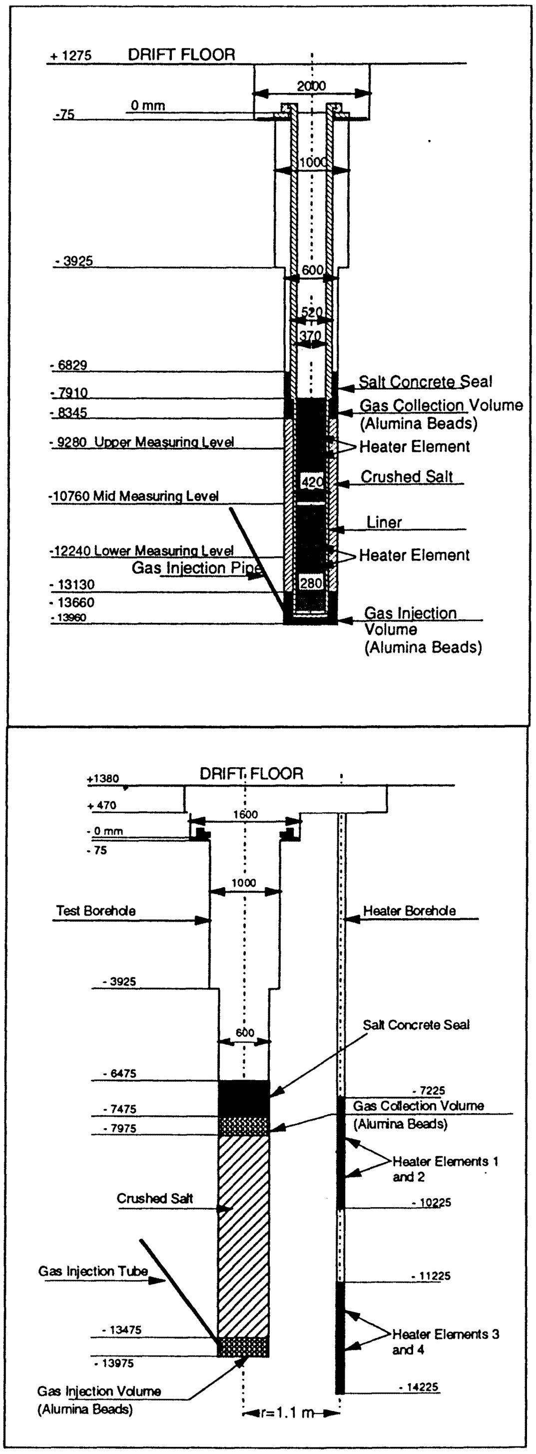

Figure 5. (a) Layout of DEBORA test 1. (b) Layout of DEBORA test 2.

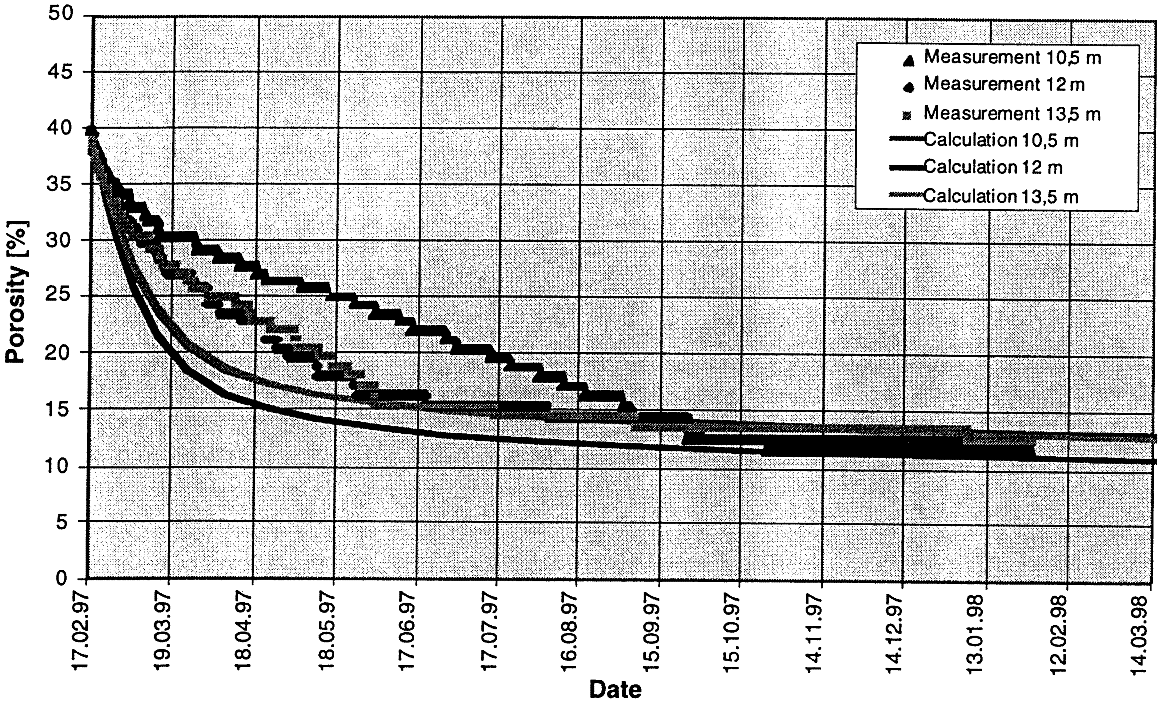

Figure 6. DEBORA 1, predicted and measured decrease of backfill porosity.

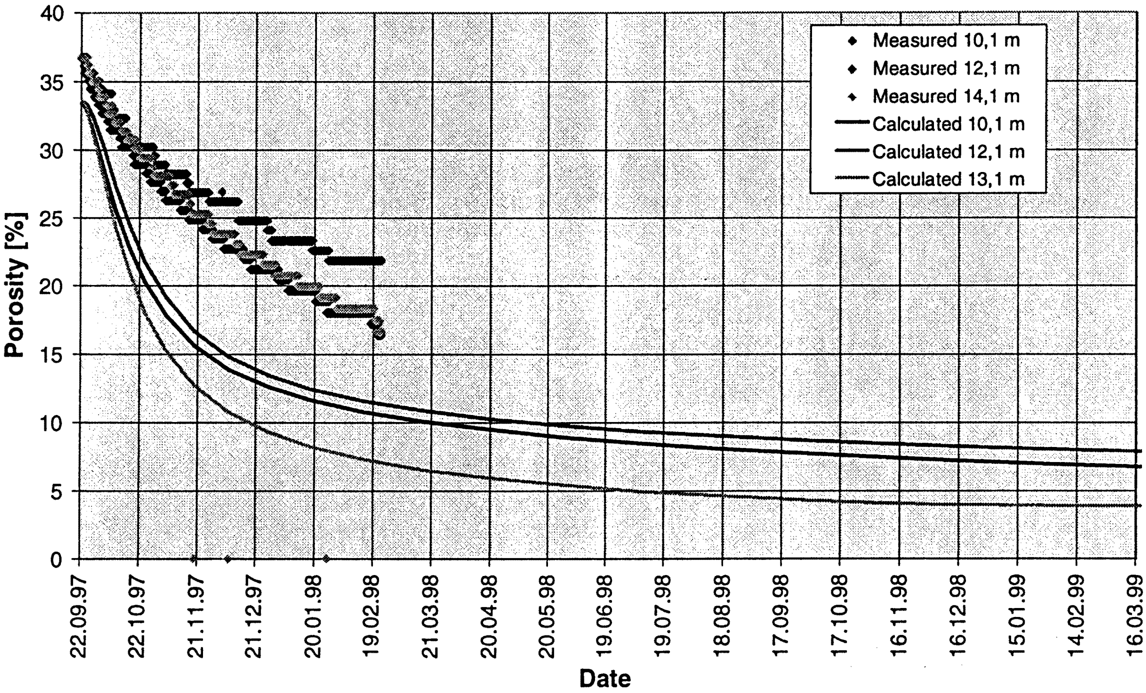

Figure 7. DEBORA 2, predicted and measured decrease of backfill porosity.

OVERVIEW OF R&D ON BACKFILL MATERIALS FOR THE HLW/TRU DISPOSAL CONCEPTS IN JAPAN

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ABSTRACT

In Japan, cement and bentonite are planned as the principal backfill materials for the engineered barrier system in the disposal concept for transuranic (TRU) waste. Bentonite is also planned for use as a backfill material in the high-level waste (HLW) repository. Cement is expected to provide favorable chemical conditions for radionuclide retardation via mechanisms such as sorption, reduction of actinide solubility, and inhibition of microbial activity in the near field over long time periods. However, the degradation of cement will result in a high pH of the near-field groundwater, which will affect the chemical and physical properties of other engineered barriers and/or the surrounding host rock. Bentonite is expected to play a physical role by ensuring diffusive solute transport and colloid filtration and it will play a chemical role by providing favorable conditions for sorption of many radionuclides. Bentonite is also expected to have a sealing effect in both the HLW and TRU waste systems and a buffering effect for overpack swelling caused by corrosion in the HLW disposal system.

This report focuses on the current status of studies concerning the role of these backfill materials in the performance assessment of the HLW/TRU waste disposal systems. The development of hydrotalcite and low-pH cement as backfill materials that are expected to increase the reliability of performance assessment results is also discussed.

1. THE WASTE MANAGEMENT PROGRAM IN JAPAN

As outlined in the overall high-level waste (HLW) management program defined by the Atomic Energy Commission (AEC) of Japan (AEC 1994), in Japan the HLW separated from spent nuclear fuel during reprocessing will be immobilized in a glass matrix and held in interim storage for a period of 30 to 50 years to allow cooling. It then will be disposed of in a repository constructed in a deep geologic formation (geologic disposal). An organization with responsibility for implementing HLW disposal will be established around the year 2000. The HLW disposal program is currently in the research and development (R&D) phase, and the Power Reactor and Nuclear Fuel Development Corporation (PNC) has been designated as the lead organization with responsibility for R&D activities (Masuda *et al.* 1998). The aim of the R&D program is to provide a scientific and technical basis for the safe disposal of HLW, but also to achieve a higher level of understanding of the concept of geologic disposal among scientists, decision makers, and the general public. As a major milestone in this program, PNC submitted a first progress report, referred to as H3, in September 1992 (PNC, 1992). H3 summarized the results of R&D activities up to March 1992 and identified priority issues for further study. The second progress report, scheduled to be submitted around the year 2000, should demonstrate more rigorously and transparently the feasibility of the geologic disposal concept. It also should provide input for the siting and regulatory procedures, which will be initiated after the year 2000. A fundamental disposal concept, applicable in a range of different geologic settings, is now being developed to maximize flexibility in the subsequent site selection phase. At present, neither a geologic formation nor a site has been selected, and no regulatory criteria have been formulated. The regulatory framework will be established in parallel with implementation, taking into account the results of R&D activities.

With regard to the transuranic (TRU) waste generated by domestic reprocessing plants, the plutonium mixed-oxide fuel fabrication plant, and overseas reprocessing plants, PNC and the utility companies have a joint responsibility to demonstrate the feasibility of safe disposal of this waste and to produce a first progress report by the end of the 1990s. This report will be based on the overall program defined by the AEC of Japan in 1994. TRU waste is defined on the basis of the criteria presented in the AEC report (total alpha activity >1 GBq/tonne). The safety of TRU waste disposal is ensured by a multibarrier system that combines engineered and natural components, similar to that being considered for HLW disposal. In collaboration with the utility companies, PNC has been pursuing its own efforts with regard to TRU performance assessment and database construction, based on the knowledge accumulated in the R&D program on HLW management.

2. WASTE DISPOSAL CONCEPTS AND THE ROLE OF BACKFILL MATERIALS

2.1 HLW

The reference engineered barrier system for HLW consists of (1) vitrified waste encapsulated in a stainless steel canister, (2) a metal container termed the 'overpack', and (3) a bentonite buffer (Figure 1). Design studies have considered two emplacement methods: horizontal emplacement in a drift and vertical emplacement in a pit.

For the next progress report, scheduled for the year 2000, further detailed consideration of these concepts is ongoing, taking into account aspects of fabrication, construction, and operation based on reasonable cost estimates. Use of concrete as a tunnel liner, providing mechanical support particularly in sedimentary rock, could be an option. Therefore, evaluation of the effects of cementitious materials on the engineered barrier system components is a key research issue.

2.2 TRU waste

When establishing the preliminary disposal concept for TRU waste, wastes have been grouped to optimize the configuration of the engineered barrier system and limit any mutual influence among the waste groups. Engineered barriers for each waste group have been designed, and relevant backfill materials were selected from the standpoint of current feasibility.

Based on the results of joint preliminary studies, waste has been categorized into four groups in terms of radionuclide inventory and the chemical form of the waste. The first group of wastes contains high concentrations of ^{129}I. The second group contains significant quantities of TRU nuclides, fission products, and/or activation products. Spent fuel cladding (known as 'hulls') is also a major component of this group. The third group contains organic materials such as bituminized and combustible wastes. The fourth group includes other miscellaneous wastes with relatively low contamination. The first and second groups will be surrounded by a combination of cementitious material (ordinary Portland cement) and Na-bentonite, while the third and fourth will be surrounded mainly by cementitious materials without bentonite.

In the preliminary stages, the planned disposal technology has been investigated from the standpoint of construction, operation, and long-term stability of the system. A performance assessment has also been conducted, taking into consideration the various features, events, and processes potentially occurring in the disposal system. The system design and the backfill material used in the engineered barrier system will be reviewed and, if necessary, modified at a later stage (Figure 2).

2.3 Role of backfill materials and key research issues

Because large amounts of cementitious materials are planned for use in the TRU waste disposal system, most of the associated research on backfill materials in the system focuses on the influences of alkaline conditions in the cement porewater as a function of degradation of the cementitious matrix. Bentonite is also planned as a principal backfill material for both the TRU waste and HLW systems, and its alteration processes are major issues to be considered in performance assessment.

Cementitious materials are expected to function as a chemical barrier with radionuclide sorption properties. In addition, the highly alkaline environment created by the cementitious materials has the potential to reduce the solubility of some radionuclides (e.g., actinides) and to restrict microbial activity in the near field over long time periods. The physical function of the cementitious barrier has not been considered in the preliminary performance assessment of TRU waste disposal. Major issues to be investigated for cementitious materials can be summarized as follows: (1) the chemical evolution of cement in contact with groundwater, (2) the construction of a sorption database taking into account cement degradation, (3) the influence of degraded materials from the waste matrix such as sodium nitrate and organic substances, (4) the reduction of microbial activity under alkaline conditions observed in cement porewater, and (5) the influence of the high-pH plume in the geosphere.

In terms of its physical role, bentonite is expected to limit solute transport to diffusiion in the engineered barrier system and to act as a filter for colloids and microbes in the long term. From a mechanical standpoint, the ability of bentonite to seal voids created by dissolution of the waste and degradation of structural materials is expected to apply in the TRU waste system. Mechanical buffering of swelling overpack corrosion products and mechanical support of the overpack are assumed in the HLW disposal concept. Bentonite is also expected to function as a chemical barrier providing radionuclide sorption. Bentonite contributes to ensuring reducing conditions because of pyrite, which is present as an accessory mineral. In the HLW disposal concept, chemical buffering resulting from calcite equilibrium, ion exchange, and protonation/ deprotonation reactions is also expected (Wieland *et al.* 1994). Major issues for bentonite research can be summarized as follows: (1) alteration behavior with and without alkaline solution, (2) database development for radionuclide sorption/diffusion, (3) filtration effects for colloids and microbes, (4) gas permeability, and (5) mechanical properties.

3. DEVELOPMENT OF THE SCIENTIFIC BASIS FOR KEY R&D ISSUES

3.1 Cement

3.1.1 Chemical evolution of cementitious material

Cement is expected to provide favorable chemical conditions over a long time period by maintaining an alkaline environment that ensures low solubility of radionuclides such as the actinides. However, for the near-field performance assessment, these positive functions should be investigated in the light of cement degradation by groundwater. Various experiments and modelling studies with cement have therefore been conducted to obtain an understanding of the following processes as a function of time (Mihara *et al.* 1997): (1) chemical evolution of cement porewater parameters such as pH, which influences the solubilities and K_d values of radionuclides; (2) precipitation and dissolution behavior of cement minerals, particularly those which may act as sorption sites for radionuclides (Shiotsuki and Pfingsten 1998). During cement degradation, both (1) and (2) are recognized as being closely linked.

Coupled codes for chemistry and transport, with an associated thermodynamic database for cement minerals such as Ca-Si hydrate (CSH), have also been developed and applied to explain the experimental results (Pfingsten and Shiotsuki 1998).

3.1.2 Solubility and sorption databases

For performance assessment of TRU waste disposal, radionuclide solubility and sorption databases need to be developed for highly alkaline conditions. Thermodynamic data to define solubilities have previously been compiled by Ewart *et al.* (1988) and Thomason and Williams (1992). Additionally, PNC has been investigating the influence of organic degradation products such as isosaccharinic acid (ISA), degraded asphalt material, and cement additives on the solubilities of actinides and technetium (Greenfield *et al.* 1997a, 1997b).

A sorption database for cementitious materials is currently being developed by Nagra/PSI (Switzerland), taking into account mineralogical alteration processes during cement degradation (Bradbury and Sarott 1993, Bradbury and Van Loon 1998). However, recent experimental results for ^{129}I sorption indicate non-linear behavior for the estimated range of iodine concentrations in cement backfill at a pH around 12.5 (Figure 3) (Mine *et al.* 1997).

Alteration of cement minerals by sodium nitrate, which is found in high concentrations in some reprocessing wastes in groups 1 and 3, is also being studied. Replacement of SO_4^{2-} by NO_3^- in monosulfate has been observed by x-ray diffraction (XRD). This alteration might decrease the K_d of anions, since monosulfate is known as the dominant accessory mineral in cement responsible for anion sorption (Atkins and Glasser 1992). Additionally, the influence of ISA, degraded asphalt material, and cement additives on radionuclide K_d has been considered (regarding results of the solubility experiments). The organic compounds that increase solubility are assumed as non-sorbing species following the assumption in Bradbury and Sarott (1993).

3.1.3 Reduction of microbial activity under alkaline conditions

In order to reduce uncertainties for performance assessment regarding the role of microbial activity in the deep underground environment, microbial activity has been investigated experimentally as a function of solution pH and Eh. Activity was seen to cease under conditions with pH greater than 12 and Eh less than -200mV. Such conditions are expected to prevail over long time periods in an engineered barrier system with large amounts of cementitious material (Fukunaga *et al.* 1993, Aoki *et al.* 1997).

3.1.4 High-pH plume in the geosphere

For the geosphere, the interaction of high-pH cement porewater (high-pH plume) with the host rock must be taken into account. Mineralogical alteration of rock by cement porewater has been investigated experimentally, and tobermorite, a CSH phase, has been observed as a secondary mineral in the altered rock.

An analytical approach using a coupled chemistry and transport code has also been initiated. Preliminary one-dimensional analyses with simplified mineralogy indicate formation of a secondary CSH phase. A thermodynamic database for CSH phase and zeolite, which are expected as secondary minerals, has been developed in parallel. The effects of the high-pH plume on bentonite should also be considered in the case of the combined backfill system of bentonite and cementitious materials (see below).

3.2 Bentonite

3.2.1 Mechanical properties

The physical functions of bentonite are important for maintaining the long-term stability of the engineered barrier system. Consolidation and shear properties were measured experimentally (Namikawa *et al.* 1997a, 1997b). The mechanical stability of compacted bentonite in the case of swelling overpack corrosion products and possible overpack sinking was analyzed using the Cam-clay model with measured properties. This model is a typical constitutive equation for increased strain of clay materials based on elasto-plastic theory (Schofield and Wroth 1968). This analysis has been used in the design study for the engineered barrier system (see Figure 1).

3.2.2 Alteration behavior and influence on other parameters

Na-bentonite (Table 1) is assumed as the reference buffer material for both the HLW and TRU waste disposal systems, and its mineralogical properties have been characterized (Ito *et al.* 1994). However, ion-exchange from Na- to Ca-bentonite is expected to occur at a relatively early stage after closure of the disposal facility, when there are massive amounts of cementitious materials in the repository. The key properties of bentonite are therefore measured experimentally not only for Na-bentonite but also for Ca-exchanged bentonite.

Physical and mechanical properties such as swelling pressure, hydraulic conductivity, unconfined compressive strength, and elastic modulus were measured experimentally. These properties are not significantly changed by Ca exchange if the Na-bentonite is highly compacted and its dry density is greater than 1.6 g/cm^3 (Maeda *et al.* 1998). Effective diffusion coefficients in compacted Ca-exchanged bentonite, measured by tritiated water, were similar to those of Na-bentonite, indicating that both bentonites have similar mass transport properties (Mihara *et al.* 1995).

Further mineralogical alteration of bentonite, potentially occurring in the long term, is a matter for concern. Bentonite alteration in contact with high-pH cement porewater has been investigated in wetting experiments with alkaline water (pH=12.5 and 14.0) at elevated temperatures (up to 200°C), in order to accelerate the alteration. The zeolite mineral analcime was identified (Figure 4). Kinetic data for smectite dissolution under a range of alkaline conditions were then obtained in batch experiments. An analcime dissolution experiment is ongoing and will be used to develop a kinetic model for smectite to analcime alteration. A natural analogue study of bentonite/cement interactions is also planned; it will be conducted in a 30-year-old tunnel that passes through a natural bentonite formation with the same mineralogy as our reference commercial bentonite, Kunigel-V1® (see Table1).

In the HLW disposal concept, the interaction between bentonite and the overpack material, including its corrosion products, is also an issue of interest. Analogue studies of steel supports in a bentonite mine indicate that Fe ions diffuse into the bentonite and that some ion-exchange sites of the smectite are then occupied by Fe ions (Mitsui *et al.* 1996). A hydrothermal experiment with bentonite and magnetite is also ongoing.

3.2.3 Sorption and diffusion database development

Sorption and diffusion databases for bentonite are being developed for the performance assessment of HLW and TRU waste disposal. An extensive literature survey and data compilation program were conducted, and sorption experiments were performed to accommodate insufficiencies in the databases, particularly for redox-sensitive elements under reducing conditions (Baston *et al.* 1997). Databases for alkaline conditions and Ca-bentonite will also be developed, taking into account the effects of high-pH cement porewater.

3.2.4 Filtration effect

The bentonite backfill is expected to act as a filter for colloids. Colloid transport experiments have been conducted using a gold colloid with a particle size diameter around 15 nm (Kurosawa *et al.* 1997). In the experiments, the filtration effect of bentonite was investigated for different ratios of sand in the bentonite/sand mixture. The colloid was filtered completely by compacted bentonite with less than 30% sand and a dry density greater than 1.0g/cm^3 (Figure 5).

Filtration of microbes has also been examined as a function of the proportion of sand in Na-bentonite buffer materials. To ensure a filtration effect, less than 50% sand and a Na-bentonite dry density of at least 1.2g/cm^3 are required, based on preliminary experimental results.

3.2.5 Gas permeability

The gas permeability of bentonite is an important issue for both HLW and TRU waste disposal. In HLW disposal, accumulation of hydrogen gas at the inner boundary of bentonite could be caused by overpack corrosion. However, this depends on the balance between the rate of corrosion and the diffusion of dissolved hydrogen. In the TRU waste system, the total amount of gas accumulation is expected to be greater than that in the HLW system because of the large amount of metallic materials present in the waste matrices and construction materials in the engineered barrier system.

Experiments have been conductred on hydrogen gas permeability to measure breakthrough pressure, which was determined to be more or less equivalent to the swelling pressure of the compacted bentonite. Pathways created by gas breakthrough are thus expected to recover (Tanai *et al.* 1997).

4. FURTHER DEVELOPMENT OF BACKFILL MATERIALS

With regard to the bentonite buffer, both bentonite and a bentonite/sand mixture have been considered for technical and economic reasons. The proportion of sand in the mixture has been optimized at around 30% for the current reference engineered barrier system design for the HLW disposal system (Figure 1).

From the results of a preliminary safety assessment of the TRU waste disposal system, anionic ^{129}I and ^{14}C are determined to be the most significant radionuclides (Mihara *et al.* 1998). Investigations of new materials, which have the potential to confine anionic radionuclides, to develop a more robust engineered barrier system have been initiated. Hydrotalcite (magnesium-aluminium-hydrate) is one of the candidate materials that incorporates anionic elements into its mineral structure and is expected to be stable under high-pH conditions.

Most R&D issues for the TRU waste disposal system are identified as being related to the high-pH environment created by cementitious materials. The applicability of several low-pH cements has thus been investigated to increase the reliability of the TRU waste performance assessment. Cementitious materials with a range of compositions are now being evaluated from the standpoint of chemical and mechanical properties.

5. CONCLUSIONS

PNC will complete the first progress report for TRU waste disposal, demonstrating the feasibility of safe disposal, by the end of the 1990s. For geologic disposal of HLW, a second progress report will be available about the year 2000. Various chemical and physical functions of backfill materials have been evaluated from the standpoint of performance assessment for HLW and TRU waste disposal. The chemical barrier function of cementitious materials and the influence of high-pH cement porewater on engineered barrier performance have been evaluated both experimentally and analytically. The physical and chemical roles of the bentonite have also been evaluated with regard to interactions with cementitious materials. Of key importance for these backfill materials is the acquisition of more reliable data and the development of more refined models, leading to development of a robust EBS concept that is applicable over a wide range of scenarios. PNC is conducting a comprehensive R&D program to examine these issues.

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Table 1. Mineralogical composition of reference Na-bentonite (Kunigel-V1)®.

Mineral Phase	(wt.%)
smectite	46 ~ 49
quartz	0.5 ~ 0.7
chalcedony	37 ~ 38
plagioclase	2.7 ~ 5.5
calcite	2.1 ~ 2.6
dolomite	2.0 ~ 2.8
analcime	3.0 ~ 3.5
pyrite	0.5 ~0.7

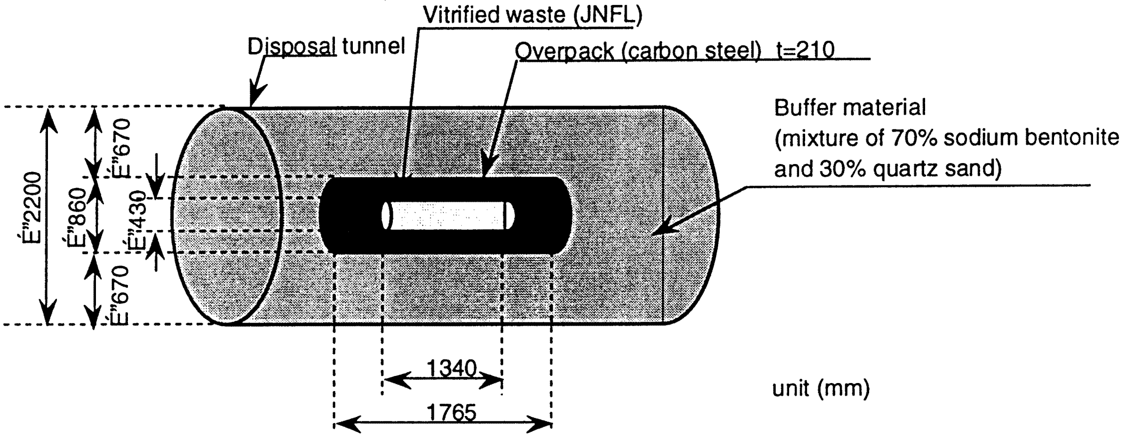


Figure 1. Current reference design for the engineered barrier system for HLW (crystalline rock case) after Iwasa *et al.* 1998.

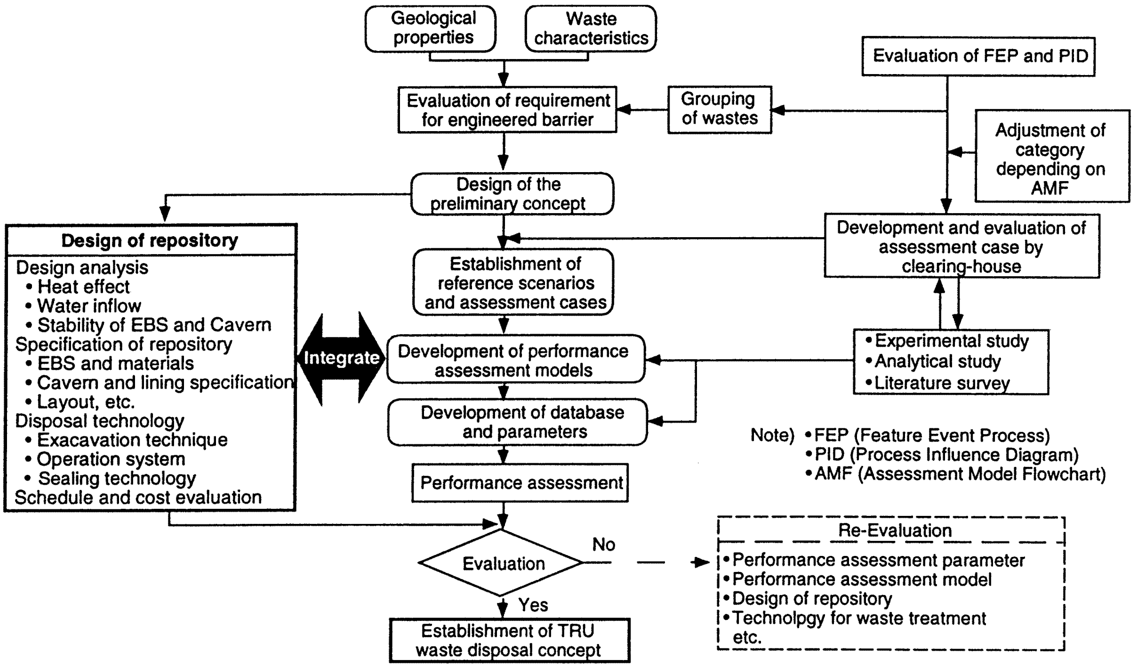


Figure 2. Approach to establishing the TRU waste disposal concept.

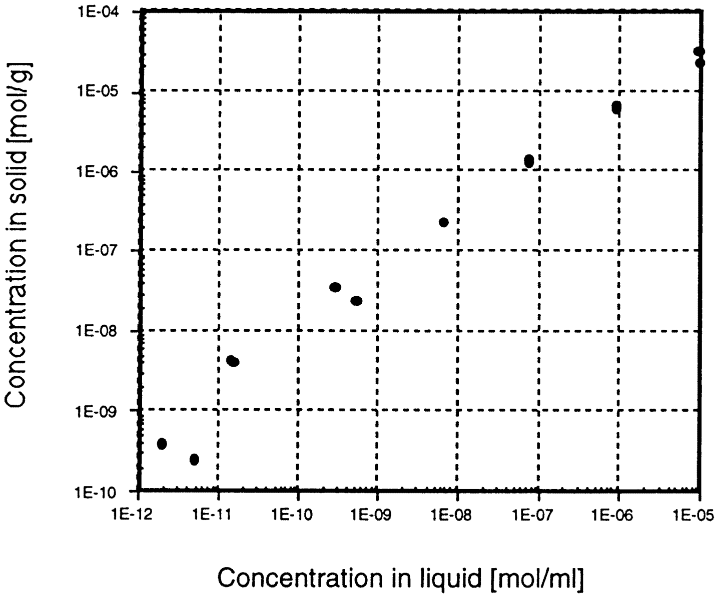


Figure 3. Sorption behaviour of iodine on cement, which shows the non linear sorption (Liquid/Solid Ratio: 50ml/g; Exp. Period: 30 days; pH: about 12.5; Temperature: ambient).

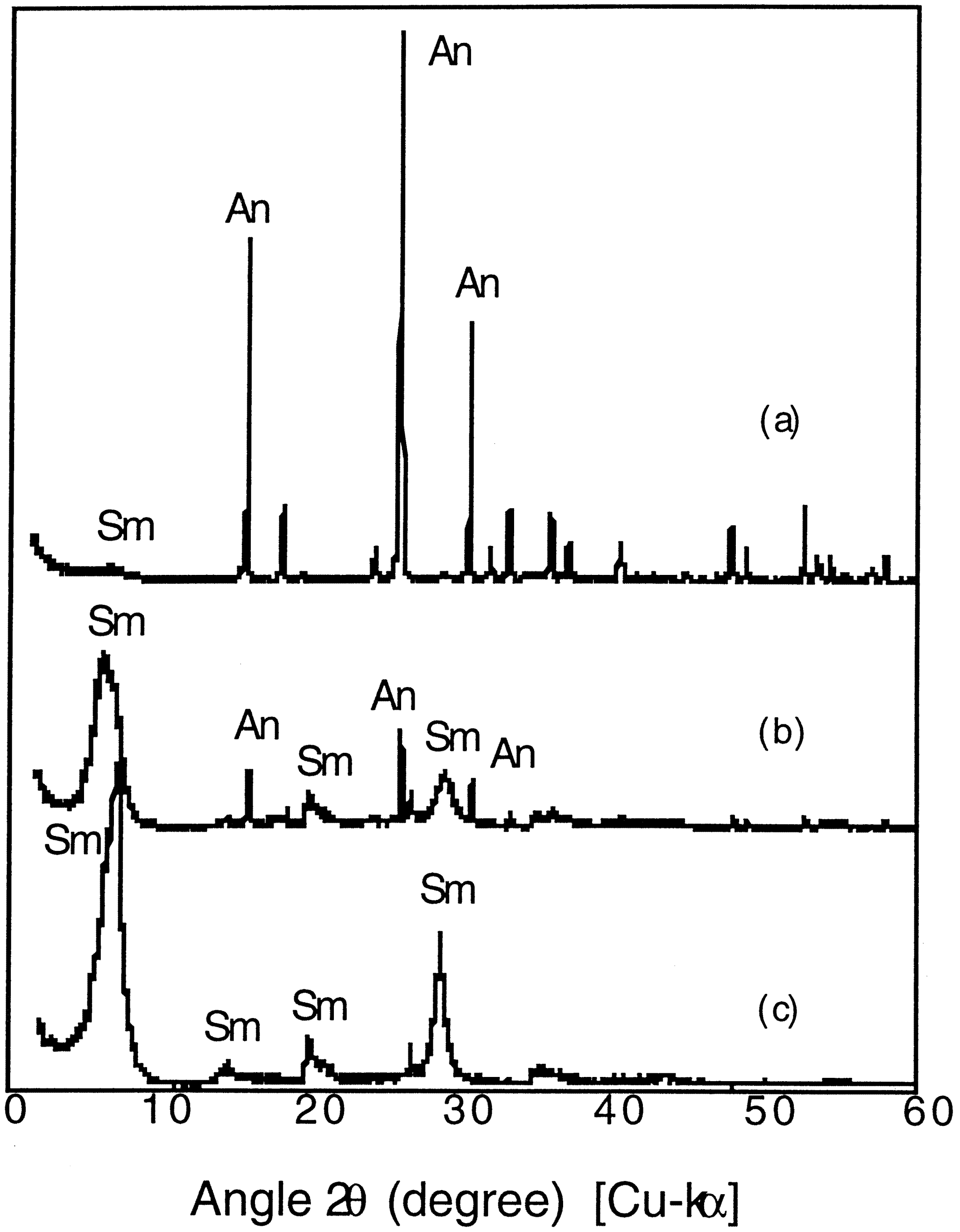
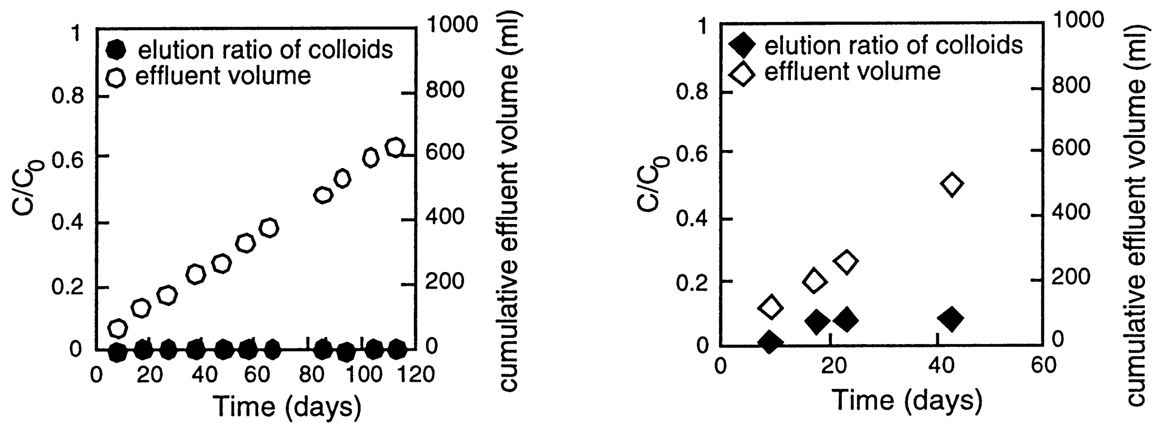


Figure 4. XRD patterns of the alteration products. Purified bentonite was treated with alkaline solution at 200°C, for 24 weeks. Liquid/solid = 10ml/g. (a) $Ca(OH)_2$ + NaOH + KOH (pH=14.0), (b) Saturated $Ca(OH)_2$ (pH=12.5), (c) Starting material (purified commercial bentonite, Kunipia-F®), Sm : smectite, An : analcime.



(a) with 30wt.% sand

(b) with 50wt.% sand

Figure 5. Colloid filtration by compacted bentonite/sand mixture (dry density 1.0g/cm^3), C = Eluted colloid concentration, C$_0$ = Injected colloid concentration (Kurosawa *et al.* 1997).

DEVELOPMENT STATUS OF BACKFILL MATERIALS FOR RADWASTE DISPOSAL IN KOREA

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ABSTRACT

In Korea, generic disposal concepts of both vault type and rock cavern type for low-level waste (LLW) and intermediate-level waste (ILW) disposal are being reviewed, and a generic non-site-specific deep repository concept for high-level waste (HLW) is being developed. To support these concepts, the research work on backfills has been performed to develop suitable domestic backfill materials. The hydraulic conductivity and the diffusion coefficient of radionuclides in Ca-bentonite were analyzed, and the effects of calcium depletion, sulphate penetration, and carbonate penetration on concrete degradation were investigated.

The relationship between the dry density and the bentonite content of the mixture that meets a diffusional barrier condition has been derived. The effect of temperatures up to 80°C on the hydraulic conductivity could be low enough to inhibit radionuclide release by advection through backfill.

The results from diffusion experiments indicate that the pathways available to ^{125}I diffusion will largely decrease with increasing dry density of the mixture, suggesting that surface diffusion is an important mechanism for the diffusion of nuclides in bentonite and/or a mixture of bentonite and crushed rock with high dry density.

To evaluate the long-term performance of the backfill material, a simple experiment under repository conditions at 80°C has been conducted. Planned tests will investigate the characteristics of some potential materials to find one suitable for retaining or retarding long-lived anions within the repository.

1. INTRODUCTION

In Korea, twelve nuclear power plants (ten pressurised water reactors (PWRs) and two CANDUs (Canada Deuterium Uranium) are in operation with a generating capacity of 10.3GWe. Six plants (four PWRs and two CANDUs) are under construction. According to the long-term nuclear power generation plan announced in 1995 by the Ministry of Trade, Industry and Energy Resources, a total of 27 nuclear power plants will be in operation by the year 2010. Total generating capacity is expected to be about 26.3GWe by 2010. By the end of 1996, 48,032 drums of LLW/ILW and 2,803 MTU of spent nuclear fuel had been accumulated; these volumes are stored in on-site storage facilities at each plant site. By the time these plants cease operation, the cumulative amount of low- and intermediate-level radioactive wastes (L/ILW) and spent nuclear fuel will reach about 211,000 drums and 29,000 MTU, respectively.

Geologic disposal concepts for these wastes are being studied. The performance of these systems is mainly based on the multibarrier concept, consisting of both natural and engineered barriers such as the waste form itself, the container, the backfill material, and the seals. Clay materials are well known for their low hydraulic conductivity, swelling, and retention properties. These characteristics make them suitable not only as host formations but also as backfill materials.

The applicability and characteristics of domestic bentonite as a base backfill material have been investigated, and an effort to find suitable additives for retention of long-lived anions is being planned.

2. CONCEPTUAL DESIGN STUDIES

2.1 Low- and intermediate-level radioactive waste

Two repository concepts (rock cavern type and vault type) for L/ILW disposal have been studied to widen the choice for siting, which is in progress (Kang *et al.* 1998). Presently, these concepts are being comprehensively reviewed by the Korea Electric Power Corporation.

The layout of the rock cavern disposal facility is shown in Figure 1. The caverns are divided into one ILW area and four LLW areas for the first construction phase. The LLW type I cavern is for disposal of spent resin, spent filters, and conditioned wastes of concentrates. Two of the LLW type II caverns are for dry active wastes. The LLW type III cavern is for dry active wastes and conditioned wastes of concentrates. The ILW cavern is essentially a large concrete vault into which remotely handled wastes will be loaded. The cavern will then be backfilled with a mixture of clay and crushed rock, or perhaps not filled.

Figure 2 shows the preliminary layout of the vault type disposal facility. There are two types of disposal vaults, depending on the durability of waste package. One is a backfilled vault where waste packages with long durability, such as concrete containers, are disposed; this vault is then backfilled with gravel. The second is a grouted vault where waste packages with short durability, such as 200 L steel drums, are disposed. The vault is then grouted with concrete.

Under the above disposal concepts, an applicable backfill concept should be adopted through comparison of the predicted dose with the performance objectives.

2.2 High-level radioactive waste

A generic disposal concept is being developed (Chun *et al.* 1997) under the assumption that an underground repository would be located in a type of crystalline rock in Korea and an appropriate multibarrier system would be provided to isolate the HLW from the biosphere.

3. RATIONALE FOR THE USE OF BACKFILL

The backfill material is a major component of the engineered barrier and has two important functions from the standpoint of radionuclide release: (1) to minimize contact between the waste container and the host environment and (2) to restrict the release of radionuclides into the host environment in the event of waste container failure.

Performance objectives applicable to L/ILW disposal in the post-closure period are defined in the MOST Notice No. 96-11 in terms of radiological risk to any individual in a critical group for L/ILW. The notice states that the predicted radiological risk shall not exceed 10^{-6} per year or its dose equivalent 0.02 mSv/yr.

The research work on backfills is aimed at developing suitable domestic backfill materials, studying their performance under repository conditions, and producing design data for an engineered barrier system.

4. RESEARCH STATUS ON BACKFILL MATERIAL

4.1 Basic properties of a domestic bentonite

Domestic bentonite collected from the southeastern area of Korea was identified as Ca-bentonite by analyzing x-ray diffraction (XRD) data and chemical composition data (Lee *et al.* 1998). The material contains mainly montmorillonite (64.7%) and smaller amounts of feldspar (34.3%) and quartz (1.0%). The chemical composition is as follows: approximately 57.4% SiO_2, 21.3% Al_2O_3, 6.4% Fe_2O_3, 2.4% CaO, 2.3% MgO, 3.0% Na_2O, and some minor elements. Its cation exchange capacity was about 50 meq/100g, and its free swell index was approximately 8.9 ml/g.

To investigate thermal effects on the functional properties of domestic bentonite, its TG/DCS curves, swelling rates, and distribution coefficients of radionuclides were studied (Choi *et al.* 1991). In the XRD patterns, (001) peak disappeared at above 200°C. The loss of swelling capacity and cation exchange capacity (CE.C) began at 100°C. The distribution coefficients of ^{241}Am, ^{60}Co, and ^{137}Cs on the bentonite showed a negligible variability as the temperature was raised; that of ^{85}Sr decreased at about 150°C.

4.2 Hydraulic conductivity of a clay/crushed rock mixture

Figure 3 is a plot of log[K(A/A')] as a function of the effective clay dry density, where A is the cross-sectional area for flow in the pure clay and A' is the cross-sectional area available for flow in the clay and crushed rock mixture (Cho *et al.* 1996). When the bentonite content was above 20 wt.%, log[K(A/A')] decreased linearly with an increase in the effective clay dry density. This indicates that, when the effective clay dry density of the mixture was similar to the dry density of pure bentonite, the hydraulic conductivity was close to that of the pure bentonite. However, the relationship may not be applicable at a very low bentonite content (less than 15 wt.%) because the bentonite is not sufficiently abundant to occupy the entire space between the crushed rock particles. The relationship between the dry density and the bentonite content of the mixture that meets a diffusional barrier condition (i.e., hydraulic conductivity $<1\times10^{-10}$ m/sec) has been derived. The results suggest that the dry density and the bentonite content increase as much as possible to have lower hydraulic conductivity than the diffusional barrier condition. However, when the mixture is applied for the backfill material of a repository, the optimum dry density and bentonite content will be determined together with the mixture's economical and engineering aspects.

4.3 Influence of temperature on hydraulic conductivity

One of the well-known classical theories for correlating the hydraulic conductivity and permeability to properties of the medium and fluid is the Kozeny-Carman Equation (Equation 5 in Carman 1939). In this equation, the permeability is proportional to $n^3/(1-n)^2$ where n is porosity. The relationship between permeability (k) and hydraulic conductivity (K) is $K=k(vp/u)$ where u is dynamic viscosity, and vp is density of fluid. After heating, the hydraulic conductivity (K') can be expressed as $K'=k'(vp'/u')$ (Cho *et al.* 1998).

The hydraulic conductivities in water-saturated bentonites at different dry densities were measured within a temperature range of 20 to 80°C. The results show that the hydraulic conductivities increase with increasing temperatures. The hydraulic conductivities of bentonites at a temperature of 80°C increase up to about 3 times as high as those at 20°C but not up to one order of magnitude. The measured values are in good agreement with those predicted. As shown in Figure 4, the permeability is nearly constant within a temperature range of 20 to 80°C, and the change in porosity of compacted bentonite is not important under the experimental conditions. Of the three factors (k, vp, u), the change in viscosity is the most sensitive to an increase in temperature, and it contributes greatly to the increase of hydraulic conductivity with increasing temperatures. The experimental results also indicate that the effect of temperature elevation up to 80°C on the hydraulic conductivity is still low enough to inhibit radionuclide release by advection through the buffer.

4.4 Diffusion of ^{125}I and ^{90}Sr in a Mixture of Bentonite and Crushed Rock

The effective diffusion coefficients of ^{125}I in a compacted mixture of 30% bentonite and 70% crushed rock were 4.9×10^{-11} m^2/sec and 4.0×10^{-12} m^2/sec when the dry densities were 1400 and 2000 kg/m^3, respectively (Lee *et al.* 1996). They were more sensitive to the dry density than the apparent diffusion coefficients because the change of porosity plus the formation factor with increasing dry density contributes to the effective diffusion coefficients. It was noted that ^{125}I diffused through 48% of the theoretical porosity for the dry density of 1400 kg/m^3 and through only 10% of the theoretical porosity for the dry density of 2000 kg/m^3. This is likely attributable to the ion exclusion of ^{125}I from the surface of solid particles with a negative charge, as reported by Murrinen *et al.* (1989) and Oscarson *et al.* (1992). Therefore, it is believed that the pathway available to ^{125}I diffusion will largely decrease with increasing dry density of the mixture.

Chun *et al.* (1995) showed in their sorption tests that the sorption of ^{90}Sr was mainly attributed to ion exchange reactions. This suggests that the diffusion of ^{90}Sr may include surface diffusion by which ^{90}Sr is allowed to diffuse along the pore surface. In comparison with the relative contribution of pore diffusion and surface diffusion to overall diffusion, the surface diffusion was negligible at a low dry density of 1400 kg/m^3, while it was comparable in significance to the pore diffusion at a high dry density of 2000 kg/m^3. This suggests that surface diffusion plays an important role in the diffusion mechanism of ^{90}Sr in the mixture at high dry density. The diffusion of ^{125}I and ^{90} Sr in a mixture of bentonite and crushed rock was primarily dominated by the bentonite independently of the crushed rock, which could be explained by the concept of effective clay dry density.

4.5 Diffusion of radionuclides in compacted bentonite

The effects of compaction density and heat treatment of bentonite on diffusion were analyzed by Choi *et al.* (1992). The apparent diffusivities of ^{85}Sr, ^{137}Cs, ^{60}Co, and ^{241}Am in the compacted bentonite of 1800 kg/m^3 were measured to be 1.073×10^{-11}, 6.705×10^{-13}, 1.226×10^{-13} and 1.310×10^{-14}, respectively. When the density of bentonite increased from 1800 to 2000 kg/m^3, the apparent diffusivity of ^{137}Cs decreased to one-quarter of that obtained at the lower density. The bentonite heat-treated up to 150°C showed little change in diffusivity. Comparing the pore diffusivity with the surface diffusivity, the surface diffusion occurring due to the concentration gradient of radionuclide sorbed on the solid phase was found to dominate greatly in the total transport process.

4.6 Sorption of TcO_4^- and I^- on calcined layered double hydroxide (LDH)

Anionic species in radioactive waste (e.g., TcO_4^- and I^-) are of serious environmental concern because they are retarded poorly by many geochemical barriers. Inorganic anion exchange materials have also been investigated by several researchers. Hydrotalcite is a rare but naturally occurring mineral that possesses an anion exchange capacity. The composition of hydrotalcite is $Mg_6Al_2(OH)_{16}(CO_3)\cdot4H_2O$, with Mg^{2+} and Al^{3+} ions randomly distributed in octahedral layers. Each layer is positively charged, and anions and water molecules occupy the interlayer sites. These materials are also called layered double hydroxide (LDH).

The sorption of TcO_4^- was found to be a stepwise ion exchange. The dominant reaction for practical applications is the first ion-exchange equilibrium. The exchange of one OH^- of the LDH with the TcO_4^- ion forms $Mg_6Al_2(OH)_{17}(TcO_4)(s)$. At higher TcO_4^- concentrations, the second equilibrium becomes more important. Two TcO_4^- ions sorbed onto LDH and $Mg_6Al_2(OH)_{16}(TcO_4)_2(s)$ are formed successively. The equilibrium constants for the first and second ion-exchange reactions were evaluated by a non-linear least squares fit and found to be K_1 = 1.40 Å 0.1 and K_2 = 0.47 Å 0.2, respectively (Kang *et al.* 1998).

The sorption of I^- onto calcined LDH is caused by ion-exchange involving the whole solid base. The dominant reaction is the first ion-exchange equilibrium, in which one OH^- ion of the LDH hydroxide exchanges with an I^- ion to form $Mg_6Al_2(OH)_{17}(I)(s)$. The equilibrium constants K_1 and K_2 for I^- are 7.40 Å 1.0, and 0.15 Å 0.4, respectively. The K_2 value is too small to evaluate the sorption behavior at higher I^- concentrations. The experimental values and calculated curve for the ratio $[X^-]_{sorbed}/[LDH]_0$ ($X^- = TcO_4^-, I^-$) as a function of $[X^-]_{eq}/[OH^-]_{eq}$ are shown in Figure 5. The I^- is much more sorbed onto the calcined LDH than the TcO_4^-, showing about five times higher equilibrium constants of I^-. This can be explained by the size of the anions. Because the size of I^- is smaller than that of TcO_4^-, the I^- is easy to intercalate in the interlayer of LDH. Evaluation of the equilibrium constants of other anions is required to determine the sorption selectivity of anions on calcined LDH.

For practical applications like the retardation of the migration of TcO_4^- or I^- from radioactive wastes, the influence of competing anions has to be studied. The influence of Cl^-, SO_4^{2-} and HCO_3^- will be investigated in future studies.

4.7 Concrete degradation

The effects of the three mechanisms of calcium depletion, sulphate penetration, and carbonate penetration on concrete degradation have been investigated (Keum *et al.* 1997). The shrinking core model (SCM) and the HYDROGEOCHEM (HGC) model have been applied to evaluate how fast the mechanisms proceed. The SCM is an analytical approximation model whereas the HGC model is a numerical mass transport model coupled with a chemical reaction. The SCM leads to more conservative results than the HGC and turns out to be very useful from the standpoint of simplicity and conservatism. During 300 years, calcium is depleted within 10 cm from the concrete outer surface, and sulphate has penetrated less than 13.5 cm into the concrete. Carbonate has not penetrated even 7 cm into the concrete in contact with the bentonite, and, furthermore, its penetration into the concrete with the groundwater is negligible. To maintain its integrity from degradation by the above mechanisms for at least 300 years (the institutional control period of the L/ILW repository) the thickness of the concrete must be more than 15 cm.

5. ASSESSMENT OF RADIONUCLIDE RELEASE FROM THE ENGINEERED BARRIER

Considering the geometry of the ILW cavern described in the conceptual design studies, the radionuclide release through the concrete structure and backfill can be approximated reasonably as one-dimensional diffusional transport through a composite slab (Cho *et al.* 1996).

$$\begin{aligned} &\partial Ci_1/\partial t = Dai_1\, \partial^2 Ci_1/\partial^2 x - \lambda i\, Ci_1 \quad -l < x < 0 \\ &\partial Ci_2/\partial t = Dai_2\, \partial^2 Ci_2/\partial^2 x - \lambda i\, Ci_2 \quad x > 0 \end{aligned} \tag{1}$$

where Ci is the solution phase concentration of nuclide i, λi is the radioactive decay constant of nuclide i, Dai is an apparent diffusion coefficient of nuclide i, and l is the thickness of the concrete structure. The subscripts 1 and 2 refer to the concrete structure and the backfill in the repository.

The outer boundary condition for backfill is replaced by an infinite medium boundary condition; for the inner boundary condition, it is assumed that the leached radionuclide maintains the equilibrium concentration (Ci_0) determined from the chemical conditions in the repository.

$$\begin{aligned} &\phi_1\, Dpi_1\, \partial Ci_1/\partial x = \phi_2\, Dpi_2\, \partial Ci_2/\partial x \quad x = 0,\ t > 0 \\ &Ci_1 = Ci_2 \quad x = 0,\ t > 0 \\ &Ci_1 = Ci_0 \exp(-\lambda i t) \quad x = -l,\ t > 0 \\ &Ci_2 = 0 \quad x \end{aligned} \tag{2}$$

where Dpi is a pore diffusion coefficient of nuclide i, ϕ is porosity and t is time.

The disposal capacity of the repository was assumed to be 100,000 drums (200 L carbon steel drums). The low- and intermediate-level wastes are composed of 72,100 and 27,900 drums, respectively. The release rates from the engineered barrier were calculated for six principal radionuclides: ^{14}C, ^{63}Ni, ^{90}Sr, ^{99}Tc, ^{129}I, and ^{137}Cs. These are the major radionuclides contained in L/ILW generated from nuclear power plants in Korea (Kim *et al.* 1994). It was assumed that 90% of total inventories are contained in ILW. The equilibrium radionuclide concentrations in the repository were estimated by the simple sorption equilibrium equation: $C_o = I_o / V\,[\phi w + (1-\phi w)\,\rho_s\,Kdc]$, where I_0 is the radionuclide inventory, V is the waste volume, ϕw is the porosity of waste matrix, ρ_s is the real density of the waste matrix, Kdc is the distribution coefficient, and ϕw and ρ_s are taken to be 0.5 and 2700 kg/m^3, respectively. The Kdc (l/kg) values were distribution coefficients of nuclides on cement, conservatively assumed to be 100 for ^{14}C; 0.1 for ^{137}Cs, ^{90}Sr, and ^{99}Tc; 0.3 for ^{129}I; and 50 for ^{63}Ni. The thickness of backfill, thickness of concrete structure, and diffusional surface area are 0.9 m, 0.6 m, and 2200 m^2 for the wall, 1.0 m, 1.0 m and 1610 m^2 for the bottom, and 1.0 m, 0.6 m and 1610 $\overset{2}{\text{m}}$ for the top, respectively. For the aperture between the concrete structure and the slab cover, the thickness of backfill is 0.9 m, and the thickness of the concrete structure and the diffusional surface area were assumed to be 1×10^{-6} m and 1 m^2.

The radionuclide release rates at the backfill edge over time are shown in Figure 6. Immediately after closure of the repository, ^{14}C begins to release, and its release rate reaches the maximum value at an early time because it is strongly sorbed onto concrete but not sorbed on the clay-based backfill. Therefore, ^{14}C is released mainly through the aperture pathway over the whole period. Because ^{63}Ni is strongly sorbed onto both concrete and backfill both contribute to the retardation of releases. Although ^{63}Ni is also released through the aperture, the release rates are lower because of its short half-life. In contrast to ^{14}C, ^{137}Cs is not sorbed onto concrete but is strongly sorbed onto the clay-based backfill, and it has a short half-life. Hence its important release pathways are the bottom and the wall because of the relatively small thickness of clay-based backfill in those locations. Release behaviour of ^{90}Sr is similar to that of ^{137}Cs.

6. PLAN FOR CONFIDENCE BUILDING IN THE BACKFILL CONCEPT

To evaluate the sorption capability of a backfill material, a long-term experiment is being conducted under a representative repository condition. The experiment is designed with the compacted bentonite of dry density 1400 kg/m^3, which is contacted with simulated borosilicate glass specimens in synthetic granitic groundwater at 80°C. For an analysis of its illitization, international collaboration could be useful for obtaining related data, e.g., the International Atomic Energy Agency's Commission for Radiological Protection programme 'Extrapolation of Short-Term Observations to Time Periods for Isolation of Long-Lived Radioactive Waste', in which KAERI has participated since July 1996.

Experiments are planned to investigate the characteristics of some potential materials to find one suitable for retaining and/or retarding long-lived anions within repository conditions, and some experiments are under way.

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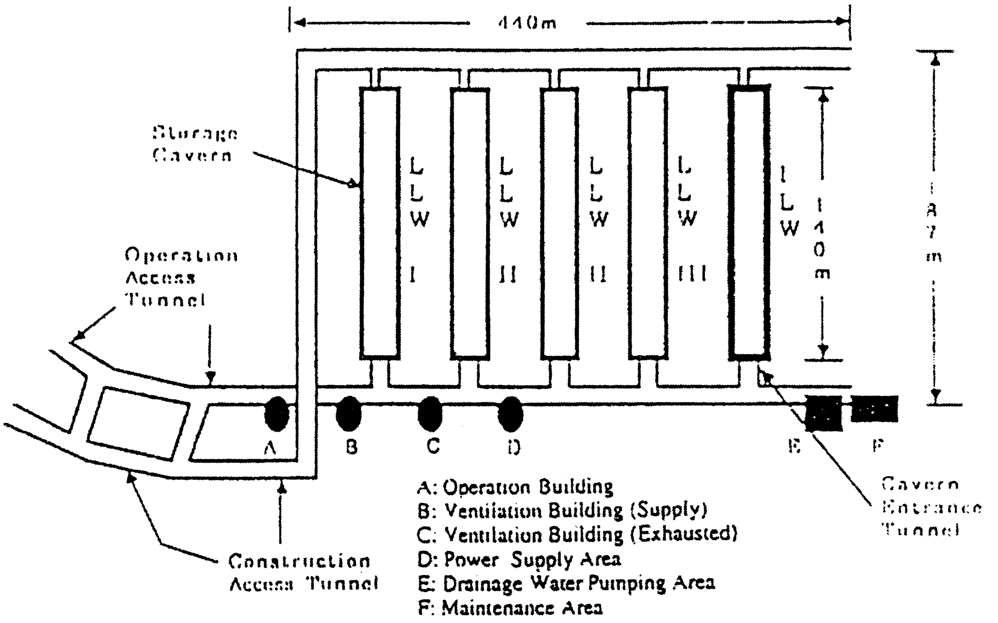


Figure 1. Layout of rock cavern disposal facility.

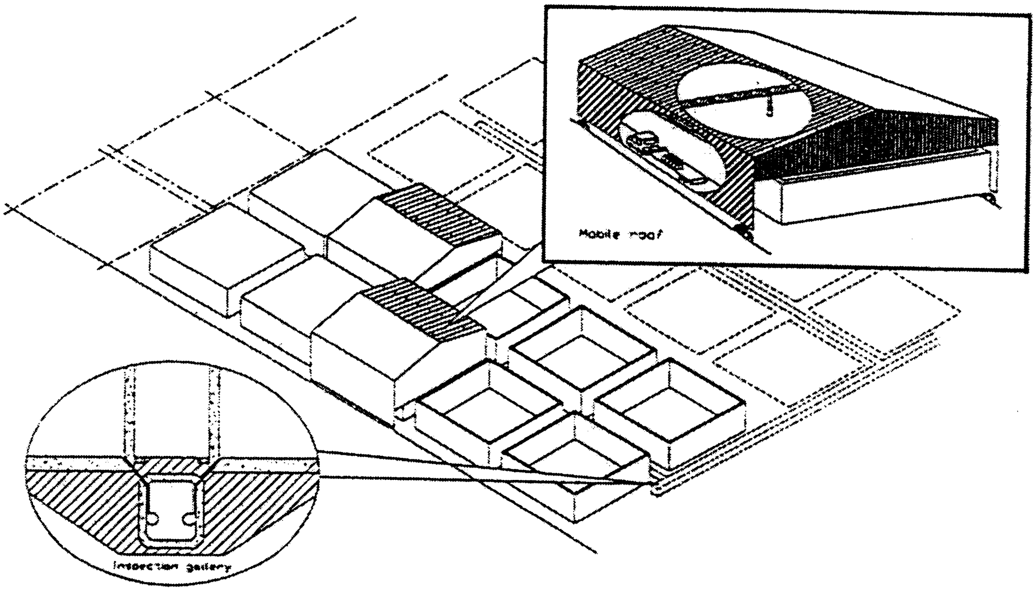
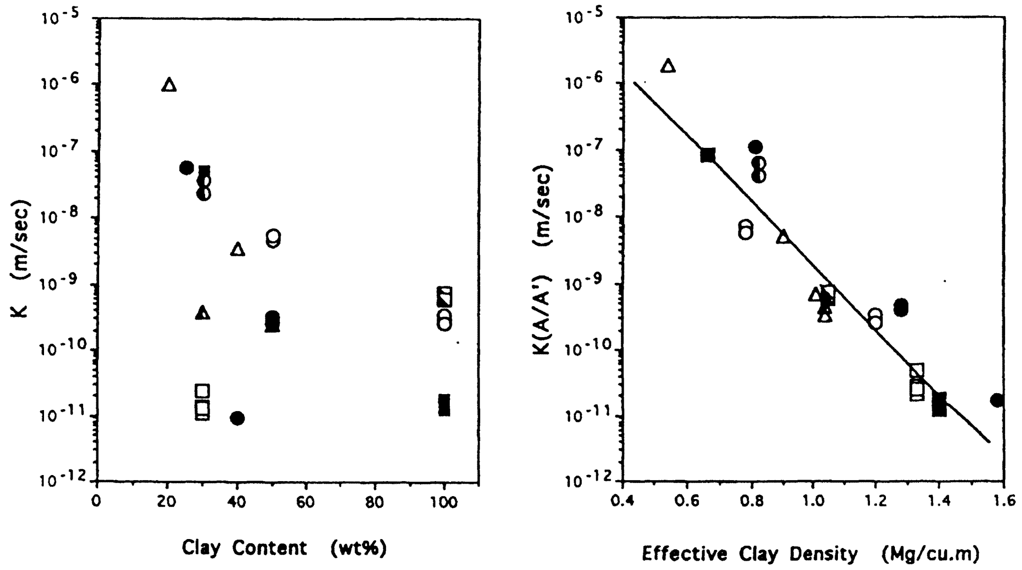


Figure 2. Layout of vault disposal facility.



(a) (b)

Fig. 3 Hydraulic conductivity of clay and crushed rock mixture as a function of (a) clay content and (b) effective clay density [ρ_d (Mg/m3) = -□-: 1.0, -○-: 1.2, -■-: 1.4, -△-: 1.5, -◐-: 1.6, -●-: 1.7, -△-: 1.8, -□-: 2.1]

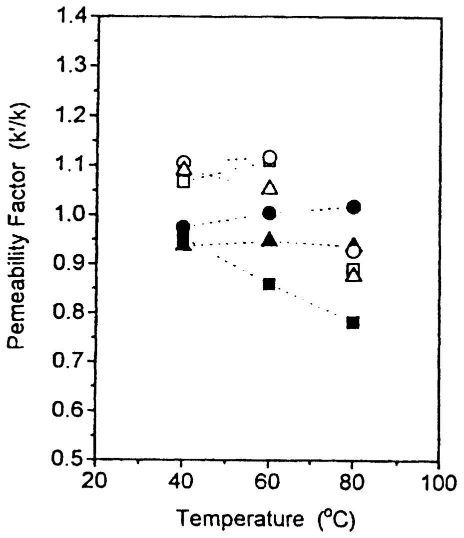


Fig. 4. Permeability factor in compacted bentonite at different dry densities as a function of temperature (-●-, -■-, -▲- : ρ_d=1.4Mg/m³, -□-, -○-, -△- : ρ_d=1.6Mg/m³)

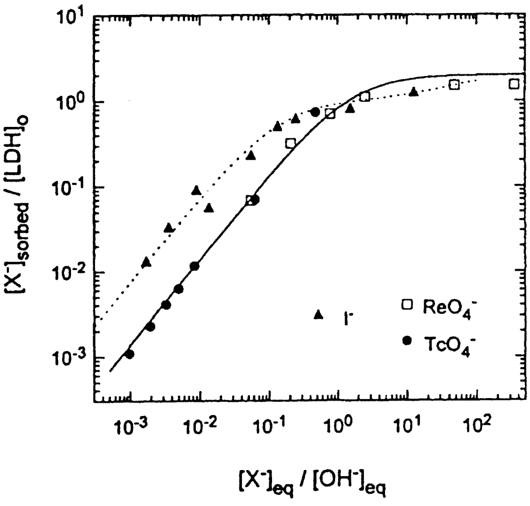


Fig. 5. Experimental values and calculated curve of the ratio $[X\ ]_{sorbed}$ and $[LDH]_0$ as a function of X and OH^- equilibrium concentrations (X = TcO_4 , I).

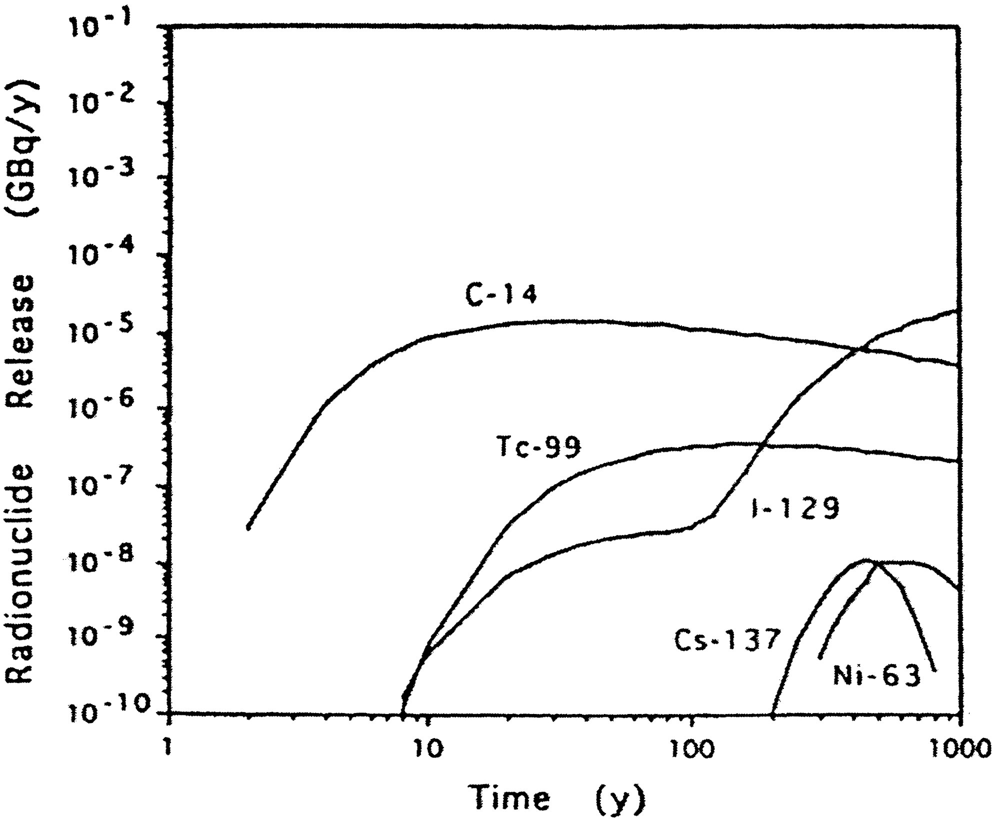


Figure 6. Radionuclide release rates from the engineered barrier in the ILW cavern.

CLAY ISOLATION OF RADIOACTIVE WASTE IN SWEDEN

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ABSTRACT

A smectitic clay is being studied for isolating radioactive waste in Sweden. In a planned future repository for spent reactor fuel, metal canisters will be embedded in very dense Na-bentonite that is practically impermeable and is self-healing because of its strong expandability. For low and medium level wastes, the same sort of clay is being used but at a lower density because lower swelling pressures are required for acceptable performance of the large concrete silo that contains the waste. This silo will be situated in the clay formation. The present paper describes this repository and its expected future performance. It was constructed about 15 years ago and is being monitored to examine major physical processes.

1. THE FORSMARK REPOSITORY

1.1 Introduction

Clay serves as an excellent isolating medium for hazardous waste and is a standard component of the multibarrier system being considered for isolating of all types of radioactive waste in Sweden. For the highly radioactive unprocessed nuclear fuel, which will be contained in copper/steel canisters, highly compacted Na-bentonite will be used as a backfill because it is almost impermeable and strongly delays diffusion of certain types of radionuclides; it also provides the ductility required for absorbing tectonically induced rock shearing (Pusch, 1979; 1985; 1994). For low- and medium-level wastes, a geologic repository (the SFR repository) was constructed about 15 years ago in rock at Forsmark, 150 km north of Stockholm. The most dangerous waste, contained in steel drums and concrete containers, will be emplaced in a concrete silo with isolated cells that extend from the bottom of the silo to its upper end, 50 m above. This paper deals with the performance of the SFR barrier system: concrete (silo), bentonite/ballast (bottom bed), bentonite (wall filling), and the surrounding crystalline rock (see Figure 1).

2. Location

The most important criterion for locating the repository was that it should not interfere with any major water-bearing or tectonically active rock discontinuity. This was particularly important for the cylindrical silo cavern, which has a diameter of about 30 m and a maximum height of 70 m. The excavation of the cavern, which is covered by about 60 m of rock, was completed using "drill and blast" techniques. The rock is granite/gneiss with primary rock stresses of 5 MPa (vertical) and about 15 MPa (horizontal). The silo cavern is located below sea level, which is some 65 m above the top of the cavern. The seawater is weakly brackish, while the groundwater, which is dominated by the seawater in its upper parts, is locally strongly brackish at deeper elevations.

1.3 Silo

The weight of the 28-m diameter slipform-cast silo, which can host about 19 000 m^3 of waste, produces a maximum foundation pressure of 1.2 MPa when filled. Presently, however, cavern drainage operations are still under way. After covering the silo with a concrete lid and a top filling, the drainage system will be shut down and buoyancy will reduce this pressure to about 0.7 MPa. The silo walls and bottom plate are 1.0 to 1.5 m thick, and the cell system makes it behave like a very strong monolith.

2. CEMENT AND CLAY BARRIERS

The concrete silo provides mechanical protection and confinement for the waste. Its chemical function is to provide an enhanced pH environment for minimizing the solubility of certain radionuclides, but this property is not a design parameter. Construction materials included Portland cement, granitic ballast, steel reinforcement, and water for preparing the concrete. Standard Swedish quality regulations for concrete of type K40 were followed. The silo was produced using the slip-form technique, and the operation was monitored by government controllers, which is standard practice.

Three clay barriers are used for isolating the silo from the surrounding rock: A 1.5-m thick bentonite/ballast bottom bed that carries the load of the silo, a bentonite fill in the 2-m wide space between the silo and the walls of the rock cavern, and a bentonite/ballast top filling (Pusch, 1994). The latter barrier has not yet been designed; the former two have been on site since 1987. The design, construction, and performance of these barriers will be discussed in this paper.

The selection of clay materials, application techniques, and design principles was based on the following major criteria:

1. The hydraulic conductivity of the clay barriers must be lower than that of the excavation-disturbed rock, which is estimated to be about 10^{-9} m/s or higher.

2. The compressibility of the bottom bed must be such that the maximum settling of the silo does not exceed a few centimeters. This amount can be compensated by applying an expandable top fill for maintaining contact with the rock. Furthermore, the maximum vertical movement of the silo must not exceed 10 cm in 500 years.

3. The effective (swelling) pressure exerted by the wall filling must not exceed 0.7 MPa and must not vary by more than ±0.3 MPa for the adjacent 10-m^2 wall element areas. This will moderate the stresses in the silo wall and eliminate the risk of silo tilting.

4. The silo backfill must be able to vent gas at an overpressure that does not cause microstructural changes leading to an increase in hydraulic conductivity. The silo will be equipped with gas vents, but gas will also have to penetrate the bentonitic top cover.

5. The entire system of silo, clay isolations, and rock must operate without significantly altered properties for 500 years.

2.1 The bottom bed

The settling and conductivity criteria are contradictory in the sense that low compressibility and expandability require high density but low smectite content, while a low hydraulic conductivity suggests a high smectite content (Pusch, 1994). The optimum composition was determined to be a mixture of 10% Na-bentonite and 90% graded granitic ballast (crushed rock), thoroughly mixed (dry mixing) and applied in 0.3-m layers compacted by ten runs of 2-ton and 3.5-ton vibrating rollers. Frequent determinations of density were made during construction of the 1.5-m thick bed, and they showed that the minimum dry density (ratio of mass of solid substance and total volume) was 2050 kg/m^3. Testing of the compressibility was made in the laboratory and by plate loading on site, and it was determined to yield a maximum settling of the filled silo of 1 to 2 cm. The hydraulic conductivity was measured on samples exposed to hydraulic gradients of 30 to 100, using distilled water and strongly brackish calcium-dominated Forsmark groundwater (11000 ppm salt). Hydraulic conductivity was found to be 1.2 x 10^{-10} m/s at the maximum (i.e., about one order of magnitude lower than that of the surrounding rock).

The postulated criteria with respect to compressibility and hydraulic conductivity were thus fulfilled. No checking of the conductivity in situ can be made, but the settling of the silo has been measured for almost 10 years and the results indicate that the silo (which is now filled to approximately one-third of its total volume) has settled by about 1.4 cm. The settling takes place according to a log time creep law, and extrapolation gives a settling after 500 years of some 2 to 3 cm, considering buoyancy effects, which meets the specified criterion.

2.2 The wall filling

Previous large-scale tests have shown that the most economical and technically feasible way of filling the 50-m high space between the silo and the rock would be to fill a hopper with granulated bentonite and move it along the upper edge of the silo while emptying it through a 15.2-cm flexible tube that reached down to the bottom or to the already emplaced fill (Pusch, 1994). This technique was applied, and uniform filling was obtained by continuously moving the open end of the tube. No compaction was made because the bulk density had to be relatively low to satisfy the load design criteria specified for the concrete silo. The average dry density of the 7000-ton fill was predicted to be about 1020 kg/m^3 in the lowest 20-m interval, 1000 kg/m^3 between 20 and 40 m from the bottom, and around 980 kg/m^3 in the uppermost 10-m interval. If conservative density and electrolyte variations are taken into consideration, this will yield a swelling pressure of 0.2 to 0.5 MPa at the lower end of the filling and 0.05 to 0.3 MPa at the upper end. The recorded pressure (still with no piezometric component due to the drained conditions) has its highest value of 0.08 MPa in the lowest part of the fill. This pressure is hence lower than predicted.

3. LONG-TERM PHYSICAL PERFORMANCE OF THE REPOSITORY

After completion of the waste emplacement in the silo, the drainage will be stopped and the piezometric level will rise to the original groundwater level after several tens of years. The regional hydraulic gradient, which is estimated to be about 0.01 to 0.02, will then drive groundwater horizontally through the rock around the clay-isolated silo. Assuming the same hydraulic conductivity of the rock and the concrete, the two different flow patterns shown in Figure 2 are expected for the case of slot fillings consisting of rock and bentonite, respectively.

Another long-term effect might be tectonically induced shearing along major discontinuities, by which large rock blocks could be released and exert a load on the wall filling (Figure 3). This case of a sliding rock wedge would increase the pressure locally by about 80 kPa if the slot were empty or contained crushed rock. However, with the clay fill saturated, the swelling pressure will be sufficient to prevent initiation of such sliding. Other tectonically generated forces are estimated to be absorbed by the relatively soft clay fill.

Gas production in the silo is expected to be quick and rather extensive. The exact design of the gas vents in the concrete silo top has not yet been decided, but one solution may be to put ceramic filters in the 1.5-m thick concrete lid and cover it with a layer of sandy silt over which a clay layer of the same type as the bottom bed is applied. With 10% bentonite in this bed, the threshold pressure to release gas is less than 100 kPa, excepting the piezometric pressure (Pusch, 1983; Gray, 1996). Gas will move through a very small number of channels up to the roof, where it will proceed through a few major fractures to the sea bottom. Penetration of gas through the top bed is not expected to cause permanent microstructural changes, but this possibility will be further investigated.

3.1 Long-term chemical effects

There are three major questions: (1) Will the smectite component be converted to nonexpanding minerals like illite? (2) What will be the effect of strongly brackish water, with calcium as the dominant cation, on the physical state of the bentonite clay? (3) Will smectite and concrete, or rather cement, react to break down either of these substances?

The first question is answered by the comprehensive international investigations on this issue: there is no indication, either by natural analogues or by common theoretical chemical models, that significant alteration of the smectite will take place in 500 years under isothermal conditions with the temperature being around 15°C (Nadeau, 1986; Pusch, 1993).

The second question is answered by the systematic laboratory research work that has been conducted in the last 15 years in Sweden. This work shows that for the clay densities prevailing in the bottom bed and deeper than about 10 m from the surface of the wall filling, the swelling pressures will be in the ranges given in the preceding text. In the uppermost part of the wall filling there may be some settling.

The third problem is one of general interest and it is being investigated in several countries including Sweden. Its treatment in the planning of the SFR repository concerned the degradation rate of the concrete and contacting smectite clay. The major ideas and findings can be summarized as follows:

3.1.1 Concrete degradation

For the required 500 years of performance of the Forsmark repository, the loss in mechanical strength of the silo was determined to be of limited importance, as indicated by studies of natural analogues and application of a simple but conservative chemical model (Pusch, 1982). This model implies that $Ca(OH)_2$ in the cement component of the concrete is dissolved layerwise from the contact surface and inwards and that the dissolved components diffuse away from the contact into the clay without being absorbed. This process creates a concentration of Ca that drives the process, which is based on the assumption that the solubility of Ca in equilibrium with calcium silicate hydrates is 2×10^{-3} kmol Ca/m^3. Using this model, 95% destruction of the concrete will have taken place in about half the concrete wall (i.e., to a 90-cm distance from the clay/concrete contact in 500 years). To evaluate this model, chemical analyses (scanning microscopy with an energy dispersive spectrometer) were performed on samples of concrete and contacting clayey silt samples from the Washington Ship Canal in the United States. At the time of sampling, the concrete construction, which had been cast in fresh water, was 70 years old.

The analyses showed that the relative concentrations of Ca, Si, and Al varied significantly across the clay/concrete contact as illustrated in Figure 4. The broken curves represent the hypothesis that the Ca concentration in "positions 560-564" is the tail of a concentration profile that has its maximum at the clay/concrete interface, where it is determined by the solubility of $Ca(OH)_2$ in a first degradation phase and by calcium silicates and aluminates in later phases, dropping to a low value far off in the clay. A general conclusion from this study and from visual inspection of the granite in the drill core is that the concrete has survived for 70 years with insignificant deterioration. It should be noted that the major clay mineral was illite (hydrous mica) and not smectite, but this is not considered to be a major issue.

3.1.2 Clay alteration

A simple theoretical approach is to take the major smectite mineral montmorillonite to be characterized by the general pyrophyllite formula ($Al_4\ Si_8\ (OH)_4$) and consider reactions with excess $Ca(OH)_2$ emanating from the concrete.

$$Ca(OH)_2 + Al_4\ Si_8\ (OH)_2\ >\ 2CaAl_2Si_4O_{12},\ 6\ H_2O \qquad (1)$$

The reaction product is the zeolite chabazite; however, depending on the degree of flushing of alkaline solutions, other zeolites like scolecite, gismondine, and analcime may be formed. It is also possible that OH^- attack may produce $Al(OH)_3$, $Mg(OH)_2$ and $SiO(OH)_3$ or amorphous substances and gel complexes. X-ray diffraction (XRD) analyses support the hypothesis that the latter reaction products are formed or that possible zeolite crystals are XRD-amorphous because of their very small size.

The chemical analyses and visual inspection of the Washington Ship Canal clay samples demonstrated that the clay had been significantly altered beyond 150 µm from the concrete contact.

3.2 Long-term overall performance of the repository

A scenario that has an impact on the long-term performance of the repository has been considered. The scenario postulates the effect of land upheaval due to tectonics and to unloading by the deglaciation that ended some 10,000 years ago.

From a radiological point of view, the design criterion has been set at 100 μSv/year as maximum permitted individual dose for the most strongly exposed group of people in the area, considering the activity of the silo waste and the decay rate (SKB, 1991). Assuming 2-D conditions and focusing on the groundwater flow through Zone H2 and a major fracture in Zone 3 that is parallel to Zone 9 (see Figure 3), the flux through the repository will be 5 l/m^2 per year after 1000 years and 15 l/m^2 per year after 2500 years when the uplift has moved the shoreline eastward to a position that makes farming possible rather close to the repository. The flow pattern is shown in Figure 5 for the case of a deep water well at the farm site, and the concentration of radionuclides in the well water is calculated to be 30 μSv/year after 2500 years. This is much lower than the present value for many wells in Sweden.

The SKI authority (i.e., the Swedish nuclear inspectorate) demanded that a general mechanical model for silo degradation should be developed for a 5000-year period after closure. It was outlined on the basis of an assumed rate of corrosion of the reinforcement steel bars of 10 μm per year, which is very conservative. This would cause substantial reduction in the performance of the reinforcement after 500 years, but collapse of the concrete silo would not be expected until after about 1500 years. Because of the relatively high porosity of the waste, the degrading concrete construction, driven by the swelling pressure of the surrounding bentonite, would then tend to move toward the center of the silo but would not become strongly disintegrated until after around 3000 years. After 5000 years the concrete would have turned into a mass of sand and gravel, and the overlying rock would start to fall because of the lack of support from below. Since the next glaciation is expected to start at about this time, further extrapolation of the degradation is highly hypothetical.

4. CONCLUSIONS

The prediction of the physico/chemical performance of the silo repository based on theoretical models is supported by the measurements with respect to the mechanical behavior, and current research on chemical changes and gas transport suggests that the clay isolations will serve more than acceptably. The overall performance of the repository with respect to radiological conditions is concluded to be acceptable, in particular because the degradation rate of the concrete is expected to be sufficiently low to leave a large part of the silo intact for at least 500 years. A substantial mechanical stability in a longer time perspective will prevail for at least 1500 years if the corrosion of the steel reinforcement is the controlling factor.

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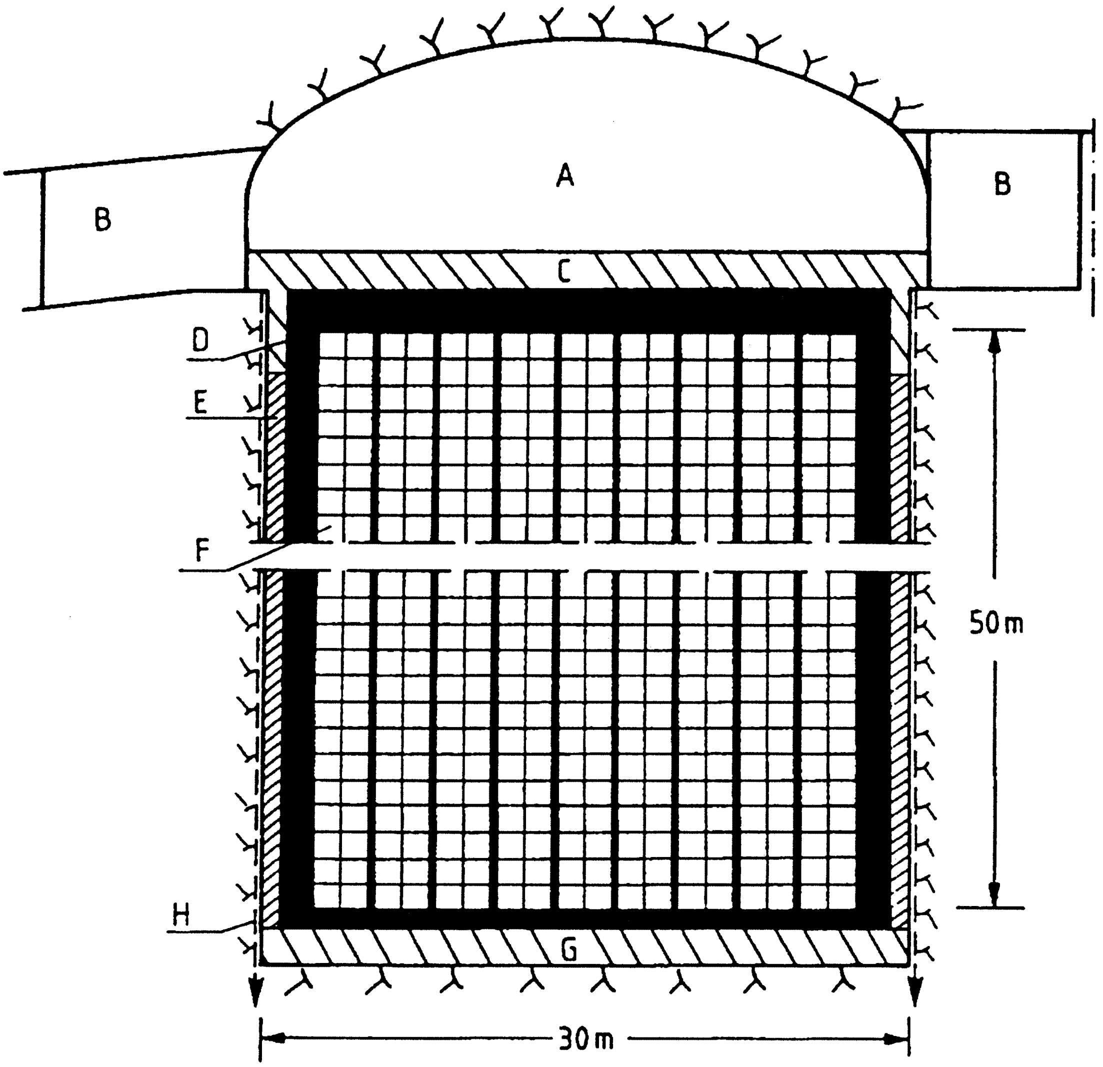

Figure 1. Schematic section of the SFR silo. (A) Compacted, cement-stabilizedsand backfill. (B) Concrete plugs. (C) Bentonite/sand top bed. (D) Concrete silo. (E) Bentonite wall filling. (F) Waste. (G) Bentonite/sand bottom bed. (H) Drains connected to tunnel system.

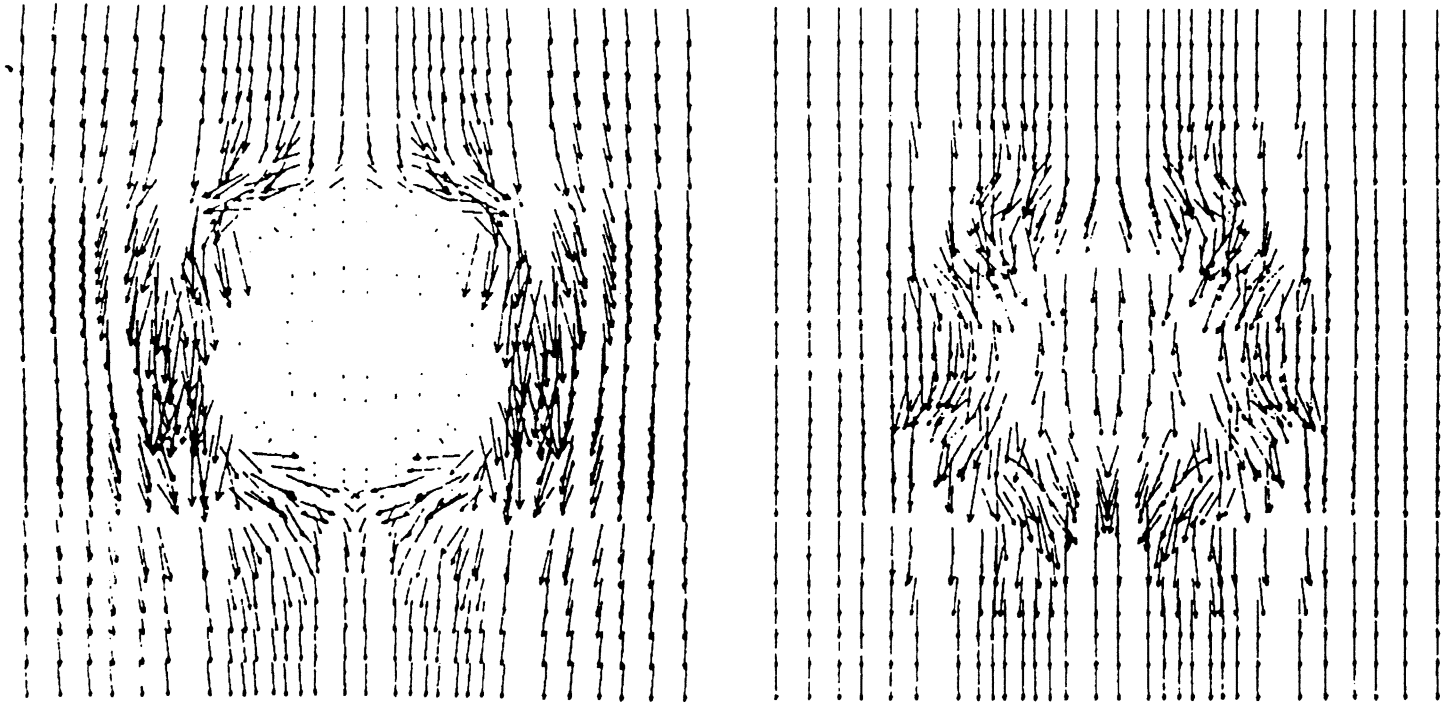

Figure 2. Finite element-calculated difference in horizontal groundwater flow through the silo repository for the case of very permeable slot between silo and rock (Upper), and for the case of bentonite-filled slot (Pusch 1994).

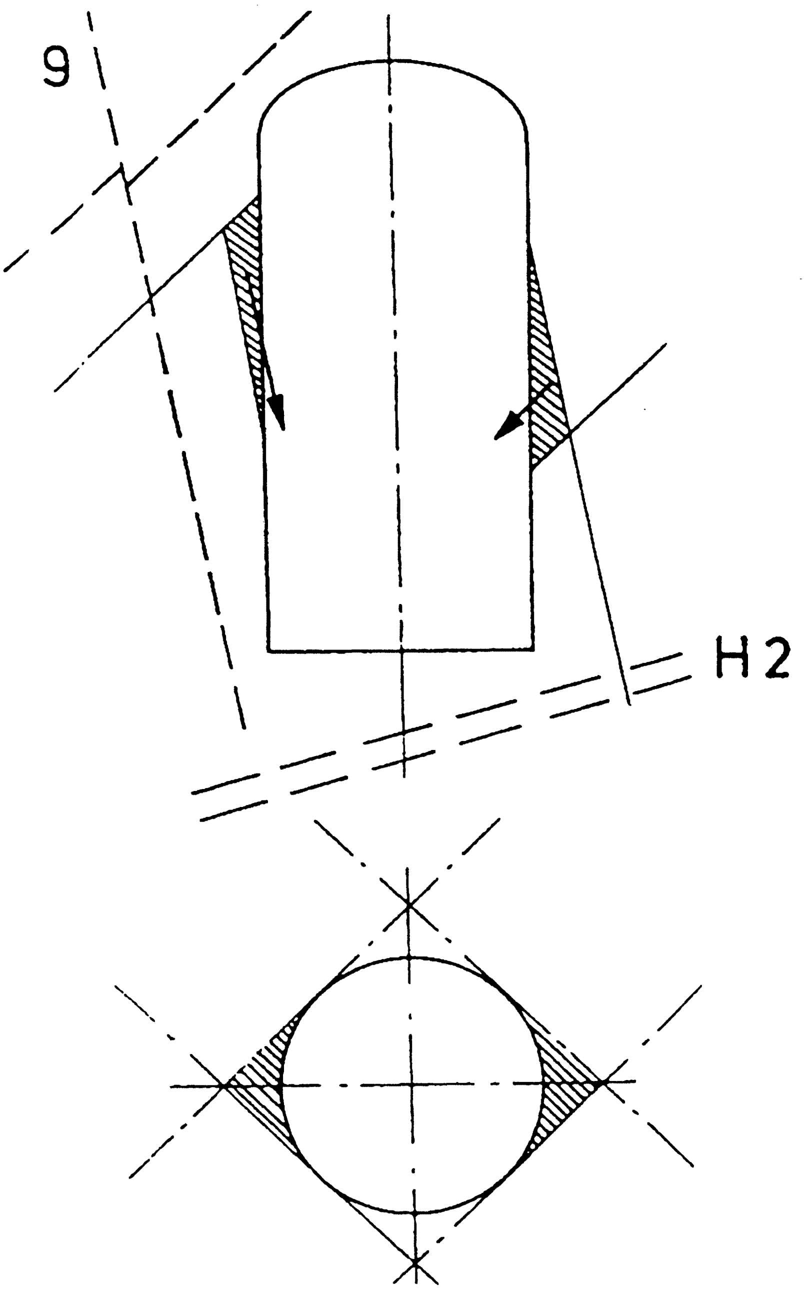

Figure 3. Schematic section of the rock with identified potentially slipping rock wedges. Two major fracture zones 9 and H2 that can form wedges are indicated (Pusch 1994).

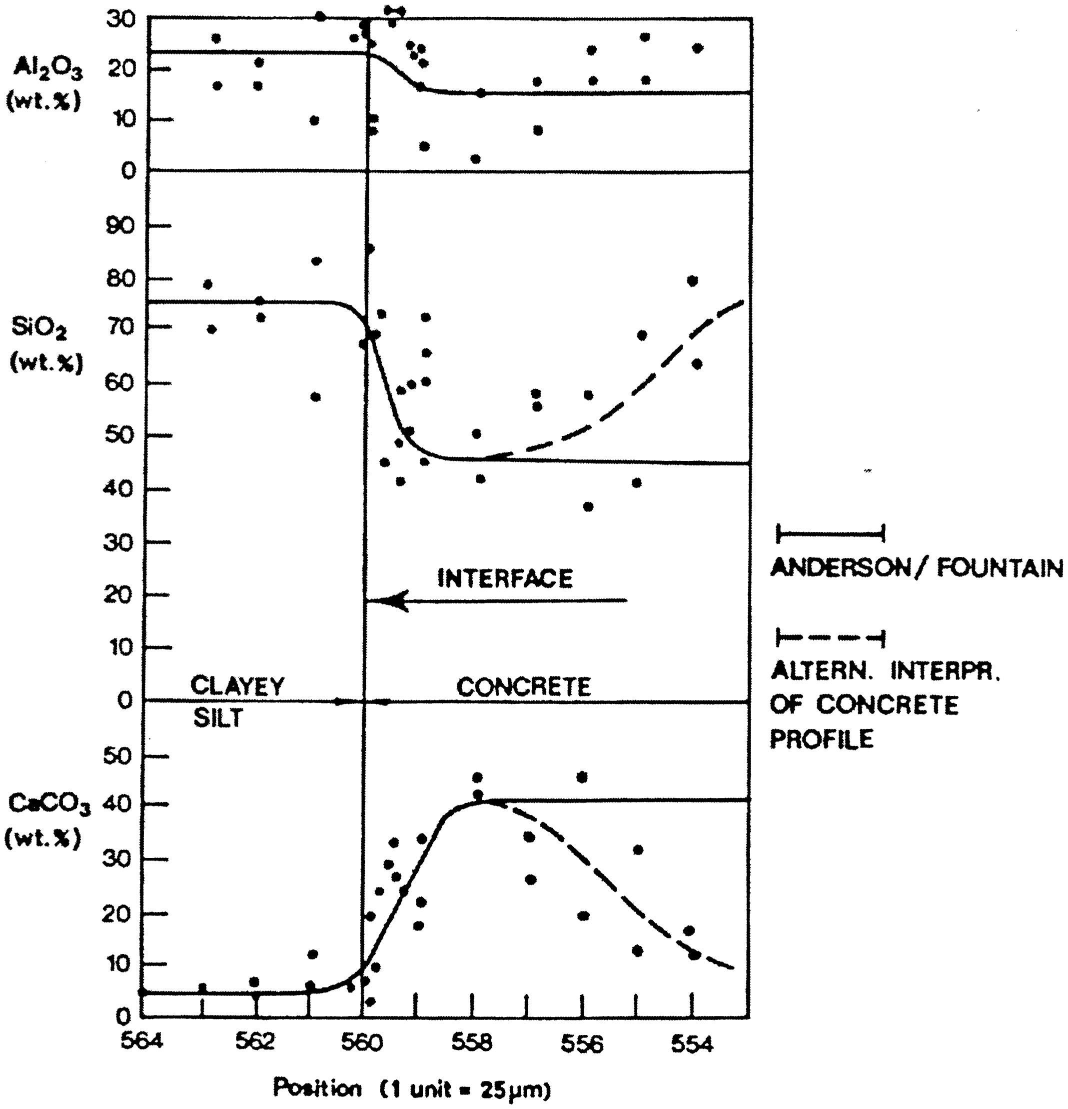

Figure 4. Contact of clayey soil and concrete depicting the results of chemical analyses. The discussion in the text refers to the broken curves (Alt. interpr.). The full lines refer to a preceding, unpublished study by Anderson/Fountain.

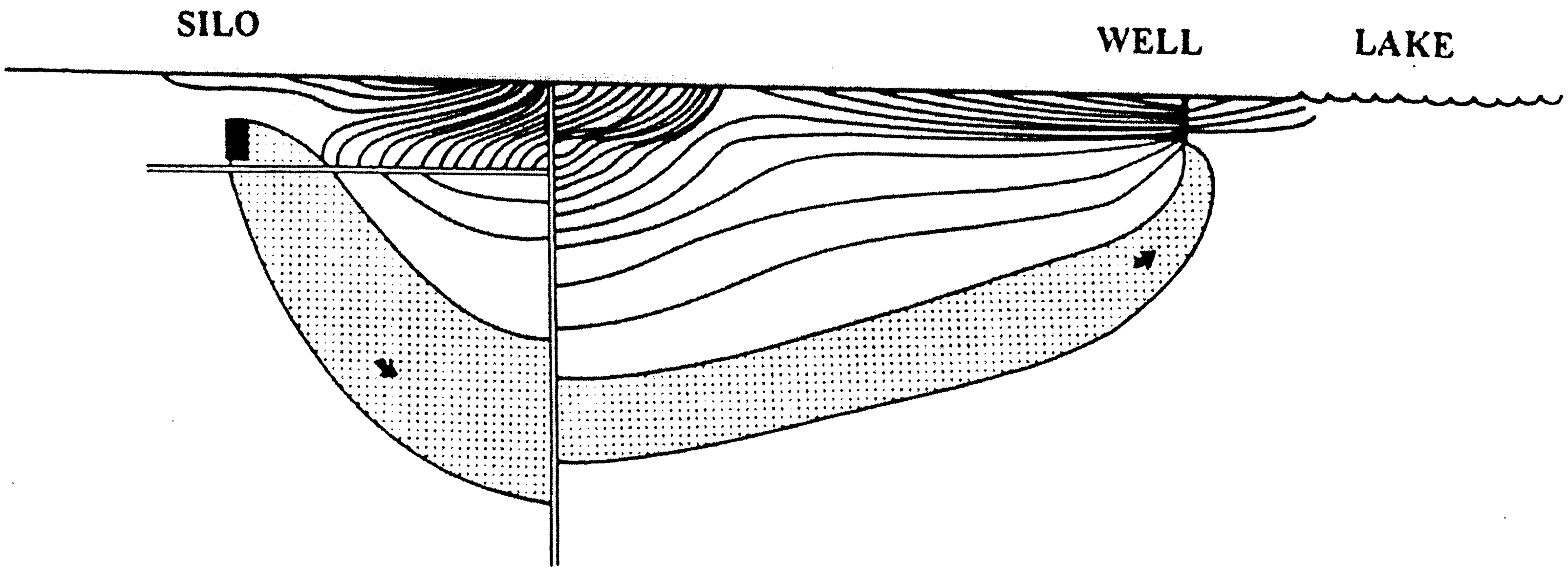

Figure 5. Stream-tubes from inland to a well after 2500 years. The dotted area represents pathway of radionuclidebearing water. The horizontal double-line just below the silo and the vertical one to the right represent major fracture zones (H2 and 3, respectively).

CEMENTITIOUS BACKFILL: THE SWISS VIEW

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1. SOME GENERAL REMARKS ABOUT CEMENTITIOUS MATERIALS FOR REPOSITORIES FOR L/ILW

Cementitious materials are widely used as construction materials in underground structures (shafts, tunnels, caverns, etc.). Cementitious construction materials are widely available, and much experience exists for a wide range of their applications. They show good workability and are inexpensive.

Cementitious materials are also widely used in the management of low- and intermediate-level radioactive wastes (L/ILW), particularly for solidification of radioactive fluids, sludges, resins, and solids. Furthermore, cementitious containers and overpacks have successfully been fabricated and used.

The properties of cementitious materials can be modified over a very wide range. This means that recipes for cementitious backfills can be developed that fulfill very specific requirements for a broad spectrum of projects. Because several of the other materials in a L/ILW repository will also be based on cementitious binders (waste matrix, overpack/container, liner, etc.), chemical compatibility of the backfill with these materials is assured. Therefore, cementitious materials are often considered to be the adequate choice for backfilling a repository for L/ILW.

Adequately designed cementitious materials show favourable properties with respect to radionuclide retention. As a consequence of their large (micro-)porosity and internal surfaces, and their high pH, these materials usually support chemical immobilization through sorption and chemical conditions resulting in low solubilities.

When using a cementitious backfill, attention must be given to the interaction with other materials. Such interaction can have favourable effects (e.g., a decreased corrosion rate of steel leads to a longer overpack lifetime and lower gas generation rates), but in some cases the effects of the interaction need more in-depth evaluation (e.g., the interaction with clay-based sealing materials or with the surrounding host rock is still an open question).

The use of an adequately designed cementitious backfill can create a chemical environment that, together with the physical properties of the backfill, will mitigate some of the perturbing effects in a repository for L/ILW including the generation and release of gas, the generation and degradation of complexants and their effect on radionuclide mobility, and microbial activity and growth. However, the use of cementitious materials in a repository also creates some challenges, especially for assessing the long-term performance of such a system. These include:

- the potential cracking and fissuring of cementitious materials and questions about self-healing (calcite precipitation);

- the accuracy of predictions of the chemical and—more problematic—the physical evolution of the system, taking into account the interaction with the natural groundwater and waste degradation products as well as the mechanical effects (e.g., rock creep); and

- the general understanding of geochemistry under alkaline conditions such as speciation (including the role of organic complexants), surface chemistry, solubilities and solid solutions, and the role of colloids (including their stability and the possibility of irreversible radionuclide uptake).

2. THE SWISS DISPOSAL CONCEPT

In the Swiss disposal concept, two repositories are foreseen (Nagra NTB 92-02):

- a repository for L/ILW; and

- a repository for vitrified HLW, spent fuel, and long-lived ILW.

Disposal of L/ILW is foreseen in horizontally accessed caverns, whereas disposal of long-lived ILW will be either in silos or tunnels. For both the L/ILW and the long-lived ILW repositories, the current design includes a cementitious backfill. In the repository for L/ILW, wastes from nuclear power plant (NPP) operations, NPP decommissioning, medicine, research, and industry, as well as low-level waste from reprocessing will be disposed. The repository for long-lived ILW will contain ILW from reprocessing. The L/ILW and the long-lived ILW is solidified by cementitious grouts, except for a small fraction which is either bituminized or solidified by polystyrene. The volumes and properties of wastes to be disposed of are described in the Swiss model waste inventory (Nagra NTB 93-21).

The L/ILW repository is planned to be sited at Wellenberg (Community of Wolfenschiessen, Canton of Nidwalden) in a sedimentary host rock (marl), and a general license application was submitted in 1994. A detailed safety analysis report was prepared to support this application (Nagra NTB 94-06). Despite the positive response by the regulatory authorities, the project is currently blocked because a concession for the use of the underground (which is required in the Canton of Nidwalden) was rejected in a public vote in 1995.

Disposal of vitrified HLW, spent fuel, and long-lived ILW is not planned until well into the next century. The host rocks considered for this repository are the crystalline basement and Opalinus Clay.

3 THE USE OF CEMENTITIOUS MATERIALS IN THE REPOSITORY FOR L/ILW

For the repository for L/ILW, specific measures are taken to create an optimum environment for the cementitious backfill. To minimize geochemical perturbations, those wastes containing potentially adverse materials (organics, complexants, etc.) are separated from the other wastes (Nagra NTB 94-06, chapter 2.2). Fortunately, the wastes with such adverse materials have normally low specific activity, and a sufficient performance can be achieved even when the cement is severely perturbed and degraded (which was reflected in the performance assessment by taking no credit for any sorption). For all other wastes, geochemical perturbations are expected to be minor.

To ensure long-term geochemical stability, the cementitious backfill will be placed in a low-flow environment. Furthermore, enough cement will be made available to provide sufficient buffering capacity for any throughflowing carbonate-rich groundwater.

Because the level of confidence in the low hydraulic permeability of the cementitious liner is very limited, in the safety concept the low-flow environment is provided by the low-permeability host rock. No credit is taken for the hydraulic resistance of the liner.

Because of the degradation of L/ILW, these wastes are expected to generate gas. In order for the gas to be released without compromising the performance of the near field, a backfill with enhanced permeability will be used (see, e.g., Senger et al., 1993). An example of such a high-permeability backfill is described in Nagra NTB 92-11. Such a backfill will also lead to 'channelled' flow through the engineered barriers: Groundwater flow will be around the waste containers, and radionuclide release from these containers is diffusive in nature with subsequent advective transport through the higher-permeability backfill.

The performance assessment prepared to support the general license application for the L/ILW repository at Wellenberg has shown that for such a system the near field is a very efficient radionuclide barrier (Nagra NTB 94-06). In this analysis, a broad spectrum of scenarios was investigated. For the near field, flow and radionuclide transport perpendicular as well as parallel to the cavern axis were modelled. In the analysis, the effects of colloids were also assessed, albeit in a very simplified manner.

Currently, more detailed models are being developed which allow the heterogeneous nature of the near field to be modelled in more detail.

To summarize, the current experiences with cementitious backfills show that they are a very good geochemical barrier. Furthermore, recent laboratory research has indicated that in future performance assessments a less conservative approach can be used to account for the effects of organics (see, e.g., Nagra NTB 96-04). The cementitious backfills will last for a very long time, provided they are emplaced in a low-flow environment. To ensure such a low-flow environment, it may be advisable to place the repository caverns in a low-permeability host rock because the reliability of a (cementitious) cavern liner as a hydraulic barrier is considered to be insufficient.

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STABILITY OF CONCRETE INSIDE THE CHERNOBYL UNIT-4 SHELTER

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ABSTRACT

A thermodynamic model of Portland cement, solved using the innovative Gibbs energy minimization approach, is described and applied to predict the interaction of concrete, water, and contaminants within the Chernobyl Unit-4 Shelter. Sufficient chemical stability of concrete was confirmed with respect to chloride-bicarbonate, potassium-sodium, the alkaline waters of the shelter, and carbonate aqueous leaching reagents. The only changes within the cement construction materials were that carbonate minerals replaced the high-calcium phases of concrete. The important role of cement materials in the physicochemical conditions of the shelter interior was demonstrated. In particular, precipitation of radionuclide-bearing secondary minerals (such as calcium-strontium carbonate and UO_2^{+2}- minerals on the concrete surface) was modeled. Calculations were conducted for the aquatic concrete-uranium-boron system to estimate the behavior of the neutron moderator under present conditions of the shelter interior, as well as during possible activities involving removal of the fuel-containing materials (e.g., in leaching technology). Equilibration of uranium- and boron-bearing alkaline carbonate solutions with high-calcium cement materials is expected to result in formation of weakly soluble minerals ($Na_2U_2O_7$, danburite, and datolite) on the concrete surfaces. Although possible leaching losses of this kind need to be monitored, coprecipitation of uranium with boron clearly will not increase criticality and nuclear danger.

1. INTRODUCTION

In 1986, a shelter ('Sarcophagus') was erected over the destroyed Unit-4 of the Chernobyl nuclear power plant (NPP) to isolate the highly radioactive compounds from the environment. Concrete is a basic construction material that ensures stability of the shelter. Contaminated concrete also accounts for the major part of radioactive waste within the shelter site. Of the total amount of concrete, high-level waste (HLW) comprises 90,000 tons, and intermediate- and low-level waste (ILW/ LLW) comprise about 300,000 tons (Aljoshin *et al.* 1998).

The presence of moisture inside the shelter and the existence of gas exchange in the environment causes intensive chemical processes and redistribution of radionuclides within the interior of the Chernobyl shelter (Khodorivski *et al.* 1996). Understanding the influence of these processes on chemical stability and the radioactive contamination of concrete is important for developing measures to stabilize the shelter and solve the practical problems of transforming it into an environmentally clean state. Conditions inside the Sarcophagus, mainly very high levels of radioactivity, impose serious restrictions on *in situ* and experimental investigations. Therefore, thermodynamic modeling is one of the most important methods for studying chemical interactions inside the shelter.

In the work described here, a thermodynamic model of Portland cement based on the innovative Gibbs energy minimization algorithms (Karpov *et al.* 1997) is described and used to predict the interaction of concrete, water, and contaminants within the Unit-4 shelter.

2. CONCRETE AND AQUEOUS SOLUTIONS INSIDE THE SHELTER

There are two main types of concrete in the Unit-4 shelter. The first is 'old' concrete used during construction of NPP Unit-4; the second is 'fresh' concrete that forms the shelter walls, which were erected in 1986. The fresh cement materials were also used in 1986 to cover some accumulations of highly radioactive fuel-containing materials inside the shelter.

Selected results of concrete strength studies (Zhidkov *et al.* 1993) are shown in Table 1. The lower strength of the fresh, non-irradiated concrete is attributed to technological departures that were made in the process of concrete emplacement during Sarcophagus construction, when conditions were extremely challenging. The influence of temperature and high doses of radiation on concrete strength corresponds to previously determined patterns (Dubrovsky and Ablevich 1983, Bazhenov 1978). Neither factor affects the structural stability of the shelter. Deformation and overloading of certain elements of the building that resulted after shelter completion are thought to comprise the main danger.

The presence of moisture (about 3000 m^3) inside the shelter could cause chemical corrosion of construction materials such as concrete. Several studies of the chemical stability of concrete in the shelter were conducted during the last few years (Khodorivski *et al.*1996, Kulik *et al.*1996, 1997, 1998). Abramis *et al.* (1998) studied the chemical composition of the shelter waters and showed that these waters are mainly of the chloride-bicarbonate, potassium-sodium, alkaline (pH 7.6 to 10.6) type; suboxic (*in situ* determined values of Eh are -83 to -112 mV); and with total dissolved solids (TDS) from 1 to 13 g/L. The concentration of radionuclides in the shelter waters places them in the classes of liquid LLW/ILW. The compositions of three typical water samples are given in Table 2.

3. MODELING APPROACH

Physical-chemical calculations have been performed to assess possible chemical interaction of Portland cement materials with shelter waters as well as with carbonate aqueous solutions, which can be regarded as prospective leaching reagents for removal of the fuel-containing materials (FCM). A Gibbs energy minimization (GEM) method, based on an interior points method (IPM) convex programming algorithm (Karpov *et al.* 1997) was implemented in the *Selektor-A* code (Kulik *et al.* 1997). The code finds explicit (meta)stable phase-component speciation x (including aqueous, gas, and solid-solution components); values of chemical potentials of chemical elements u; pH, Eh, and pP(gases). Input parameters are temperature T, pressure P, bulk elemental chemical composition of the whole system b, partial molal (molar) Gibbs energies for all species g^0_{TP}, and a set of equations for the non-ideality models θ (if appropriate). One aqueous electrolyte, one gas mixture, and any number of crystalline and dispersed (single- or multi-component) solid phases can be included in the system. Because of this, the solubility, gas-aqueous, and redox equilibria in a complex solid solution-aqueous solution (SSAS) system can be calculated by GEM in a single run, without invoking auxiliary techniques such as Lippmann's diagrams.

In this study, model calculations were performed for ambient conditions (25°C, 1 bar) in the system Na-Ca-Mg-Fe-Al-Si-U-Sr-C-S-B-H-O. Activity coefficients of individual aqueous species were calculated using the extended Debye-Hueckel equation, with a common third parameter set to 0.064. Solid solutions and gas phases were taken as ideal mixtures. The total chemical composition of the modeled systems was specified using quantities of solid salts and minerals per 1 kg of water.

4. THERMODYNAMIC DATABASE

An extensive consistent set of thermodynamic data, which includes more than 200 species, was used in the calculations. The standard Gibbs energies of formation ($\Delta G^o_{298.15}$) for gas, aqueous, and solid species were taken from the built-in thermodynamic database of the Selektor-A code (Kulik *et al.*, 1997).

4.1 Aqueous species

The aqueous solution is represented with a comprehensive set of aqueous species for the ion-association model, including dissolved gases and solutes for the system Na-Ca-Mg-Si-Fe-Al-U-Sr-B-C-S-H-O. The thermodynamic properties of most species are listed elsewhere (Sinitsyn *et al.* 1998a). The sources of thermodynamic values for uranium complexes, as well as carbonate complexes of Na, Ca, Mg, and Fe, are cited in Sinitsyn *et al.* (1997). The $\Delta G^o_{298.15}$ values for aqueous species of boron are presented in Sinitsyn *et al.* (1998b).

4.2 Gas phase

The gas phase is represented by an ideal mixture of ideal gases (CH_4, CO, CO_2, H_2S, NH_3, NO_2, SO_2, SO_3, H_2, N_2, O_2), which can cover a wide range of redox conditions. The thermodynamic properties of gases were taken from Robie and Hemingway (1995).

4.3 Minerals

Minerals were included in calculations of the 'solid-water-atmosphere' equilibria as the ideal solid solution phases $(Ca,Sr)CO_3$ and $(Ca,Sr)SO_4$ and as single phases (kaolinite, gibbsite, quartz, brucite, amorphous SiO_2 [Robie and Hemingway 1995], serpentine, hydrogoethite, hydromagnetite, mackinawite, whitlockite, disordered dolomite [Melnik 1986, Kharaka *et al.* 1988, Ball *et al*, 1991], salts in the subsystem Na-K-Ca-Mg-CO_2-SO_3-H_2O [Robie and Hemingway 1995, Kharaka *et al.* 1988, Ball *et al.* 1991]). Uranium phases were represented by the uranium oxides Na_2UO_4, $Na_2U_2O_7$, Na_3UO_4, $NaUO_3$, ß-$UO_2(OH)_2$, UO_2CO_3, and $Na_4UO_2(CO_3)_3$ (Grenthe 1992). The $\Delta G^o_{298.15}$ values for the boron-containing solids ($CaB_3O_3(OH)_5{\bullet}4H_2O$, $CaB_3O_4(OH)_3{\bullet}H_2O$, (hydrobaracite - Hb) $Ca(BO_2)_2$, $Ca_2B_2O_5$, $Ca_3(BO_3)_2$, CaB_4O_7, $CaB_2Si_2O_8$ -datolite, $CaBSiO_4OH$ -danburite (Db), $Na_2B_4O_7$, $Na_2B_6O_{10}$, $NaBO_2$, $Na_2B_4O7{\bullet}10\ H_2O$ -borax, B_2O_3 and H_3BO_3) are listed in Sinitsyn *et al.* (1998b).

4.4 Mineral phases of fully hydrated Portland cements

The thermodynamic model of fully hydrated Portland cements is described in Sinitsyn *et al.* (1997, 1998a). It includes single-component (ettringite *Ettr* - $Ca_6Al_2S_3O_{12}(OH)_{12}$, hydrotalcite *Htc* - $Mg_4Al_2O_7(H_2O)_{10}$, portlandite *Portl* - $Ca(OH)_{2,cr}$) and solid-solution phases (CSH1 and CSH2 phases of amorphous calcium silicate hydrogel and "hydrogarnet" solid solution *HGr*). Thermodynamic models of CSH phases are developed in Sinitsyn *et al.* (1998a) and Kulik *et al.* (1998). For the purposes of this work, ideal solid solution models with sodium end-members (Sinitsyn *et al.* 1998a) were used, namely: CSH1 solid solution with SiO_2, $Ca_{0.9}H_{1.8}SiO_{3.8}$ and $CaH_2SiO_4 \cdot NaOH$ end-members; and CSH2 with $Ca_{0.9}H_{1.8}SiO_{3.8}$, $Ca_{1.7}H_{3.4}SiO_{5.4} \cdot 4H_2O$ and $CaH_2SiO_4 \cdot NaOH$ end-members. The *HGr* solid solution is represented by three components: $Ca_3Al_2O_6 \cdot 6H_2O$, $Ca_3Fe_2O_6 \cdot 6H_2O$, and $Ca_3Al_2Si_3O_{12}$. Thermodynamic properties for the fully hydrated Portland cement single-component phases and end-members are given in Table 3.

In previous work (Sinitsyn *et al.* 1998a), the proposed multiphase thermodynamic model of Portland cement was tested using published experimental data on the solubility of single cement phases and CSH as well as available experimental compositions of cements and pore solutions of different aging times. Model calculations were performed by means of the Selektor-A code and have shown reasonable consistency between predicted and experimental data. Hence, the model can be used for predictions of the concrete-water-contaminants interaction within the Chernobyl Unit-4 shelter.

5. MODEL CALCULATIONS

5.1 Concrete/shelter water interaction

Concrete/shelter water interaction was modeled to estimate the corrosion stability of the main construction materials in the shelter. Because the actual composition of the concrete in the shelter is unknown, the following composition of Portland cements was assumed (in wt.%): CaO - 65, SiO_2 -23, Al_2O_3 -7, Fe_2O_3, - 3, MgO - 1.5, SO_3 - 0.5. In the first step, aqueous solution compositions corresponding to real shelter waters (Table 2) were equilibrated with air. Next, the modeling was performed for different solid/water ratios ranging from 10^{-7} to 1. At each point, the equilibrium phase assemblage, quantities of phases, and compositions of solutions were determined.

The calculations (Figure 1) show that the interaction of concrete with carbonate-bicarbonate shelter water results in carbonation of high-calcium cement phases, accompanied by a decrease in dissolved carbonate. As a consequence, secondary uranium minerals precipitate and Sr_{aq} concentration drops as a result of $(Ca,Sr)CO_3$ formation. Also, Mg_{aq} concentration in the shelter water is close to saturation with concrete phases. Si_{aq} and Al_{aq} exceed, while Ca_{aq} does not approach the concrete saturation values. Evidently, this can lead to Ca leaching via portlandite dissolution, although aluminosilicate phases of the concrete are sufficiently stable in this environment. These results are confirmed by observations of real concrete after a 10-year period of interaction with water inside the shelter. Corrosion of the concrete was never observed to deteriorate the structural stability of the shelter.

5.2 Concrete/aqueous solution/boron interaction

The concrete/aqueous solution/boron system was modeled to estimate the behaviour of a dissolved neutron moderator in an interaction pathway inside the shelter. This is important for the development of possible technological approaches for removal of fuel-containing materials (FCM) from the shelter, which is a crucial step towards transforming it into an environmentally safe site. At present, chemical dissolution (leaching) of some FCM varieties is suggested as a feasible approach to solve this problem.

The shelter waters (Table 2) and carbonate reagents used for *in situ* uranium leaching (Mamilov et.al. 1980) are comparable with respect to alkalinity and ionic composition. Although the leaching reagents are 2 to 5 times more concentrated, the calculated models show that during interaction between Portland cement and the typical soda reagent, the concrete remains stable. To investigate the behaviour of dissolved boron interacting with concrete, 200 g of H_3BO_3 per 1000 g of H_2O were added to the model system (Portland cement and 0.8 m Na_2CO_3 + 0.25 m $NaHCO_3$ aqueous solution). Figure 2 demonstrates some results of the calculations for different solid/water ratios ranging from 10^{-4} to one. At log (solid/water) up to -2, the phases of ordinary Portland cement (OPC) are not stable and only secondary minerals are present, such as ferrihydrite, kaolinite and Ca, Mg carbonates. B_{aq} is controlled by sodium (borax) and calcium ($CaB_3O_4(OH)\cdot 3H_2O$) borates. In the narrow solid/water range, danburite is stable. At equilibrium with borax, B_{aq} concentration is about 8 g/L, decreasing to about 5 g/L with Hb and Db precipitation. When OPC phases become stable, datolite is formed, accompanied by a sharp drop of B_{aq} (<0.1 mg/L).

6. CONCLUSIONS

The proposed multiphase solid solution-aqueous solution thermodynamic model for Portland cement, based on Gibbs energy minimization, provides a simple yet rigorous description of published solubility data. The model can be used to predict the chemical equilibria of concrete in complex systems such as the hydrochemical media of the shelter interior.

The model results show that Portland cements are sufficiently stable in the aqueous environment of the shelter, as well as with respect to carbonate chemical reagents, which could be used for leaching of uranium and other radionuclides from FCM.

The calculations demonstrate that concrete can essentially influence physical-chemical conditions in the shelter interior. The interaction of contaminated shelter waters with cement materials could cause precipitation of radionuclide-bearing secondary minerals. This process would decrease dissolved strontium and uranium concentrations, although the surface of the concrete will be contaminated.

In the application of leaching technology for FCM removal, the equilibration of uranium- and boron-bearing alkaline carbonate reagents with high calcium cement materials may result in the formation of the weakly soluble minerals $Na_2U_2O_7$, danburite, and datolite on the concrete surfaces. However, coprecipitation of uranium with boron clearly will not increase criticality and nuclear danger.

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Table 1. Results of strength studies of the shelter concrete (Zhudkov *et al.* 1993)

N	Type of concrete	Temperature	Dose (Roentgen)	Strength MPa
1	"Old"	ambient	Low	35-45
2	"Old"	250-300 °C	?	27
3	"Fresh"	ambient	Low	16-28
4	"Fresh"	ambient	$(2\text{-}6)\bullet 10^7$	47
5	"Fresh"	ambient	$(1\text{-}4)\bullet 10^8$	52

Table 2. Composition of typical shelter water (Abrams *et al.* 1998)

Sample #	pH	Na^+ mg/l	K^+ mg/l	Ca^{+2} mg/l	Mg^{+2} mg/l	Fe mg/l	U mg/l	Si mg/l
13	7.61	862	46	24.4	12.7	<0.1	1.7	12.5
20	9.72	273	526	5.2	9.5	<0.1	1.4	8
21	10.58	5346		43.5	21.4	<0.1	7.7	n.d.

Sample #	Cl^- mg/l	SO_4^{-2} mg/l	CO_3^{-2} mg/l	HCO_3^- mg/l	PO_4^{-3} mg/l	TDS mg/l	Oxidant demand, mg/l O_2
13	839	130	<5	321	46.2	2281	48
20	138	200	200	687	4.8	2045	31
21	963	880	1814	4300	8.4	13380	n.d.

(n.d. = not determined)

Table 3. Values of $\Delta G°_{298.15}$ for $Ca(OH)_2°$ and Cement Hydrate Solid Components

Components	*Cement Nomenclature	$\Delta G°298.15$ (J/mol)	Comments
$Ca(OH)_2°(aq)$	CH	-884819	Estimated (Sinitsyn et al. 1998a) from portlandite solubility
$CaH_2SiO_4 \cdot NaOH$	$CN_{0.5}SH_{1.5}$	-2194864	Estimated (Sinitsyn et al. 1998a) using solubility of CSH in NaOH solutions and cement pore water compositions data
$Ca_{0.9}SiH_{1.8}O_{3.8}$	$C_{0.9}SH_{0.9}$	-1681325	Estimated (Sinitsyn et al. 1998a) from published data on solubility of CSH in water
$Ca_{1.7}H_{3.4}SiO_{5.4} \cdot 4H_2O$	$C_{1.7}SH_{5.4}$	-3351539	Estimated (Sinitsyn et al. 1998a) from published data on solubility of CSH in water
$Ca_3Al_2O_6 \cdot 6H_2O$	C_3AH_6	-5020021	From solubility data (Bennett et al. 1992, Atkins et al. 1992)
$Ca_3Fe_2O_6 \cdot 6H_2O$	C_3FH_6	-4147549	From $LogK_{sp}$ [1]
$Ca_3Al_2Si_3O_{12}$	C_3AS_3	-6237668	Estimated (Sinitsyn et al. 1998a) from solubility of gehlenite (Bennett et al. 1992, Atkins et al. 1992)
$Ca_2Al_2SiO_7 \cdot 8H_2O$	C_2ASH_8	-5716998	From solubility data (Bennett et al. 1992, Atkins et al. 1992)
$Ca_4Al_2SO_{10} \cdot H_2O$	$C_4A\underline{S}H_{12}$	-7779300	From solubility data (Atkins et al. 1992)
$Ca_6Al_2S_3O_{12}(OH)_{12}$	$C_6A\underline{S}_3H_{12}$	-9050701	From solubility data (Bennett et al. 1992, Atkins et al. 1992)
$Mg_4Al_2O_7 \cdot 10H_2O$	M_4AH_{10}	-6402149	From solubility data (Bennett et al. 1992, Atkins et al. 1992)

* A - Al_2O_3, C - CaO, F - Fe_2O_3, H - H_2O, M - MgO, $\underline{S}$ - SO_3, S - SiO_2

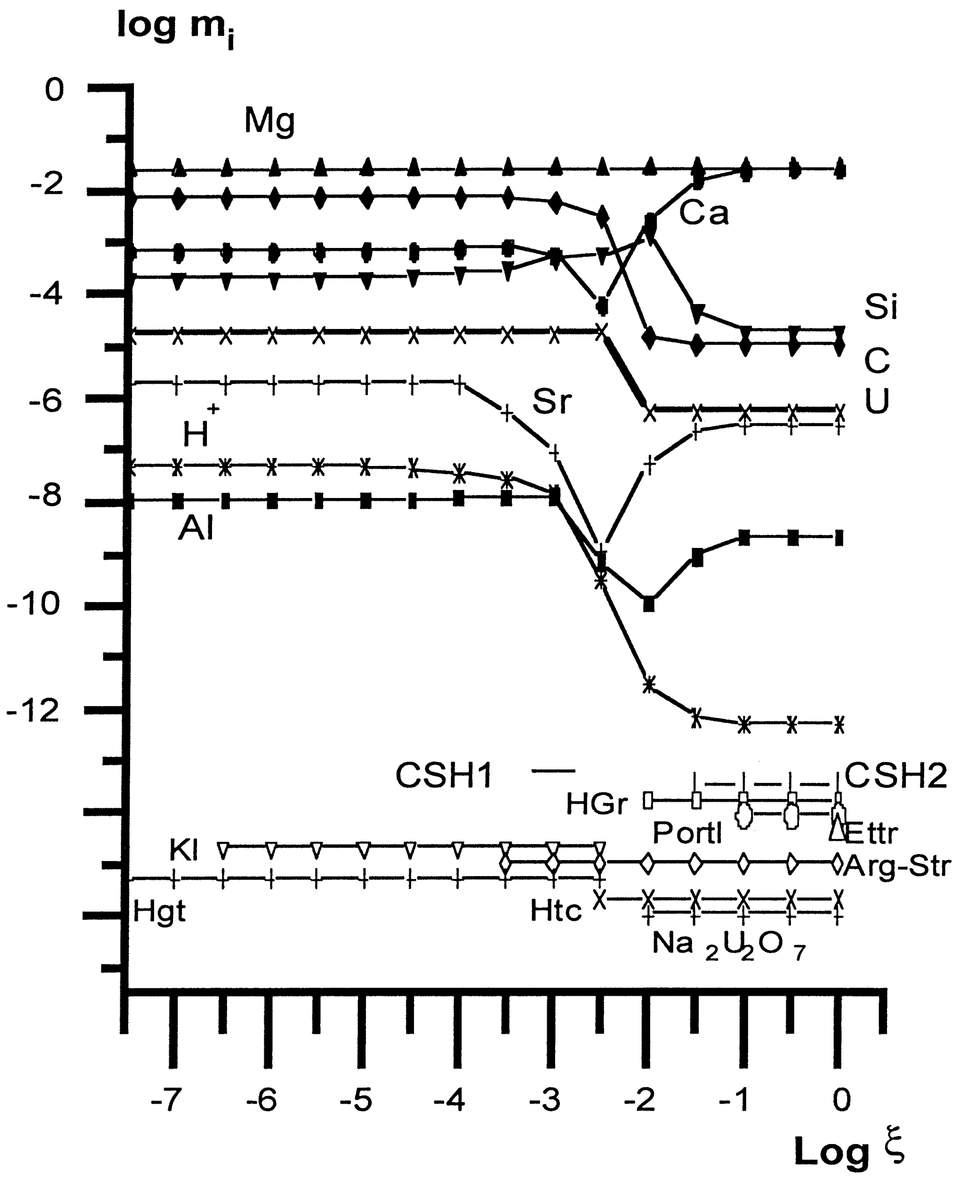

Figure 1. Modelled equilibrium total dissolved element concentrations (mol/kg H_2O) and phase assemblages formed as a result of interaction of Portland cement with the shelter water sample #13 as function of the solid/water mass ratio ξ at 25°C, 1 bar. The equilibrated solid phases are CSH1 and CSH2 (solid solution phases of amorphous calcium silicate hydrogel), HGr (hydrogarnet solid solution), Portl (portlandite), Ettr (ettringite), Htc (hydrotalcite), Kl (kaolinite), Hgt (hydrogoethite), and $Na_2U_2O_7$.

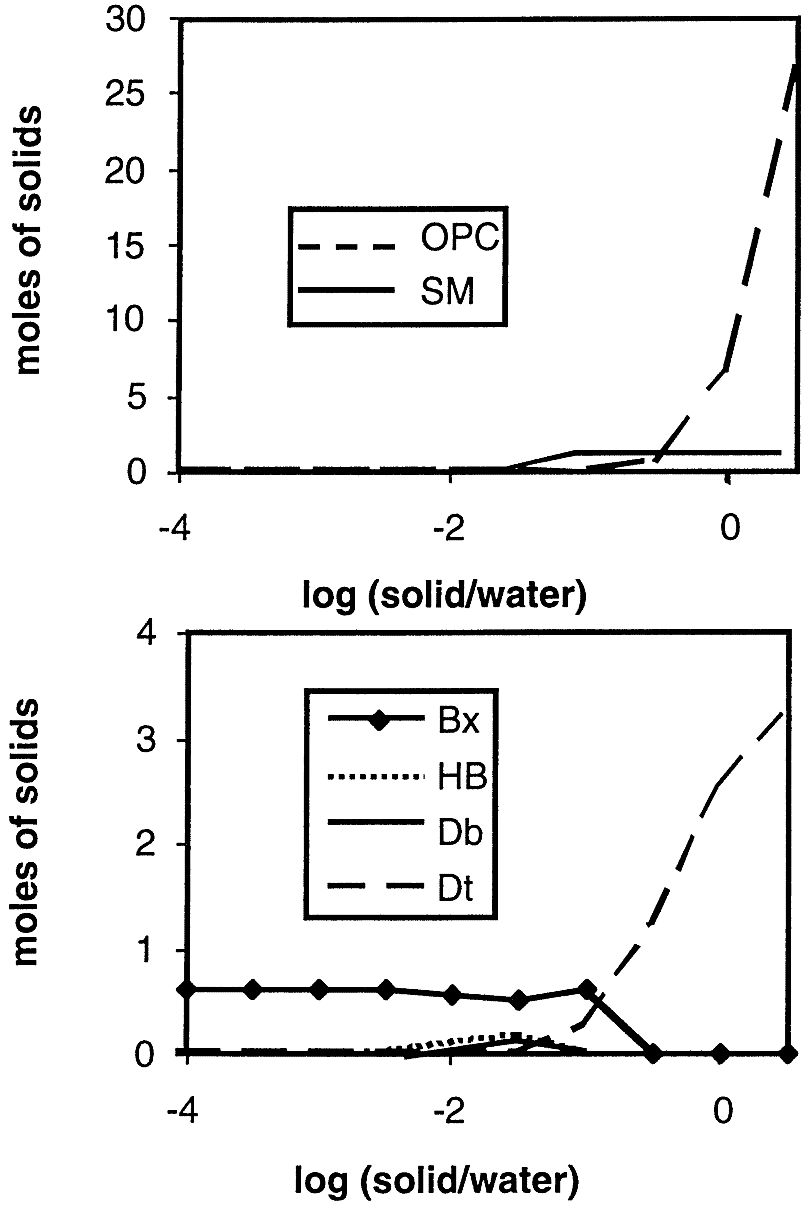

Figure 2. Modeled equilibrium phase assemblages formed as a result of interaction of Portland cement with the soda aqueous solution (0.8m Na_2CO_3 + 0.25m $NaHCO_3$) and 200g H_3BO_3 at 25°C, 1 bar. A: equilibrium total number of moles of Portland cement phases (OPC) and secondary minerals (SM). B: equilibrium number of moles of boron-containing minerals: borax (Bx), hydroboracite $CaB_3O_4(OH)_3 3H_2O$ (HB), danburite (Db), and datolite (Dt).

RADIOACTIVE WASTE DISPOSAL IN THE UNITED KINGDOM: USE AND APPLICATION OF CEMENTS AND BACKFILL MATERIALS

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1. INTRODUCTION

1.1 Regulation of radioactive waste disposal in the UK

In the United Kingdom, disposal of solid radioactive waste requires an authorization under the Radioactive Substances Act of 1993 (RSA93). Responsibility for granting such authorizations rests with the Environment Agency of England and Wales (in the case of disposal facilities in England and Wales), and with the Scottish Environment Protection Agency (SEPA) and the Department of the Environment for Northern Ireland (for disposals in Scotland and Northern Ireland, respectively). An authorization will be granted if the relevant agency judges that the applicant has given adequate assurance of protection of the public and the environment from hazards that might arise as a result of the disposal. Operational nuclear safety, and planning aspects, are regulated separately.

The developer or operator of any facility is solely responsible for preparation of submissions in support of an application for disposal of solid radioactive waste under RSA93, and the Environment Agency will assess these submissions against the requirements of the Act. The Environment Agency, SEPA, and the Department of the Environment for Northern Ireland have issued guidance on the principles and requirements against which the agencies will assess an application for authorization under RSA93 relating to a disposal facility on land for low and/or intermediate level radioactive wastes (Environment Agency *et al.* 1997). The principles and requirements in the guidance document will be applied in setting limits and conditions of authorizations for any new development and when reviewing current authorizations for future disposals at existing facilities.

1.2 Categorization of radioactive wastes in the UK (RWMAC, 1998)

Very low-level waste

This is waste that can be safely disposed of with ordinary refuse.

Low-level waste (LLW)

This is waste containing radioactive materials not acceptable for disposal with ordinary refuse, with <4 GBq/tonne alpha activity or <12 GBq/tonne beta/gamma activity.

Intermediate-level waste (ILW)

This is waste with radioactivity levels exceeding the upper boundaries for low-level wastes, but which does not require consideration of heat generation in the design of storage or disposal facilities. A significant proportion of the wastes categorized as intermediate level are produced as a result of reprocessing the spent nuclear fuel from the United Kingdom's first generation of gas-cooled 'Magnox' power reactors. Consequently those wastes contain relatively high quantities of long-lived actinides and correspond broadly to transuranic (TRU) wastes as defined in other national programmes.

High-level waste (HLW)

This is waste in which the temperature may rise significantly as a result of its radioactivity so that this factor must be taken into account in designing storage or disposal facilities.

1.3 Current position on solid radioactive waste disposal in the United Kingdom

1.3.1 High- and intermediate-level radioactive wastes

No sites have been identified within the UK for the final disposal of either HLW or ILW. The House of Lords Select Committee on Science and Technology is undertaking an enquiry into the management of nuclear waste in the UK. This investigation was prompted by the decision not to give planning approval for an underground research laboratory near Sellafield and subsequent curtailment of the development of a deep disposal facility for ILW. The starting point for the enquiry is The Parliamentary Office of Science and Technology (POST) report (1997). The Committee is considering all possible options for the management of the UK's ILW and HLW. The outcome of the enquiry, expected in the latter part of 1998, may feed into any subsequent government paper, which will be subject to a period of public consultation.

1.3.2 Low-level radioactive waste

The majority of the LLW generated within the UK is disposed of at the Drigg site in Cumbria. This site is operated by British Nuclear Fuels Limited (BNFL) and has accepted LLW since 1959. The waste is from a wide range of sources, including the BNFL Sellafield reprocessing and waste management site, nuclear power stations, nuclear research sites, Ministry of Defence facilities, hospitals, research establishments, and other industrial organizations. The type of waste is varied, including paper, plastics, scrap metal, rubble, protective clothing, soil, and redundant equipment.

2. USE OF CEMENT-BASED MATERIALS IN DEEP GEOLOGICAL DISPOSAL OF INTERMEDIATE AND LOW-LEVEL RADIOACTIVE WASTES

2.1 Background

United Kingdom Nirex Limited (Nirex) is responsible for the development of a deep geologic repository for the disposal of the UK's intermediate-level and certain low-level, solid radioactive wastes.

Consistent with other national programmes, Nirex has developed a multiple-barrier disposal concept whereby engineered and natural barriers would work in conjunction to provide the necessary long-term isolation and containment of the radionuclides in the wastes to ensure their safe disposal. Typically the wastes would be encapsulated within a cementitious grout inside an engineered steel or concrete waste container. The waste form itself, the encapsulating grout, and the waste container would each be expected to afford some degree of containment of the radionuclides in the wastes, according to the radionuclide content and the physical and chemical characteristics of the wastes. However, the main contribution to containment of long-lived radionuclides by the engineered barrier system is sought from a specially formulated cement-based backfill, which would be placed around the packaged wastes in disposal vaults. The backfill material, Nirex Reference Vault Backfill (NRVB), is described in more detail in Section 2.3 and in the patent application (UK Patent Office 1997).

2.2 Rationale for the use of backfill materials

The UK's inventory of ILW currently designated for deep disposal has a projected planning-basis volume of 260,000 m^3. The appreciable volume of ILW would contain materials of diverse physical and chemical forms, including metals and alloys - some of which are relatively reactive (e.g., magnesium), ceramics, sludges and resins, and organic materials such as paper and manmade polymers (Nirex 1996). With reference to the "groundwater pathway" for the potential transport of radionuclides from a deep repository, it has been considered impracticable to invoke high-integrity physical barriers to contain the radionuclides in such wastes over the necessary long-term period, during which they would undergo considerable physical and chemical evolution. Consequently, it was determined that the principal contribution to long-term containment in the repository near field would derive from chemical conditioning, both of the groundwater that would infiltrate the near field and of the surfaces of materials in the near field. The NRVB was specified to achieve those objectives; it is described in more detail below and in the development report (Nirex 1997a).

2.2.1 Chemical Properties

pH buffering

The NRVB has been specified to ensure that any water contacting radionuclides in wastes will be buffered to a relatively high pH so that the solubility of the key actinide radioelements will be suppressed. The two radioelements of particular interest in this regard, given their relatively high inventories in the UK's ILW, are plutonium and uranium. The backfill is designed to buffer the pH of water within its porous structure over the long time periods of interest (more than a million years). The approximate range of pH is required to be 12.5 to 10, over which the solubilities of plutonium and uranium are at a minimum as a function of pH (Nirex 1995a). Further, the NRVB is designed to generate a sufficiently high concentration of hydroxyl ions to suppress the effects of dissolved concentrations of ligands, such as carbonate ions that could increase the solubilities of the radioelements.

Radionuclide sorption

The NRVB is also specified to have a high surface-active area to exploit the sorptive properties of certain minerals in cementitious materials toward a number of important radioelements. By creating a highly sorptive medium as a backfill, the containment achieved by suppression of radioelement solubilities would be enhanced (Nirex 1995b).

Homogeneous conditioning

The heterogeneous physical and chemical characteristics of the UK's ILW could result in the creation of widely different water chemistries through the repository near field. This situation would lead to a lack of predictability of the dissolved radionuclide source-term when considering the safety of disposal. Using a backfill that would create homogeneous conditions of water chemistry throughout the near field has obvious benefits in this regard. The required conditions are achieved as a consequence of the backfill having a chemical buffering potential in combination with suitable mass transport properties, in particular a relatively high connected porosity and a suitable hydraulic conductivity (Harris and Nickerson 1995). Such backfill properties could ensure that the required chemical containment would be available throughout a repository and that this containment could be evaluated reliably in associated performance assessments.

Corrosion of steel

Once a deep repository has been filled with wastes, backfilled, and sealed, the oxygen introduced in air and dissolved in the groundwater surrounding the excavations would be consumed relatively rapidly by corrosion, leading to anaerobic conditions. Naish *et al.* (1995) concluded that under these conditions only uniform corrosion of steels can occur, and the rates of such corrosion for steels in simulated groundwater equilibrated with NRVB are below 1 μm per year for any of the expected conditions in the near field. Naish *et al.* (1995) found that the corrosion rates of the stainless steels from which a large proportion of the waste containers are to be fabricated are less than 0.01μm per year, even under extreme conditions of temperature and groundwater salinity. This finding has led to predictions of times in the range of 9,000 to 16,000 years before the stainless steel waste containers would be consumed by corrosion (Porter *et al.* 1994).

In the period before anaerobic conditions would be established (i.e., under aerobic conditions), localized corrosion of steels is considered more significant than uniform corrosion. This is particularly relevant under conditions of relatively high groundwater salinity, which are often encountered in deep geological formations. The alkaline conditions provided by a suitable backfill serve to protect steels from such localized attack to the extent that hypersaline conditions would be required to cause pitting of stainless steels. The protection mechanism depends on the creation of a passive oxide film at the steel surface, which is broken down when the chloride to hydroxyl ion chemical activity ratio exceeds a certain value (Verbeck 1975). Carbon steels are more sensitive, and their corrosion would require less extreme salinities at elevated temperatures (>50°C), but even in that case the alkalinity afforded by NRVB has been shown to limit the development of pitting.

Microbial activity

Although microbial action may be beneficial in the long term with respect to repository performance because it could destroy soluble organic complexants, it is considered undesirable to have the potential for rapid, microbially mediated reactions. Using a backfill that creates an extreme chemical environment (high pH) compared with common terrestrial environments may help to ensure that only a small proportion of the total microbial population initially present in the wastes would survive in contact with the cementitious pore water in the backfill.

2.2.2 *Physical protection*

The large number of waste packages that would be involved in the disposal of the UK's ILW demands that in any practicable repository the packages would be stacked vertically and that the stacks of packages would be in a close proximity to one another. By surrounding the stacked packages with a backfill that would retain some physical integrity, even after long-term evolution in advecting groundwater, the packages would be protected from damage by contact with other packages.

2.2.3 *Control of mass transport*

By developing a backfill with suitable mass transport characteristics, in particular hydraulic conductivity, the flow of groundwater through the repository near field could be controlled. Given the relatively large dimensions of the disposal vaults that are envisaged for a repository for ILW, it is likely that localized inflows of groundwater would be experienced in the vault walls. A suitably designed backfill could ensure that the adjacent waste packages would be protected from the adverse effects of exposure to such localized flow.

Transport of radionuclides in particulate or colloidal form has the theoretical potential of producing a more significant release than transport in solution. A backfill can be designed to limit the transport of particulates and colloids within and away from the near field of a repository. This has an added benefit when considering the potential accumulation of particulates of fissile materials in wastes as a scenario within a criticality safety assessment.

2.3 Specification of NRVB

The NRVB is a four-component mixture (including water), comprising:

Ordinary Portland Cement	450 kgm^{-3}
Limestone Flour	495 kgm^{-3}
Lime	170 kgm^{-3}
Water	615 kgm^{-3}

A four-component mixture is favoured because it enables a number of required characteristics to be achieved by adjusting the relative proportions of the components.

As noted in Section 2.2.1, a prime requirement of the NRVB is that it should act as a chemical barrier to the migration of long-lived radionuclides by providing a high pH in infiltrating groundwater to suppress the solubility of key radioelements. This requirement was converted into a specification that in the long-term the pore water within the NRVB should be maintained at pH 10.5 or greater. It was found that this buffering capacity would be achieved by a mixture containing a minimum of 400 kgm^{-3} ordinary Portland cement (OPC) or its equivalent in terms of calcium hydroxide. The content of OPC and lime satisfied that requirement.

Engineering requirements of the cured backfill material were that

- it should develop relatively high early strength so that, if necessary, it could provide adequate support for the placement of successive waste packages and backfilling layers; and
- it should develop relatively low long-term strength to facilitate retrieval of wastes should this be deemed desirable.

The first of these requirements was met by using a relatively high water to cement ratio of (1.37:1), and the second was met by using OPC, which was known to have only a small long-term gain in strength.

Engineering requirements of the backfill in fluid form were that

- the workability should be suitable for flow without vibration into a horizontal space 5 m × 3 m × 75 mm (high), taken as typical of the space under a package;
- the mix should be suitable for pumping along a horizontal pipeline at least 250 m in length, taken as a typical maximum delivery distance along a disposal vault; and
- bleeding/settlement should not exceed 2%, to reduce the possibility of under-package void formation and surfaces of weakness in the cured backfill.

To achieve the balance between fluidity and bleed, and at the same time retain the required pH buffering and physical strengths, a fourth component, limestone flour, was required.

The high water to cement ratio in the NRVB results in a relatively porous material with a large proportion of the pores forming an interconnected network. This structure is consistent with a number of highly desirable properties identified in Section 2.2 (e.g., high surface-active area for sorption) and others such as relatively high permeability with respect to gases (to allow gases generated from the wastes to escape from the repository without significant over-pressurization and possible disruption of the engineered repository system).

2.4 Status of research into NRVB

Since its development was initiated in 1989, the NRVB has been the subject of substantial research programmes. This strategy reflects its importance in the overall Nirex repository concept. The research programmes cover the following areas: engineering performance; pH buffering performance, radionuclide solubility, radionuclide sorption, microbial activity, mass transport properties, colloid formation, thermal properties, and hydrothermal ageing. It is beyond the scope of this paper to record the details of research work in each area; a brief summary is given below.

2.4.1 Engineering properties

To demonstrate that the NRVB can be produced and placed, to the required quality, in large quantities under realistic repository operation conditions, the following tests have been carried out (Nirex 1997a):

(a) large-scale mixing (of the four-component mixture) using a commercially available grout mixer;

(b) long-distance pumping under adverse conditions of low-line pressure and narrow pipe diameter;

(c) free-flow testing under simulated large waste packages, giving good quality contact with the simulated package base;

(d) large-scale, free-flow testing in a simulated array of waste packages, representing the largest single backfilling operation currently envisaged; and

(e) demonstration of package retrieval from cured backfill, using water-jetting techniques.

Research has also been conducted to identify the principal mechanisms that could lead to the development of cracks in the cured backfill (Nirex 1997a). The cracks generated by different mechanisms have been characterized in terms of their dimensions and mass transport properties for use in repository performance assessment studies.

2.4.2 pH buffering performance

Clearly it is very important to test whether the NRVB would deliver the required chemical containment through pH buffering of infiltrating groundwater under realistic conditions of long-term evolution. Thermodynamic modelling has been conducted to determine the evolution of phases within the NRVB and the pH which they would establish in equilibrium with contacting groundwater (Harris 1997). This modelling takes account of the following factors:

- dissolution of chemical constituents in the advecting groundwater system;

- reactions with dissolved species in the groundwater;

- reactions with acidic products generated from the degradation of organic materials in the wastes (including generated carbon dioxide gas);

- "pozzolanic" reactions with cement minerals present in some waste encapsulants.

This modelling has been tested by characterizing the products of relevant reactions, by measuring the pH of simulated groundwater in equilibrium with phases of interest, and by conducting accelerated tests representing the flow of groundwater through backfill over the very long time scales of interest (Nirex 1997a).

A simpler, empirical buffering model has been developed, employing the assumption that pH buffering is initially achieved through the presence of portlandite (calcium hydroxide) and thereafter by calcium-silicate-hydrate (CSH) gels of varying compositions. This model is used to guide decisions in studies to optimize repository design.

2.4.3 Radionuclide solubility

The solubilities of all important radioelements have been determined in simulated groundwater equilibrated with NRVB. The solubilities have been determined as a function of the pH of the aqueous system, to simulate the evolution of the NRVB/groundwater chemistry, and as a function of ionic strength and temperature (Baston *et al.* 1996). To ensure a proper understanding of the solubility data, the controlling thermodynamic processes are modelled using the HATCHES thermodynamic database (Cross and Ewart 1990) in conjunction with the geochemical program HARPHRQ (Haworth *et al.* 1995).

2.4.4 Radionuclide Sorption

The distribution ratio between the NRVB and simulated groundwater has been determined for important radioelements (Bayliss *et al.* 1996). Both batch-sorption and through-diffusion experimental procedures have been used to ensure an understanding of bias in the results through the creation of reactive surfaces or the use of unrealistic water/backfill ratios in experiments.

2.4.5 Microbial activity

The growth of microbial organisms in association with NRVB has been tested under a range of conditions to characterize conditions favourable to growth (Nirex 1995a). This allows the effects of the predominant forms of growth on chemical containment performance to be evaluated.

2.4.6 Mass transport properties

To test the key mass transport properties required variously to deliver chemical containment and conditioning throughout the repository near field, and to allow gas to escape without significant over-pressurization, detailed studies have been undertaken to determine the porosity, water and gas permeabilities, and the diffusion coefficients of marker species (Harris and Nickerson 1995). A number of the measurements made in these experiments provide data that are required for models used in repository performance assessment studies.

2.4.7 Colloid formation

The potential of the NRVB to act as a source of colloids has been investigated through leaching experiments using various water chemistries (Nirex 1995a). Although very low concentrations of colloidal particles were generated, even under extreme conditions favourable to their generation, the sorption of key radioelements to the colloidal material has been characterized to define the potential for radionuclide transport (Nirex 1997a).

2.4.8 *Thermal properties*

Radiogenic heating and the heat generated during NRVB hydration must to be taken into account when assessing repository safety in both the operational and post-closure periods. With respect to the operational and early post-closure periods, it is necessary to note that the material may not be water-saturated. The heat of hydration, thermal conductivity, and specific heat capacity of NRVB have been measured using an appropriate range of experimental methods and conditions (Nirex 1997a).

2.4.9 *Hydrothermal aging*

Over an extended time, the NRVB will age such that the metastable, poorly crystalline CSH gel will tend to crystallize to form more stable mineral phases, which may have modified properties with respect to the pH buffering performance, sorptive behaviour, and surface area. Preferential leaching of calcium from the NRVB into groundwater would lower the net calcium to silicon ratio in the repository, and this would influence the crystallization process. Accordingly, CSH gels of various calcium to silicon ratios have been hydrothermally aged in experiments designed to investigate the pH buffering behaviour of mineral phases that would be expected to be present at long times in the future (Atkinson *et al.* 1995).

2.5 REPRESENTATION OF NRVB IN PERFORMANCE ASSESSMENT

Nirex has developed a probabilistic systems analysis program, MASCOT (Sinclair and Agg 1995) to calculate post-closure performance indicators with respect to a deep repository. The repository system is modelled as consisting of three compartments, consisting of the near field, the geosphere, and the biosphere. The NRVB is represented in terms of its key characteristics within the representation of the near field. The model derived for representation of the near field is a source-term model, describing the flux of radionuclides as a function of time, that would be transported out of the near field into the surrounding rocks. The brief description of the approach given here is from the most recent performance assessment (Nirex 1997b); earlier assessment studies adopted different approaches in some aspects.

2.5.1 *Base-case source-term model*

The source-term model assumes that the contents of each category of repository vault (there are different conceptual vault designs for different waste packaging arrangements) are homogeneous. This means that the model conservatively assumes no initial period when groundwater would displace any air in the near field, infiltrate waste packages, dissolve radionuclides within the waste packages, and come to equilibrium with water in the surrounding backfill. The model accounted for radioactive decay and ingrowth, solubility limitation and the effects of sorption to NRVB, and the effects of complexation of radionuclides by products resulting from the degradation of organic materials in wastes. The flux of radionuclides from the repository near field was calculated by multiplying the calculated uniform concentration of the radionuclides in the porewater of the repository vaults by a groundwater flux. Key features of the source-term model relevant to the representation of the NRVB are summarized below.

It was assumed that groundwater flow through the near field removed radionuclides in proportion to their equilibrium concentration. Equilibrium between radionuclides in the pore water and those sorbed onto solid phases was assumed to be continuously re-established by rapid dissolution from the waste or desorption from the backfill. The processes of dissolution and desorption were assumed to continue until the inventory of each radionuclide was completely exhausted by radioactive decay and groundwater leaching. This approach ignores the potentially beneficial processes of irreversible sorption or mineralization. It was assumed that the near-field pore water was conditioned to a high pH and low redox potential. The behaviour of each element was characterized by a solubility limit and by a sorption coefficient appropriate to the chemical conditions. These parameters were defined as probability density functions to take account of relevant uncertainties. The chemical conditions, and hence the solubility and sorption of each element, were assumed to remain constant for the entire period addressed.

When deriving sorption distribution coefficients for radionuclides, consideration was given to the aging of the backfill surfaces prior to radionuclide sorption by assuming a significantly reduced sorption capacity compared with that measured in experiments. Account was also taken of results of some experiments on the mass transport properties of NRVB, which indicated that the process of anion exclusion might cause anionic species to have access to only a fraction of the total pore volume in the NRVB.

2.5.2 *Bias audit*

The Nirex 97 post-closure performance assessment included a bias audit and reported quantitative and qualitative evaluation of the biases identified. The studies relevant to the NRVB are summarized below:

(a) An evaluation was conducted of the physical containment that would be afforded by the waste packages. This evaluation included an examination of the effects of the permeability contrast between encapsulating grouts and the NRVB.

(b) An evaluation was conducted of the non-uniform distribution of wastes in a repository vault.

(c) The time evolution of pH corresponding to evolution of the NRVB was evaluated. This highlighted the importance of understanding sorption of some radioelements on mineral phases that would be present at a lower pH.

(d) The effects of the formation of different types of cracks in the NRVB were evaluated, in particular with respect to the channelling of groundwater flow and the diffusion of radionuclides into such preferential flowpaths. An existing research programme was judged to be capable of addressing the key uncertainties identified.

(e) The absence of a treatment of mineralization in association with NRVB aging was viewed as significant, and almost certainly pessimistically biased because the potential for a radionuclide to become irreversibly incorporated in crystallizing mineral phases would be likely to afford significantly greater containment than would reversible sorption to surfaces.

(f) The effect of high-pH groundwaters, derived from the NRVB, on the surrounding rocks has not been included in performance assessment to date, although this has been the subject of considerable research. Work to date shows that the high-pH groundwater/rock interaction is likely to result in the creation of mineral phases with beneficial sorption properties. Those minerals would result in the sealing of flowing features and general reduction in the permeability of the zone around the repository.

2.5.3 Gas pathway

The parameters used in models to establish a gas pathway source term were, where relevant, the same as those used for the groundwater pathway. Relative permeabilities were derived for the modelling of gas/water fluid flow in the repository. An important feature of the assessment was the representation, based on research conducted to date, of the NRVB as a sink for carbon dioxide gas, including that containing ^{14}C generated from the degradation of the wastes.

3. THE USE OF WASTE CONDITIONING AT THE BNFL LOW-LEVEL WASTE DISPOSAL SITE AT DRIGG, CUMBRIA, UK

3.1 Background

BNFL is responsible for the operation of a near-surface disposal facility for solid low-level radioactive waste at the Drigg site in Cumbria, northwest England. Historically, waste had been dumped into trenches excavated into glacial sediments overlying a sandstone aquifer. These trenches are now covered by an interim cap incorporating a plastic membrane to minimize water ingress. The last of the trenches was filled in 1995. Waste is now containerized, compacted, and grouted prior to consignment to a concrete-lined vault. BNFL has plans to build additional vaults to accept future wastes. The site is expected to remain operational until around the middle of the next century. Ultimately, the disposal area will be covered by a long-term closure cap.

A major consideration in site development is the objective of significantly increasing the projected lifetime of disposal at Drigg, and in particular ensuring a solid, low-voidage waste form to support the long-term site closure cap. Therefore, BNFL has adopted the following steps to pretreat and condition waste at the Waste Monitoring and Compaction (WAMAC) Plant at Sellafield (Donn *et al.* 1994):

- the waste is precompacted into 1 m^3 boxes;
- the 1 m^3 boxes and 200 l drums are volume-reduced by high-force compaction (typically with pressure equivalent to 1000 tonnes on a 200 l drum of waste) into pucks;
- the pucks and oversized waste are loaded into 20 m^3 external volume half-height ISO freight containers.

The containers are transferred to the Drigg where:

- the ISO containers are grouted; and

- the dense waste form is stacked in the vault.

To eliminate point loads on the base of the vaults originating from stacks of containers (weighing up to 42 tonnes each) as well as the weight of the overlying cap, the load is distributed through the waste form itself rather than through the container structure. To facilitate this, the top of the waste in the containers is grouted to ensure an even surface. A schematic of a grouted ISO freight container containing supercompacted LLW is shown in Figure 1.

Efficient stacking in the vaults means that void volume between the containers is very small. Any remaining spaces, for example adjacent to walls, will be filled with granular fill to minimize voidage.

3.2 Rational for the use of grout materials

The grout has been designed on a process engineering basis so that the:

- slurry prior to setting has very low viscosity, making it conducive to process handling; and

- the material is capable of filling accessible void spaces around the waste.

The primary purpose of filling in voidage space with grout is that the final waste form will minimize the potential for significant settlement of the final site closure cap.

The grout is composed of a 3:1 PFA:OPC ratio-based formulation with a relatively high water content and use of a plasticizer to improve operability.

3.3 Representation of the grout in performance assessments

There are four main reasons why grout may be represented in performance assessment (Figure 2). All of these reasons relate to its influence on radionuclide migration, and all can be represented in performance assessments if required. The following sections discuss how the Drigg grout is represented in performance assessments for the site.

3.3.1 Physical properties

The Drigg grout has been designed for its flow properties, which make the grout relatively brittle and therefore likely to crack. Therefore, the grout is **not** considered to provide a *physical* barrier to radionuclide migration in Drigg performance assessments. Considering the internal stresses and strains likely to be generated within the waste package and the vault in general through processes such as corrosion, this assumption is not unreasonable.

The major contribution made by the physical properties of the grout to the Drigg performance assessment is the reduction of voidage within the vaults. Considerable work has been devoted to investigating the void-filling properties of the grout. Prior to the construction of the facility, trials were performed on a range of scales from laboratory- to full-scale. More recently, an inactive grouted ISO freight container was cut open to demonstrate successful penetration of the grout into void spaces (Figure 3). The limitation of voidage within the vaults is a requirement for disposal. The requirement states that no waste should have a residual voidage after grouting of greater than 10%. This leads to special requirements, particularly for oversized waste, which requires direct disposal to the vault. In that case, the grouting of internal voids within waste items may also be required (Figure 4).

The concern over voidage originates from the need to reduce settlement within the site after closure. Settlement is identified as a major failure route for any post-closure cap placed on the site because settlement may lead to cap cracking, which in turn may lead to a failure of the low-permeability water-retarding layer, resulting in increased water ingress into the site and potentially increased radionuclide migration. To feed these processes through to the Drigg performance assessment, an Engineering Risk Assessment (ERA) methodology (Garrard *et al.* 1997a, 1997b) has been developed. Through the use of fault and event trees, influence diagrams, and expert elicitation, the ERA is able to take basic engineering data and generate engineering performance data that can be utilized by conventional post-closure radiological assessments.

3.3.2 Chemical properties

Chemical conditioning

The Drigg grout was not selected on the grounds of its chemistry. However, it has a chemical component to its properties, and consequently these properties are considered in the performance assessment of the site, specifically in the source-term calculations. Any grout has a conditioning effect on any groundwater or rainwater that passes through it prior to contact with the waste. Chemical conditioning works in conjunction with other processes such as metal corrosion, microbial degradation of waste components, waste chemistry, and the initial rain and groundwater chemistries to determine the evolution of the ambient geochemistry within the near field. These processes all act in concert. For example, although the grout is likely to dominate the pH of the system, the pE is more likely to be mediated by corrosion and microbial activity. These processes, however, are pH sensitive, so their magnitude, and to some extent their products, will be influenced by the chemical influence of the grout. These processes influence radionuclide migration from the near field through their influence on radionuclide speciation and precipitation. In the Drigg performance assessment, these processes are taken into account by using the biogeochemical source term model DRINK (DRIgg Near field Kinetic code) (Manton *et al.* 1995, Humphreys *et al.* 1995, 1997). This code has the ability to simulate the evolving near-field geochemistry and its subsequent influence on radionuclide migration.

Radionuclide sorption

In addition to its impact on aqueous chemistry, the grout also provides potential sites for radionuclide sorption, thereby retarding radionuclide migration from the near field. In Drigg assessments, sorption onto grout is included by the use of K_d-based sorption representations in the DRINK source-term model.

Complexation

The high pH conditions generated by traditional high-OPC-content grouts may, under certain circumstances, interact with waste, leading to the generation of complexing agents such as isosacccharinic acid (ISA) (Greenfield *et al.* 1994, 1995). These complexants result from the chemical hydrolysis of cellulosic materials and may potentially have a significant effect on radionuclide migration from the near field. The nature of the Drigg grout and the general Drigg environment means that the generation of these complexants is not an issue and therefore is not considered in the performance assessments. The principal reasons for this are:

- low ambient temperature: Drigg vault temperatures are likely to be around 10°C; and
- grout composition: the chemical composition of the Drigg grout is such that the chemistry of the interaction with leachant waters is different from that arising from other higher alkalinity grout.

This reasoning has been supported by a series of simple batch degradation experiments in which it has not been possible to identify ISA in the presence of the Drigg grout under anerobic conditions (Table 1).

3.4 Building confidence in the performance of the grout

To build confidence in the assumptions that are made about the performance of the Drigg grout and grouted waste forms in Post Closure Risk Assessment (PCRA) calculations, a series of long-term waste simulation experiments has been constructed. These Long Term Vault Experiments (LTVE) contain high-force compacted pucks of low-level waste and a range of instrumentation to allow the determination of various parameters including:

- mild steel corrosion rates;
- stainless steel corrosion rates;
- ambient temperature for calibration purposes;
- gas generation;
- time of wetness; and
- internal strain.

There are three LTVE experiments designed to test the behaviour of grouted waste under differing conditions. Two of these experiments stand in a rainwater-filled bund to simulate saturated vault conditions. The third is kept dry but is still exposed to the elements to ensure that weathering processes can take place. The LTVEs will be monitored over several years for changes in the behaviour of the waste form.

The LTVEs will provide long-term information that will test BNFL's understanding of the physical and chemical processes affecting grouted waste forms. To develop that understanding, shorter term experiments are currently being performed. These include the following investigations:

- evolution of grout chemistry;

- metal corrosion rates in the presence of grout; and

- microbial degradation of grouted waste.

4. CONCLUDING REMARKS

Cementitious materials are used in the Nirex deep disposal programme for intermediate and selected low-level radioactive waste and at the low-level radioactive waste disposal site at Drigg, Cumbria (UK). In the Nirex programme, a cementitious backfill is proposed as a chemical conditioning agent to aid long-term isolation and containment. At BNFL's Drigg site, a grout is used as a void-filling material for waste disposed in concrete-lined vaults. Both the Nirex and the BNFL research programmes include studies on cementitious materials to support site authorization submissions under the Radioactive Substances Act of 1993. The Environment Agency has also undertaken a substantial research programme on cementitious materials for use in radioactive waste disposal to support its regulatory decision making (Glasser 1998, Glasser *et al.* 1998).

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Table 1. Generation of ISA under various chemical conditions

Preparation (Cellulose +)	Temperature (°C)*	Positive ID for ISA	Average Conc (mM)	Other Products Present
$Ca(OH)_2$	80	✓	2.4	✓
$Ca(OH)_2$	≈20	✓	0.9	✓
$CaCO_3$	≈20	✗	<0.1	✗
Drigg Grout	≈20	✗	<0.1	✗
Drigg Rainwater	≈20	✗	<0.1	✗

* Laboratory temperature

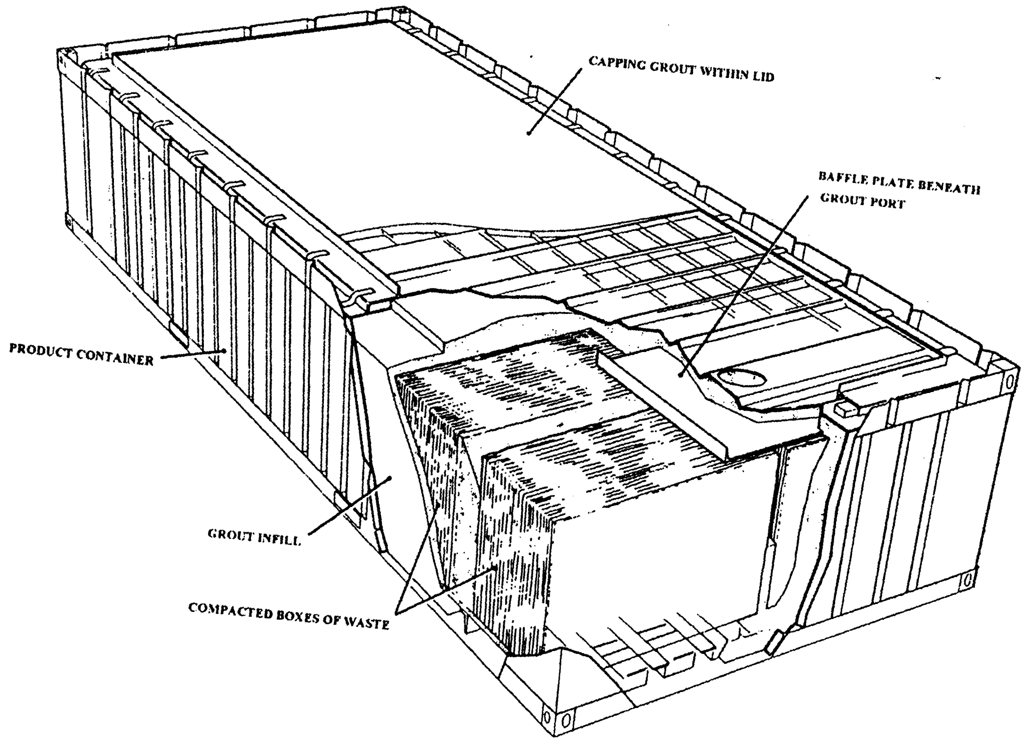

Figure 1. Schematic of grouted ISO freight container containing supercompacted LLW.

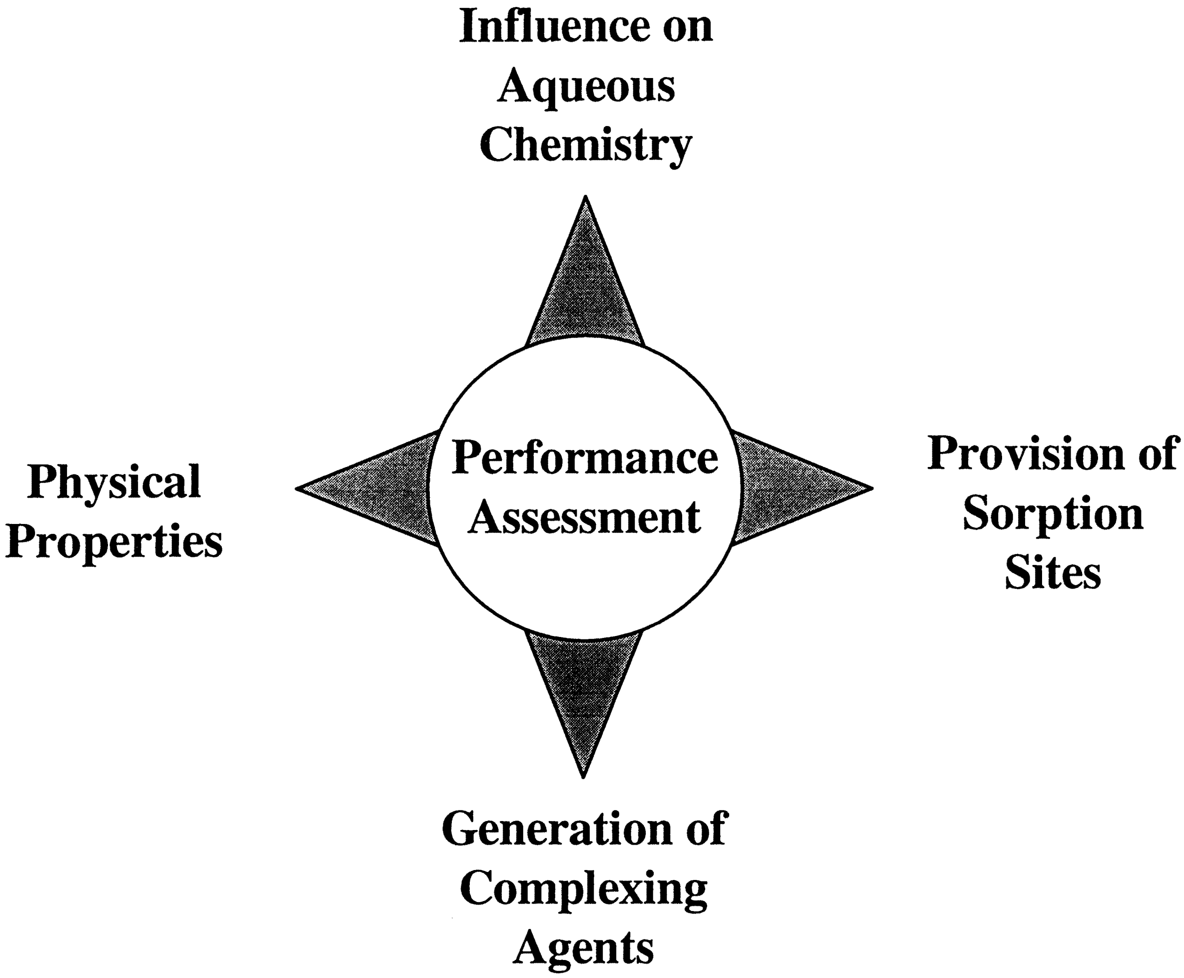

Figure 2. **Reasons for representing grout in performance assessments.**

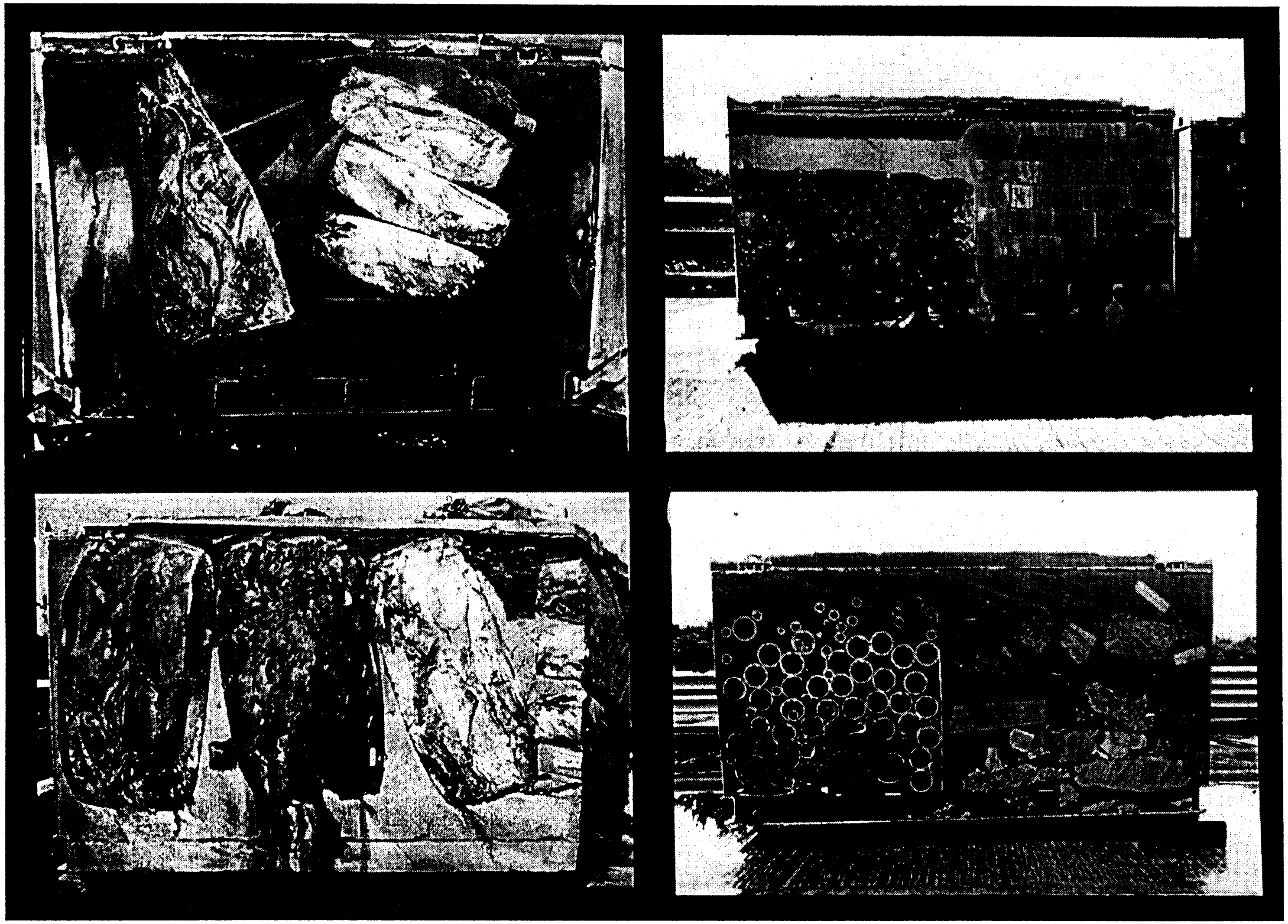

Figure 3. Penetration of grout into void spaces of an inactive ISO freight container.

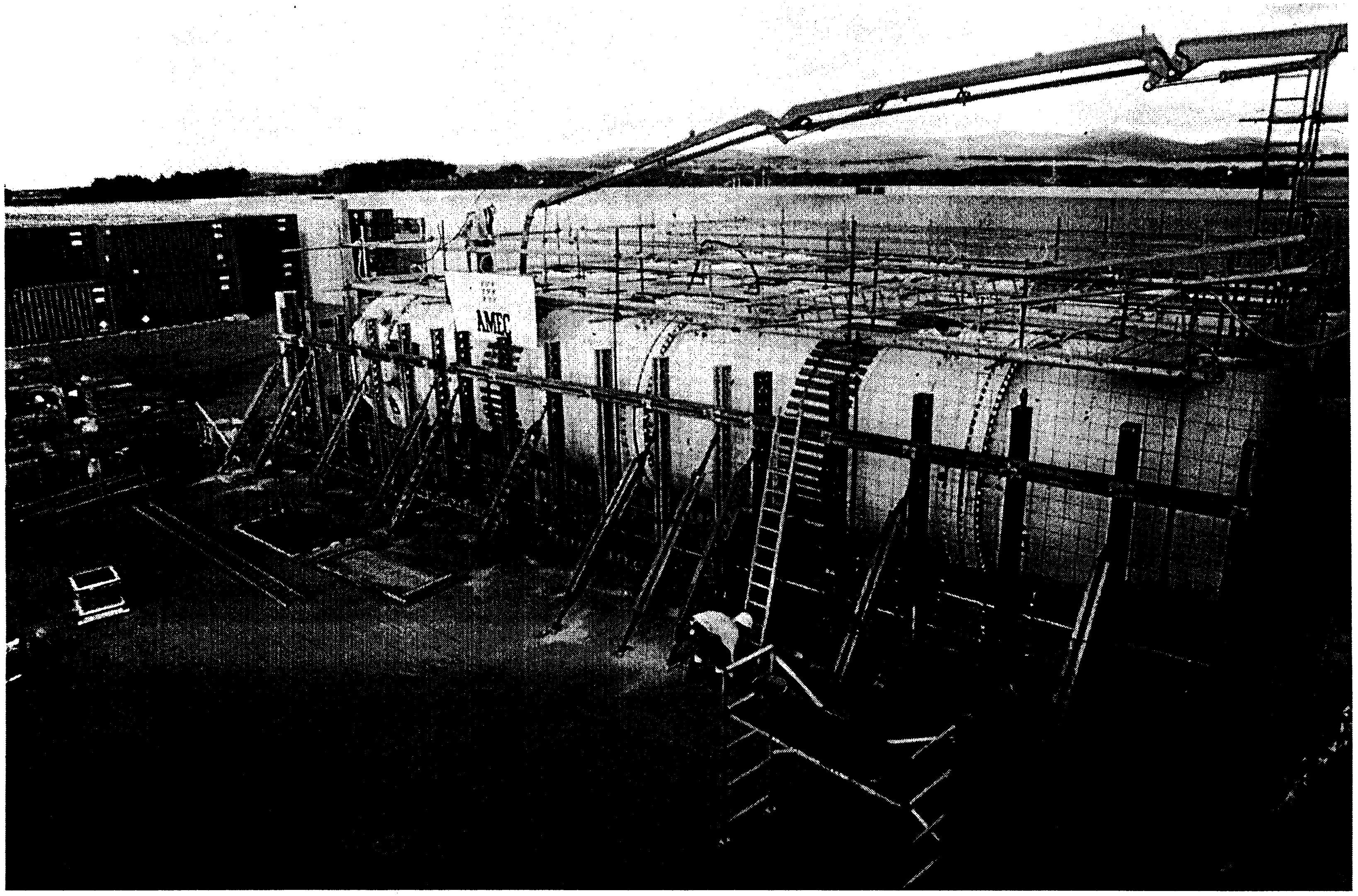

Figure 4. Grouting of internal voids within waste items.

ENGINEERED BARRIERS AND BACKFILL IN LOW-LEVEL RADIOACTIVE WASTE DISPOSAL FACILITIES

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1. INTRODUCTION

Engineered barriers and special backfills have become important components in the design, licensing, operation, and closure of low-level radioactive waste disposal facilities. This paper first outlines some key regulatory criteria and relates the role of engineered barriers and backfills as well as covers to these criteria. It then reviews some examples of engineered barriers and backfills. Finally, it identifies standard methods of predicting their long-term performance. Engineered barriers are included with backfill in this discussion because they are a specialized type of backfill and perform many of the same functions.

2. REGULATORY CRITERIA

The applicable regulation in the United States for commercial low-level waste disposal facilities is Code of Federal Regulations, Title 10 Part 61 (10CFR61), promulgated by the Nuclear Regulatory Commission (NRC). This regulation initially focused on shallow land burial in unlined earthen trenches, although the NRC later stated that it was also applicable to near-surface disposal with engineered barriers. One important section of the regulation contains performance objectives. They involve a systems analysis of site and facility features to: (i) meet an annual dose limit of 25 mrem per year for a significant time after closure; (ii) protect inadvertent intrusions after closure; (iii) protect workers; and (iv) ensure the stability of the site for a significant time after closure. A contaminant-pathways analysis covering up to 10,000 years after closure is required to satisfy these performance objectives.

Table 1 illustrates the role that engineered barriers, backfills, and covers have for compliance with the four performance objectives.

Another section of the regulation contains prescriptive technical requirements; the following relate to design features:

(i). The design features must be directed toward long-term isolation and avoidance of the need for continuing active maintenance after site closure.

(ii). The covers must be designed to minimize, to the extent practicable, water infiltration.

(iii). The disposal site must be designed to minimize, to the extent practicable, the contact of water with the waste.

(iv). Class A waste must be hydrologically segregated from the higher classes of waste.

(v). Class C waste must have sufficient intruder barriers to be effective for 500 years.

(vi). Void spaces are to be minimized.

(vii). Void spaces between packages are to be filled by earth or other material to reduce future subsidence within the fill.

Engineered barriers are particularly effective in helping to comply with the dose limit for the near term (a few hundred years), before they degrade. In contrast, backfills and covers are expected to contribute significantly to limiting of the dose for the entire period of regulatory control. Intruder protection is provided by engineered barriers and covers. Worker protection is provided by cover over the fill and possibly by engineered barriers before they degrade. It is true that the engineered barriers in place can act as radiation shields for the workers; however, often the use of engineered barriers requires more extensive worker operations which run counter to the shielding protection the engineered barriers provide. This may result in a larger collective dose to workers.

The stability of the facility and the site is provided in the near term by intact engineered barriers and is provided during the entire period of regulatory control by degraded engineered barriers and by the backfill between packages as well as the cover, although the effectiveness of the cover may diminish over time. After the engineered barriers degrade, they also act as traditional backfill, so their effectiveness diminishes, but they still play an important role. For some nuclides the high pH environment reduces their mobility due to increased absorption and adsorption, but for others the high pH increases their mobility.

Table 2 illustrates the compliance role of engineered barriers, backfills, and covers with respect to some of the key prescriptive technical requirements contained in 10CFR61. The first requirement listed is the need to provide for long-term isolation, which is provided by engineered barriers, backfills, and covers. Engineered barriers, even if they are assumed to have lost their integrity, still provide a measure of isolation in the long term.

Prescriptive requirement number (ii) is specific to covers and states that covers should be designed to minimize the infiltration of water. Requirement number (iii), minimize water contacting with the waste or standing water in the vicinity of the waste packages, is provided by engineered barriers over the near term and by the backfill materials as well as the cover materials for the long term. This is where backfill materials are usually assigned a key role. Backfill materials in new designs typically consist of either sand or gravel to facilitate the movement of infiltrating water past the waste packages and to the floor of the facility. The segregation requirement (iv) is satisfied with engineered barriers, although physical separation of any trenches is also usually required for long-term segregation.

The intruder barrier provision is satisfied both with intact engineered barriers as well as with sufficient cover material. Minimizing void space in the packages can be accomplished through grouting, for example. Backfill between packages could also be a grout or a material that fills the void space to provide structural support while still allowing the passage of infiltrating water.

About the time that 10CFR61 was issued, the US Congress passed the Low Level Waste Policy Act (in 1980). This act gave the individual states authority to handle their own low-level radioactive waste disposal problems and urged the states to form regional compacts for new waste disposal facilities. Progress has been exceedingly slow. To hasten the process, Congress passed the Amendments Act of 1986 that set milestones and established severe financial penalties for not meeting those milestones. One of the results of the Amendments Act was to greatly increase disposal fees by requiring large surcharges in addition to the normal fees if milestones were not met. Another outcome of the Low Level Waste Policy Act, particularly in the states that were developing new commercial low-level waste disposal facilities, was that state legislatures and state radiation control agencies established additional requirements to 10CFR61. The most common additional requirement was the prohibition of standard shallow land burial technology for new disposal facilities. Also, the variations among state regulations created problems of definition for some engineered barriers or engineered features. For example, an early informal opinion by NRC staff stated that modular concrete canisters into which waste packages were placed are simply another form of package. However, the size of some modular concrete canisters is about 3 m in diameter by 3.7 m in height. If these are classified as another form of a package, then modular concrete canister disposal would be classified the same as shallow land burial disposal and could not be used in states that prohibit shallow land burial.

The modular concrete canister, illustrated in Figure 1, is one of the more common engineered barriers to be used in new commercial low-level waste disposal facilities. Another very common barrier is the concrete vault. Vaults are designed to be placed either above the natural ground surface, as shown in Figure 2, or below the ground surface, as shown in Figure 3. In general, if there are questions about meeting the groundwater criteria of 10CFR61, then aboveground vaults are considered. In the humid climates of eastern states such as North Carolina and Pennsylvania, one promising concept proposed by candidate site operators is to include a modular concrete canister inside a concrete vault (Chem-Nuc 1995).

The earth-mounded concrete bunker technology, shown in Figure 4, is essentially a below-ground vault into which the waste is placed; then the void space is filled with concrete and an earth-mounded facility is placed over the concrete bunker. This concept has been applied in France. The earth-mounded portion holds containers, most frequently containers placed in concrete modular canisters, with the concrete modular canisters stacked on top of the concrete bunkers and then covered with an earth mound.

Another backfill example comes from one of the reference design options for isolation of spent fuel and high level waste in the United States (Bailey 1997). Although not suitable for a low-level waste facility, this example is interesting in its use of two types of backfill for different purposes. The design, shown in Figure 5, shows the waste package elevated on a pedestal to avoid immersion in standing water and covered with a drip shield, a type of backfill, to divert infiltrating water around the package. A zeolite layer is placed on the bottom of the emplacement drift to retard any nuclides released from the package. The pedestal and package are surrounded with a different backfill to protect the package from falling rocks or drift liner chunks and to limit the humidity and the flow of infiltrating water through the drift.

One problem that has occurred in implementing engineered barriers and backfills to the design and qualification of low-level waste disposal facilities is the inconsistent treatment and analysis of their effectiveness. For example, the state of Texas uses modular concrete canister disposal; that is, the modular concrete canister is placed directly into an earthen trench (Texas 1996). However, in North Carolina (where only 100 years of credit can be taken for engineered barriers in performance assessment analyses) the modular concrete canister is interpreted as a container. By classifying the canister as a container and not an engineered barrier, the applicant was able to utilize the integrity of the modular concrete canister for several hundred years in the performance assessment.

To provide some guidance to the states, the NRC has issued prescriptive guidance for qualifying engineered features such as concrete vaults (NRC 1988). If their particular prescriptive guidance is followed, an applicant can get between 100 and 500 years of credit. In other words, it can be assumed that their engineered barriers will maintain their integrity for up to 500 years, and it can be assumed that the barrier prevents any contact of infiltrating water with the waste and resultant release of radionuclides into the groundwater.

Several questions arise, though, when performing a detailed performance analysis to determine the long-term integrity of the barrier. For example, can an application assume that the integrity of the engineered barrier lasts beyond 500 years if they have a more conservative design (for example, if they have thicker concrete walls for the vaults or the concrete canisters, or if they use a lower water-cement ratio in the concrete)? A lower water-cement ratio lowers the porosity of the concrete, thus lowering diffusion and transport through the concrete. It also subjects the concrete member to less shrinkage cracking and generally gives it a greater strength. To illustrate the different approaches, Texas ignored the NRC prescriptions and performed detailed calculations, then checked that their results were consistent with the NRC guidance. Pennsylvania increased the prescriptive requirements significantly and added an additional performance objective that there would be zero radionuclide releases from the facility during the hazardous life of the waste (Penn 1989). Defining the time period for the hazardous life of the waste is a key issue. In North Carolina, the applicant first received NRC approval for using their particular modular concrete canister as a high-integrity container that would last 300 years. They then used expert opinion to extend the time period of performance from 300 years to 500 years, using several concrete and polyethylene experts to maintain that if this container will last 300 years it will just as likely maintain its integrity for 200 additional years. The applicant in North Carolina also initially proposed using no backfill in the vaults, but this was quickly rejected by the state regulatory agency. In Nebraska, the applicant followed NRC guidance but also performed a detailed engineering analysis of the loads on the concrete engineered barriers and performed degradation calculations to present a "best engineering judgment" of the time period for which the barriers would maintain their integrity.

3. DEGRADATION MECHANISMS

Major types of degradation to which high-quality concrete barriers are subjected are listed in Figure 6 (Chau and Rogers 1995). The most predominant types are degradation from sulphate ions or acids, calcium hydroxide leaching from the member, corrosion of the rebar, alkali aggregate reactions, and, to a lesser extent, freeze-thaw reactions. Each of these particular types of degradation is discussed below.

3.1 Sulphate degradation

Sulphate degradation results from sulphate ions in the groundwater; these ions penetrate a short distance into the concrete and react with the materials in the concrete to form etteringite or other compounds whose densities are lower than the constituent materials. They create internal pressures as they are formed, which causes the thin surface layer to spall, exposing the next thin layer to the sulphate in the groundwater, and the cycle repeats itself. Since it generally is a relatively short, defined distance into which the sulphate penetrates, it is assumed that the rest of the concrete maintains its integrity and that the initial thickness of the concrete member decreases linearly with time as the surface degrades. The American Concrete Institute has many correlations to estimate the short-term effect of sulphate degradation. These correlations are frequently extended to many hundreds of years. Another approach is to use a first principles mechanistic approach in which the sulphate ions are presumed to diffuse into the concrete and react as the diffuser. Since the sulphate transport through the concrete is diffusion-based, diffusion coefficients become very important.

3.2 Calcium hydroxide leaching

Calcium hydroxide leaching is basically a bulk property degradation mechanism; however, one also needs diffusion coefficients to determine the rate at which the calcium hydroxide leaves the concrete member. The effects of adsorption also should be included. In this case, surface conditions of the engineered barrier are important because the bulk diffusion rate depends very critically on the conditions at the surface. The most conservative assumption is to assume that sufficient water passes over the outside surface of the concrete member to keep washing away any calcium hydroxide so that its concentration does not build up at the surface.

A particularly tenuous part of the analysis is the relationship between the amount of calcium hydroxide leached out and the resulting reduction in the ultimate strength of the concrete member. Limited experimental and theoretical data are available to provide a relationship, but there is very little technical guidance. One approach yields the relationship shown in Figure 7 (Baird et al. 1987).

3.3 Corrosion

Corrosion of the rebar is a complex multistage process and is a threshold reaction. For example, there can be chlorine in contact with the rebar, but not be conditions sufficient to initiate corrosion. The chloride acts as a catalyst for the oxygen in the reaction. The oxygen must also diffuse from the surface through the concrete and to the iron to begin corrosion. In general, though, once corrosion starts it is predicted to proceed to completion within 100 years. Also, because the rebar plays such an important role in the tensile strength of the concrete members, the effect of the corrosion on concrete integrity can be very significant. One conservative approach that is frequently used is to design the concrete barriers to withstand the applied loads and movements even after the rebar corrodes.

The American Concrete Institute has correlations that are mainly applicable over the short term for the onset of corrosion and for the overall effect of corrosion of the rebar. For example, there is a correlation that is mainly used to estimate the time to corrosion of rebar in highways due to chloride from salt placed on the highways for ice and snow control (Baird et al. 1987). An example of the use of this correlation is shown in Figure 8.

3.4 Alkali-aggregate reaction

It is exceedingly difficult to quantify the effect of alkali-aggregate reactions. Some aggregate components interact with concrete products to form a resultant product that fills the pore space in the concrete. The first effect is to reduce the pore space and increase the ultimate strength of the concrete. This reduces diffusion rates and reduces the rate of degradation of other mechanisms. However, as the reactants proceed to fill a pore space, just as in the case of corrosion of the reinforcing steel, they create internal stresses that cause internal cracks that ultimately weaken the strength of the engineered barrier concrete member and that also increase the effective porosity which, in turn, increases diffusion and contaminant transport through the concrete member. The American Concrete Institute has very restrictive prescriptions for aggregate materials, but these prescriptions are only applicable for the short term. Some laboratories have attempted some accelerated testing, with mixed results.

3.5 Surface degradation

Freeze-thaw is a surface degradation mechanism for very good concrete because the low porosity restricts the depths that water can penetrate in one cycle. Several correlations exist that relate the extent of degradation to the number of freeze-thaw cycles. For most candidate sites in the United States, freeze-thaw is not considered to be a severe problem because it is relatively easily corrected with design and air entrainment additives that greatly reduce the potential for degradation from freeze-thaw.

For most cases examined for US commercial disposal facilities, sulphate attack and rebar corrosion are the dominant degradation mechanisms. Figure 9 shows an example of the cumulative effect of these degradation mechanisms for a below-grade vault in a moderate environment (Shuman et al. 1988). The rapid decline in the safety factor at year 500 is from the corrosion of the rebar. The safety factor generally decreases linearly with time because sulphate attack is the other dominant degradation mechanism.

4. THE ROLE OF ENGINEERED FEATURES

In general, backfill in low-level waste disposal facilities is used to help satisfy the restriction that water infiltrating the facility will not come in contact with the waste or minimize the contact of water with the waste. This is effectively done by providing a clear path around the waste packages through which the infiltrating water can move quickly. Sands are most effective for this, as are small gravels.

The main purpose of the backfill, however, is to reduce the potential for subsidence. It was recognized when the regulations were made that precipitation on the disposal units would greatly increase if differential settlement occurred in the waste region, allowing sink holes or cracks to open up in the cover, promoting the transport of infiltrating water directly to the waste units. Very little has been done for commercial disposal facilities to use backfill materials as absorbers or adsorbers of contaminants from the waste that are released from the leaching processes. This has been considered but has not yet been implemented because the requirement for providing a rapid path for infiltrating water to move down past the waste has been the dominant consideration.

There are other engineered barriers or engineered features that are used in low-level waste disposal facility designs that serve the same purpose as engineered concrete barriers or backfills. These features are: (1) high-density polyethylene liners that are placed in covers and below the facilities, (2) multilayer covers, (3) epoxy coating on the rebar, and (4) waterproof coating on the concrete. Even though the layers of a multilayer cover may all consist of earthen materials, different layers serve different functions. For example, a sand layer placed over a clay layer promotes the transverse migration of water around the waste facility. Further, the clay layer inhibits infiltration into the disposal units.

High-density polyethylene liners are required in hazardous waste facilities, but in that application the requirement is that they must maintain their integrity for only 30 years. These liners degrade from exposure to ultraviolet rays and to oxygen. It is difficult to quantitatively estimate the rate of degradation of high-density polyethylene liners that have an earthen cover over them. Most frequently, no credit is given for synthetic liners in meeting the NRC's criteria, other than they are considered to be an additional feature that helps satisfy the "as-low-as-reasonably achievable" criterion. Multilayer covers also often have a graded cobble layer to discourage animal and plant biointrusion. In some regions of the country, the potential for disrupting the cover from biointrusion greatly increases the infiltration into the waste units. A cobble layer is one method that appears to show promise as a long-term effective barrier against animal and plant intrusion.

Because these multilayer, multifunction covers generally are made from earthen materials, standard infiltration computer codes such as the Environmental Protection Agency's HELP Code are often used to predict a present condition performance as well as degraded cover condition performance. However, the common approach is to assume that the cover will perform as designed and as initially analyzed, that its performance will be constant for a given number of years, such as 300 years, and that the cover will degrade to the regional natural infiltration rate for subsequent years.

5. CONCLUSIONS

In summary, engineered features such as concrete engineered barriers and backfills play an important role in the performance of low-level waste disposal facilities. Because the process of licensing, building, and operating new low-level waste disposal facilities is mainly state-regulatory driven, there is a significant degree of inconsistency in the regulatory approach, even though each of the agreement states have the required degree of compatibility with the NRC rules.

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Table 1. Compliance Role of Engineered Barriers, Backfill and Covers for Performance Objectives.

Performance Objectives		EB	B	C
i	Dose Limit	short term	✓	✓
ii	Intruder protection	✓		✓
iii	Worker protection	?		✓
iv	Stability	short term	✓	✓

Table 2. Compliance Role of Engineered Barriers, Backfill and Covers for Technical Requirements.

Prescriptive Technical Requirements		EB	B	C
i	Long-term isolation	✓	✓	✓
ii	Minimize infiltration			✓
iii	Minimize water contacting waste	short term	✓	✓
iv	Segregate Class A	✓		
v	Intruder barriers for 500 yrs	✓		✓
vi	Minimize void spaces	✓	✓	
vi	No voids between packages		✓	

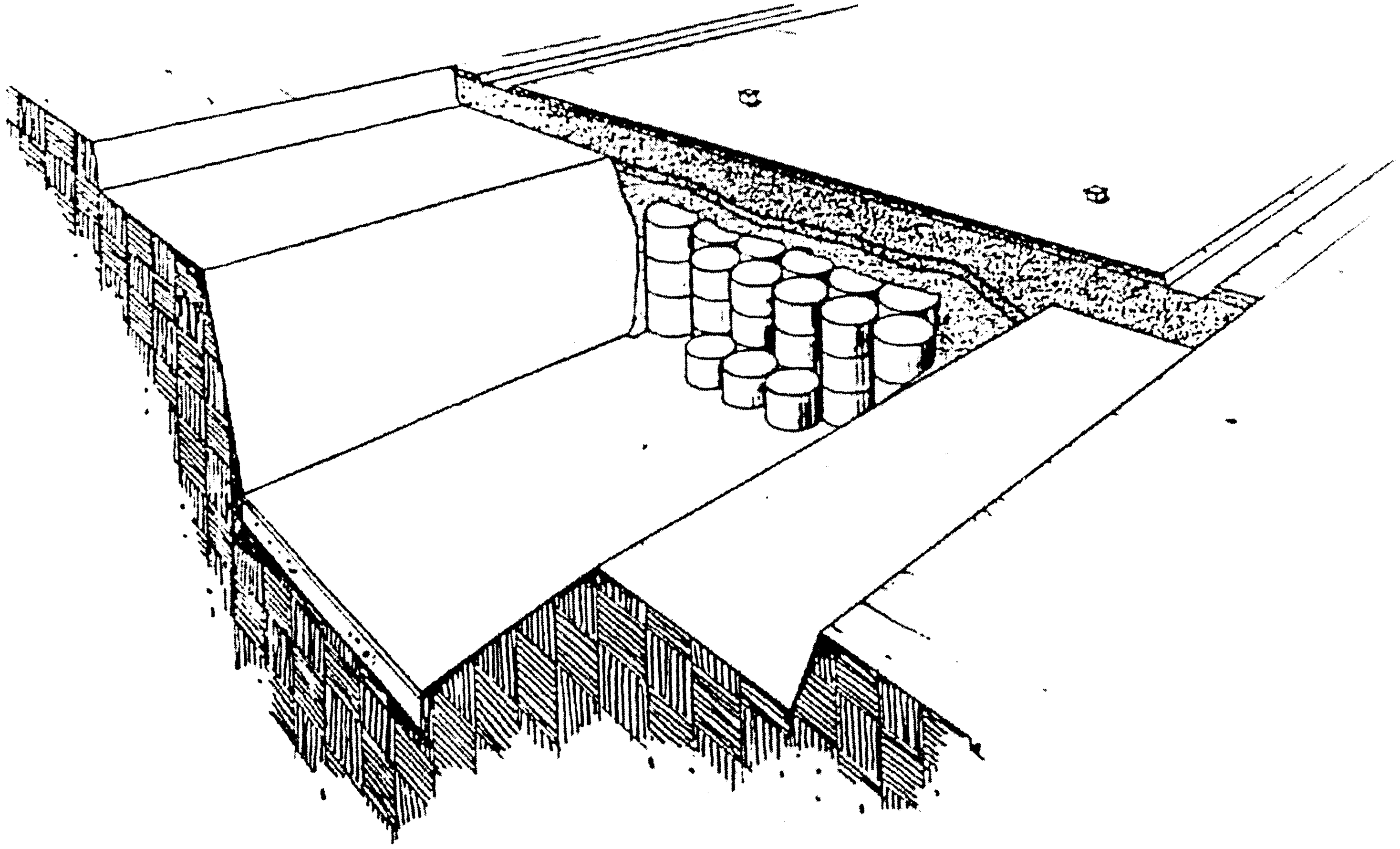

Figure 1. Schematic representation of modular concrete canister disposal unit.

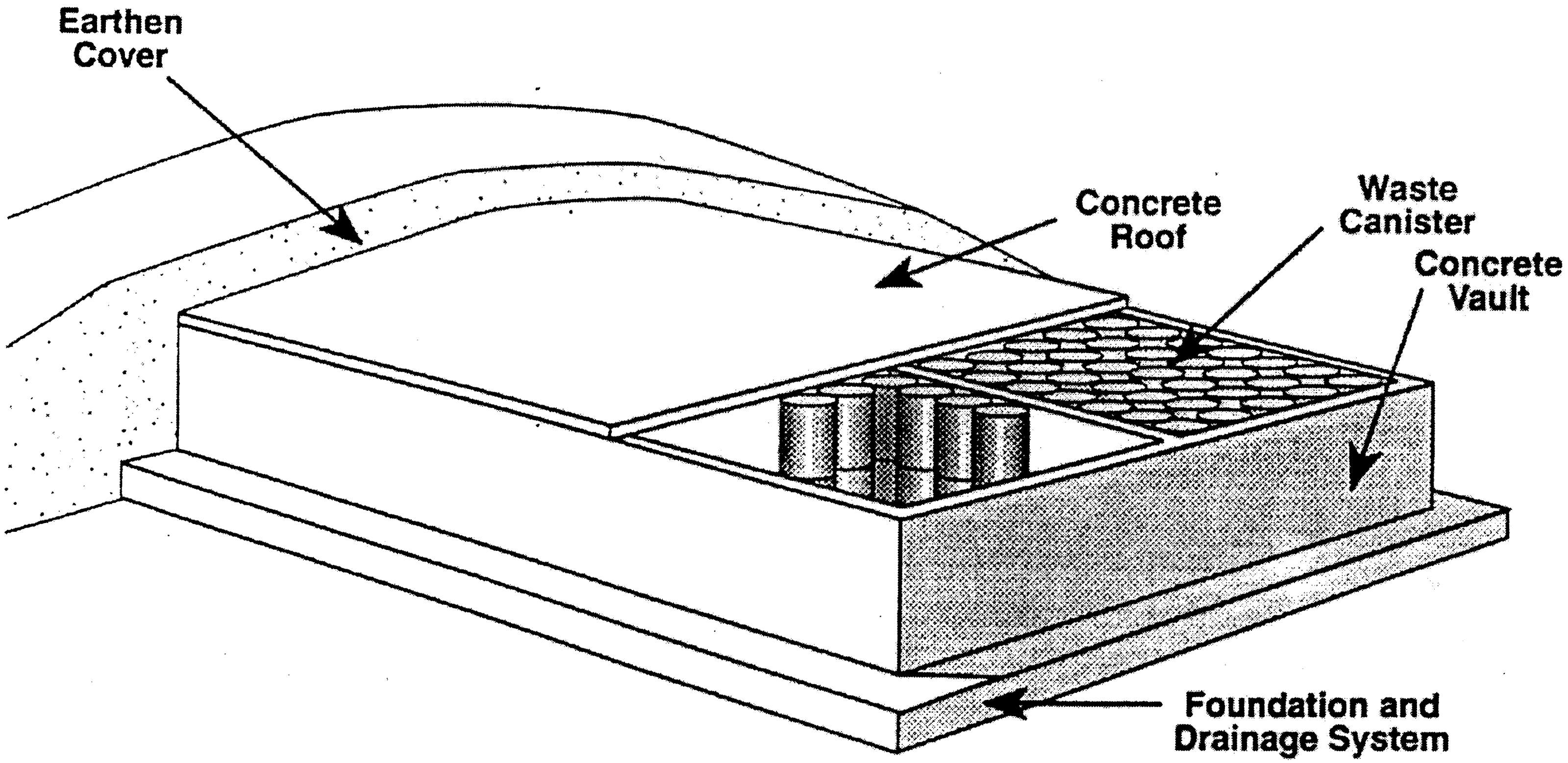

Figure 2. Schematic representation of covered above-grade concrete vault.

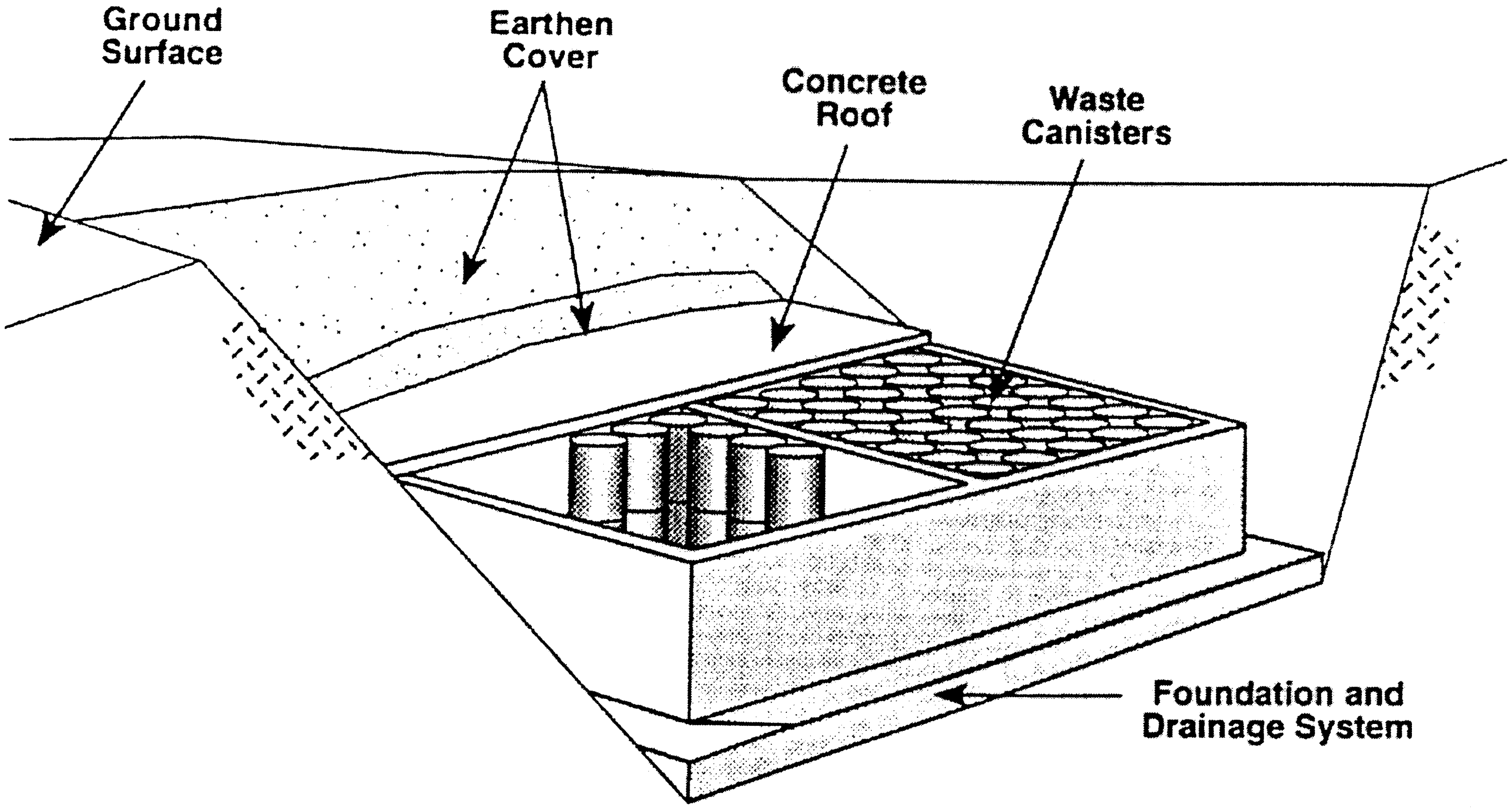

Figure 3. Schematic representation of below-grade concrete vault.

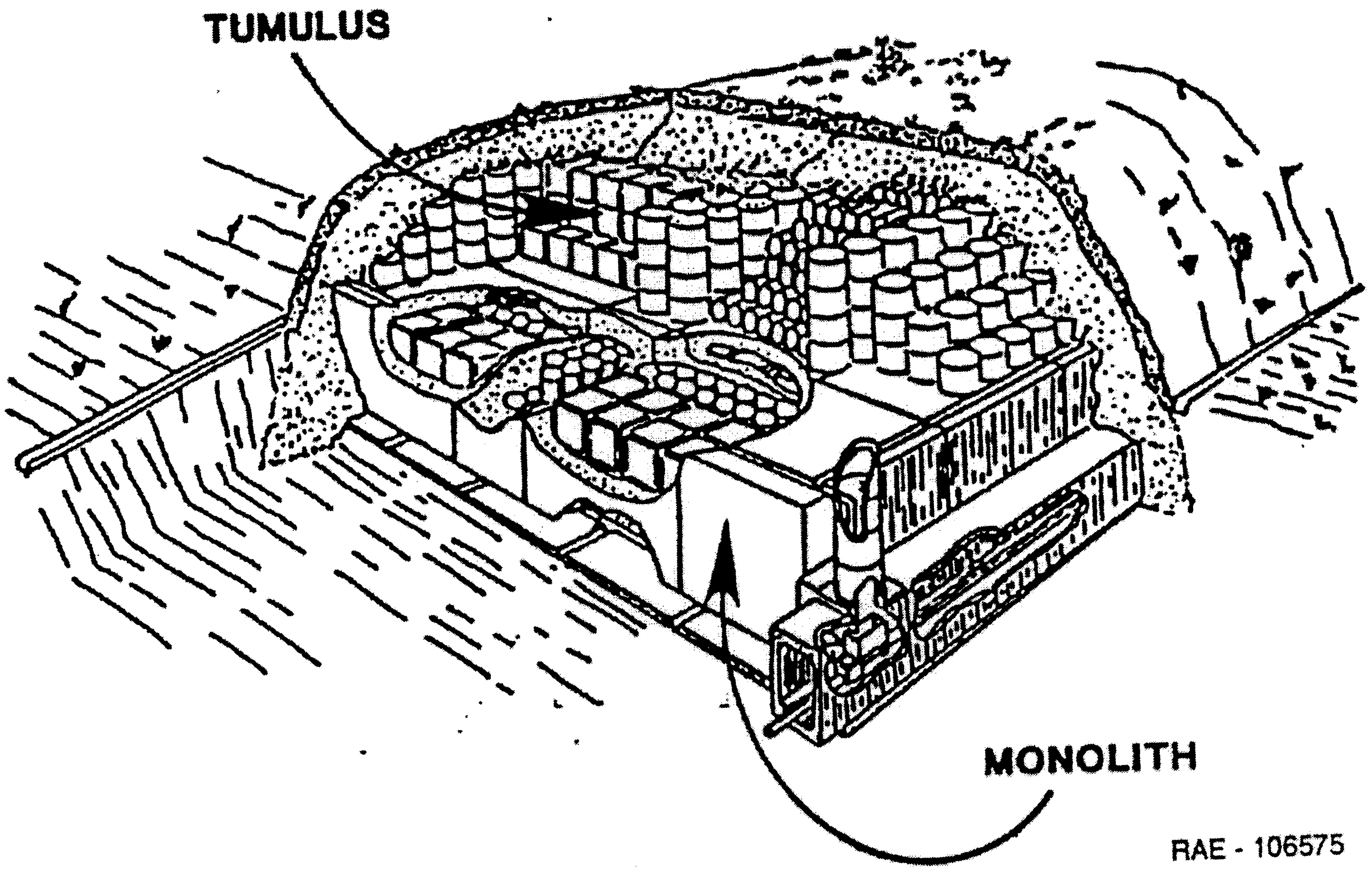

Figure 4. **Schematic representation of earth-mounded concrete bunker disposal unit.**

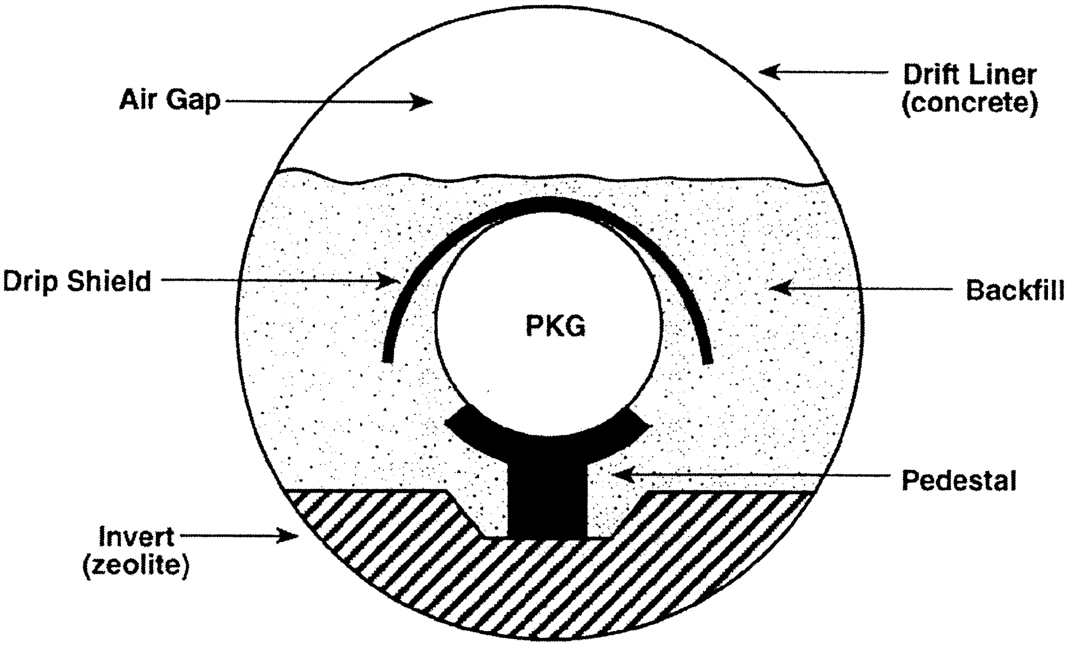

Figure 5. Use of backfill in reference design option for the Yucca Mountain high level waste disposal facility.

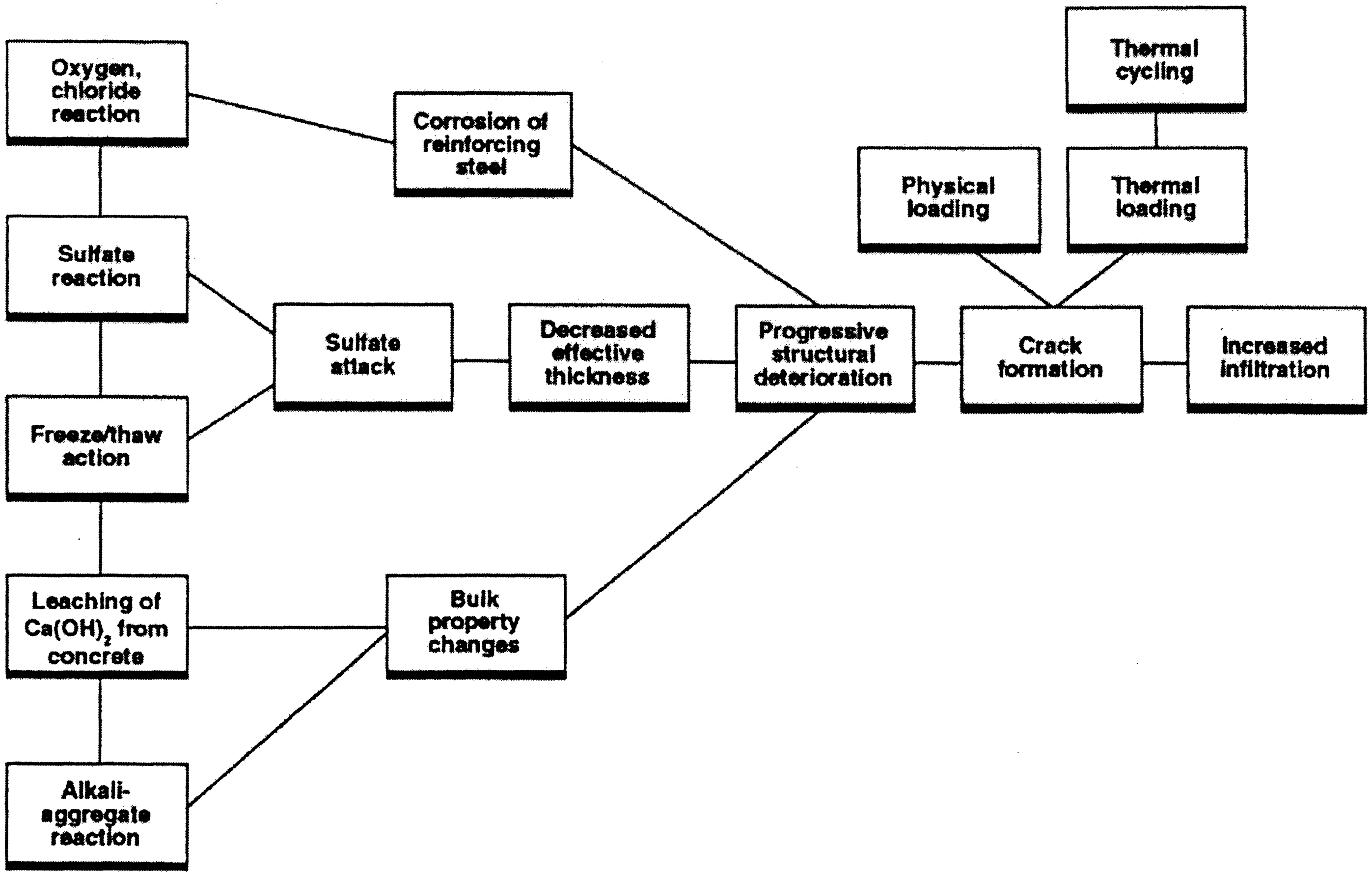

Figure 6. Concrete performance tree.

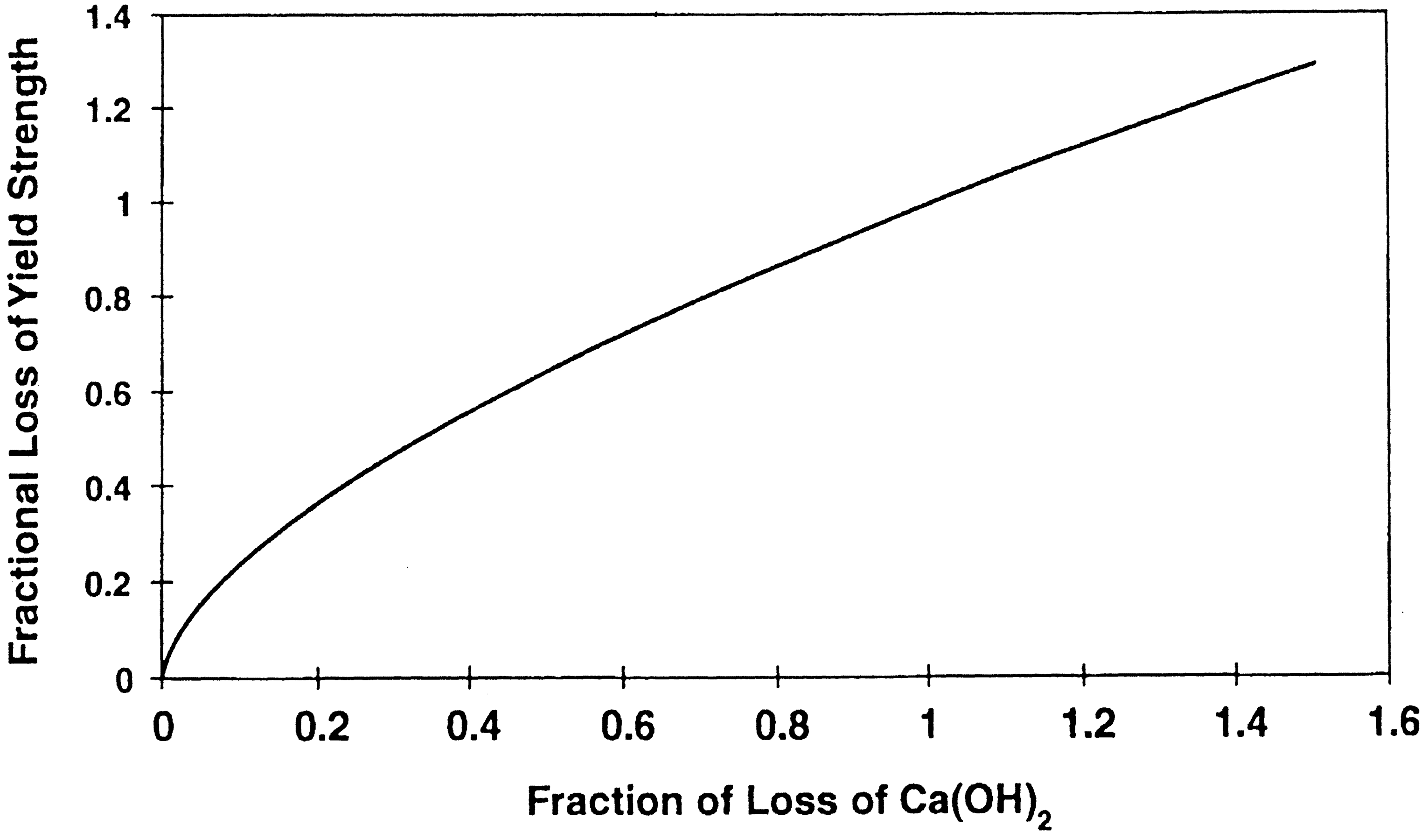

Figure 7. Fractional loss of yield strength with $Ca(OH)_2$ loss.

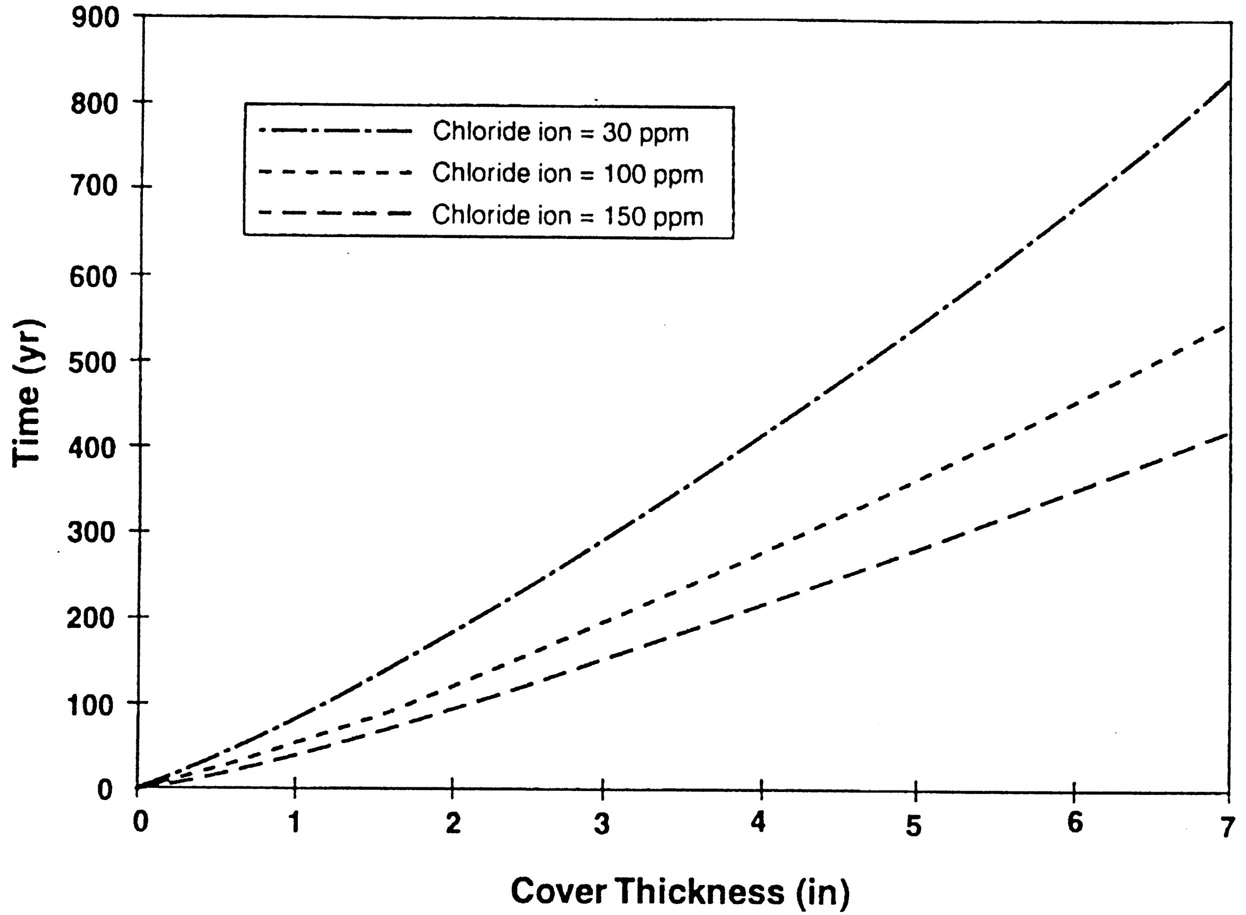

Figure 8. Prediction of time-to-onset of corrosion from the clear equation.

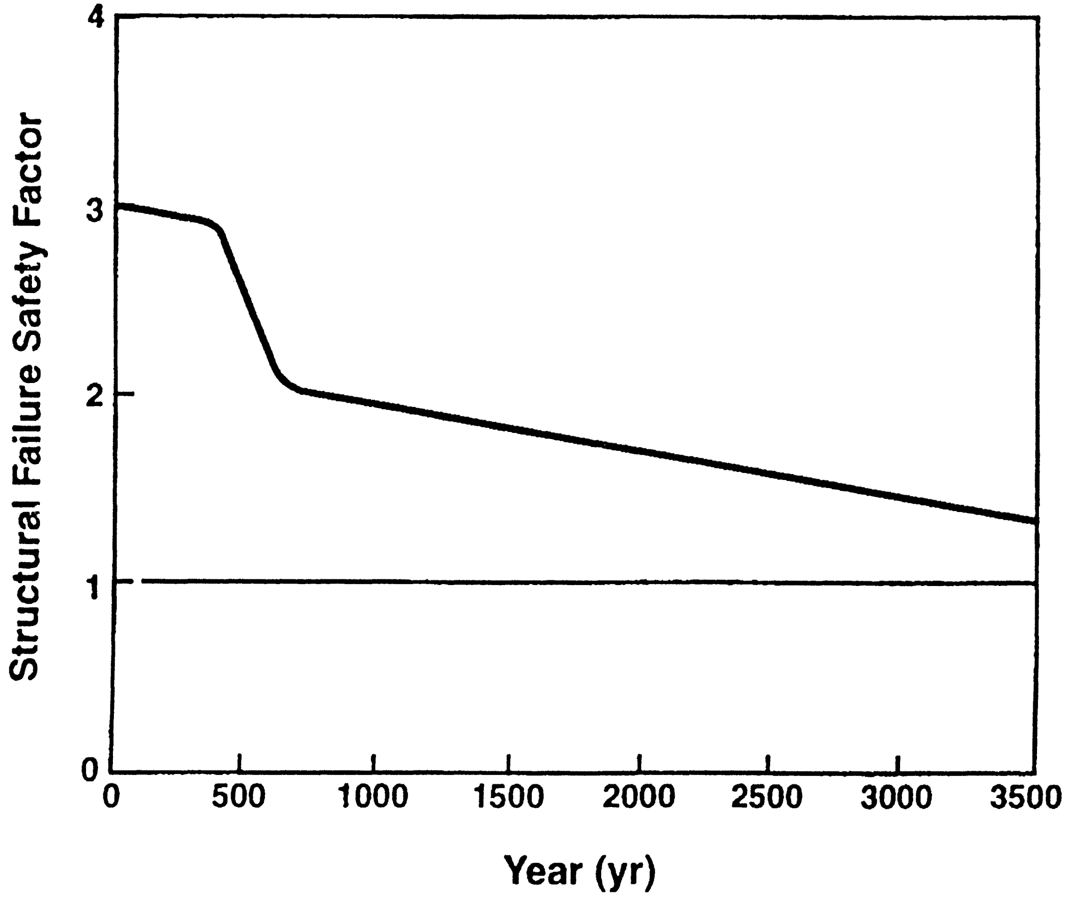

Figure 9. Structural safety factor as a function of time for the below-ground vault facility.

IDENTIFICATION AND EVALUATION OF APPROPRIATE BACKFILLS FOR THE WASTE ISOLATION PILOT PLANT (WIPP)

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ABSTRACT

A backfill system has been designed for the Waste Isolation Pilot Plant (WIPP), which will control the chemical environment of the postclosure repository to a domain where the actinide solubility is within its lowest region. The actinide solubility is highly dependent on the chemical species that constitute the fluid, the resulting pH of the fluid, and the oxidation state of the actinide which is stable under the specific conditions. The use of magnesium oxide (MgO) as the backfill material not only controls the pH of the expected fluids, but also effectively removes carbonate from the system, which has a significant impact on actinide solubility. The backfill selection process, emplacement system design, and confirmatory experimental results are presented.

1. INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) is a repository for the disposal of transuranic element (TRU) wastes. The WIPP is located in southeast New Mexico, USA in a natural bedded salt formation approximately 655 meters below ground surface The wastes destined for WIPP are typically a highly heterogeneous assortment of materials such as ordinary laboratory refuse, construction and maintenance waste, and process wastes contained in steel drums or waste boxes.

There are many processes expected to occur within the WIPP repository that may influence the chemistry of the system, resulting in significant impacts on the actinide solubility and corresponding source term. Principal among these processes is the microbial degradation of carbon-containing materials, primarily cellulosics, plastics, and rubbers. The microbial degradation of these carbon-containing materials may proceed by many processes (Berner, 1980; Brush, 1990; Wang and Van Cappellen, 1996). In the WIPP repository, the available electron acceptors will soon be exhausted, and methanogenesis is expected to become the dominant mechanism. Methanogenesis proceeds according to the following generalized reaction:

$$C_6H_{10}O_5 + H_2O \rightarrow 3CH_4 + 3CO_2 \qquad \text{(Eq. 1)}$$

Methanogenesis, if indeed significant microbial action occurs at all, will lead to the production of large quantities of carbon dioxide (CO_2). The formation of CO_2 has a significant impact on the solubility of the actinides through one of the following processes: (1) Carbon dioxide reacts upon contact with water, forming carbonic acid. Carbonic acid, although a relatively weak acid, is capable of driving the pH of the repository into the acidic range, where the solubility of the actinides is typically greatly increased. (2) Carbonic acid undergoes dissociation in water, forming carbonate and bicarbonate species. The carbonate ion is known to bind very strongly to the actinides, forming stable, relatively highly soluble species. The presence of CO_2 in any significant quantity therefore drives the actinide solubility to much higher values due to lowering of the pH or forming soluble actinide carbonate complexes.

Based on there being an estimated 2.7×10^7 kg of carbon-containing compounds to be emplaced in the WIPP (US DOE, 1996), the fugacity of CO_2 (fCO_2) could vary within the range of 0 (in the event that there is insufficient microbial action to overcome the buffering effect of the cementitious material (which is in the waste itself or used as a sealing material) to approximately 60 atmospheres. This wide range of fCO_2 is accompanied by a correspondingly wide range of pH values (approximately 4–13) and carbonate concentrations. The net effect of these processes is that the actinide solubility, and thus the source term, could vary widely over an unacceptably large range.

To mitigate the detrimental effects of possible CO_2 generation, a material is required to maintain the pH of the brines in the alkaline region *and* to remove CO_2, thus minimizing the ability of the carbonate ion to participate in complexation reactions. The alkaline earth oxides (e.g., MgO) were identified as fulfilling these two functions.

The alkaline earth oxides react with water according to the following equation:

$$MgO(s) + H_2O \rightarrow Mg(OH)_2(s) \qquad \text{(Eq. 2)}$$

The reaction with water to form the hydroxide also potentially benefits the repository performance by maintaining a dry repository in the event of limited brine inflow. The hydroxide thus formed, in this case brucite, is available to react with any carbonic acid that may be available,

$$Mg(OH)_2(s) + H_2CO_3 \rightarrow MgCO_3(s) + 2H_2O \qquad \text{(Eq. 3)}$$

thus effectively removing the carbonate from the system due to the low solubility of $MgCO_3$. Through the implementation of MgO backfill, the range of chemical conditions pertinent to the performance assessment of the WIPP is constrained, and additional assurance of the repository's compliance with the applicable disposal regulations (as specified in Title 40, Code of Federal Regulations, Part 191) is obtained.

1.1 Evolution of Backfill at the WIPP

The concept of utilizing a backfill at the WIPP has been discussed in many forums with many intended objectives essentially since the idea of the WIPP was first conceived. Early in the WIPP conceptual lifetime, backfill was envisioned for the reduction of the fire hazard within the mine (through the reduction in the potentially flammable volume available), and for subsidence mitigation. As more was learned of the system, the use of backfill was given more compliance-oriented roles. For example, in the late 1980s, salt backfill was considered in order to speed the entombment of the waste through the reduction of the void volume, which had to be overcome by the salt creep of the surrounding formation salt. In the late 1980s, the disposal regulations applicable to the WIPP had not been finalized (i.e., the consideration of the human intrusion scenario had not been recognized as a requirement), and the repository was anticipated to be effective for isolating the waste once the surrounding formation salt had closed in around the waste. However, it was later learned that the room closure was not significantly hastened by the presence of the backfill to justify its emplacement, and the baseline design for the repository did not include any backfill material.

Toward the end of this period (approximately 1985–1990), laboratory evaluations (Lappin and Hunter, 1989) were performed on the utility of clay materials for backfill. These studies included the evaluation of clay to adsorb any brine that could enter the repository from the surrounding Salado Formation, and also a sorbing clay barrier to transport. These concepts were later dropped due to the discovery of pressurized brine pockets in underlying formations, which dominated the release mechanisms (and would overwhelm the ability of the clay to sorb water) and the inability to assure a required minimum thickness of sorbing clay to survive the room closure process. The concept of clay backfill as a brine inflow barrier and transport impediment was revisited in 1993–1994. The concept was again dropped due to uncertainties in assuring a contiguous clay barrier and the perception that no additional measures were needed in order to demonstrate compliance with the now finalized regulations.

Concurrently, other WIPP researchers were evaluating alternative backfill materials such as grouts, gas getters, and materials that might prevent the formation of some anticipated repository gases (Molecke, 1990; Molecke and Nowak, 1980). There was also much interest in the ability of the backfill materials to inhibit transport of the radionuclides through sorption in clay materials that are naturally present or artificially present as backfill (e.g., Nowak, 1978; Nowak, 1980). Many other studies relating to backfill, including its mechanical properties and the materials' utility in shaft seals, for example, have been performed. A bibliography (Powers and Martin, 1993) referencing many of these early studies has been prepared and is available from the National Technical Information Service.

As the preliminary calculations for the WIPP Compliance Certification Application (CCA) were being performed during late 1995 and early 1996, it was determined that a compliant complementary cumulative distribution function (CCDF) could only be assured, given the combination of other parameters and conceptual models being used at that time, when the actinide concentrations were less than approximately 10^{-5} molar. Concurrently, the experiments providing the thermodynamic parameters for the actinide source term model were still being developed, but the preliminary results, given the presence of extremely high CO_2 pressures and a wide range of pH, indicated that these relatively low actinide concentrations might be unattainable. This unfavorable situation was further compounded by the actinide source term model having difficulties addressing the extremely high CO_2 conditions and the far field transport program having preliminary indications that the presence of organic ligands reduced the retardation factors to unacceptably low levels. At that point, implementing a backfill that controlled the chemical conditions to one where the actinide solubility is low and assisted in the effective removal of the organic ligands from the system appeared necessary and a rapid evaluation and design was performed, resulting in the implementation of MgO backfill as the design basis for the WIPP CCA. It is important to note that with maturing of the parameters, databases, and conceptual models, which occurred prior to the CCA being finalized, it was demonstrated that the repository indeed complied with the disposal regulations even in the absence of the MgO backfill and that the MgO backfill would be placed in the repository only as an additional assurance measure.

1.2 Basis for Selection of Backfill Material

There are four principal mechanisms by which a backfill could chemically control the actinide source term. These mechanisms are:

- sorption;
- redox control;
- precipitants; and
- pH and $f\mathrm{CO}_2$ controllers.

These were evaluated to determine which mechanism (or mechanisms) would lead to the most stable repository environment and provide the most significant contribution to demonstrating repository performance. A preliminary screening was performed to narrow the scope of materials that were to be evaluated. For this screening, the following qualitative criteria were applied:

- ability to efficiently effect the desired change;
- available in bulk;
- no significant health hazards;
- no significant safety concerns (e.g., pyrophorics, or materials that will consume oxygen and/or generate toxic gases); and
- ability to emplace a sufficient quantity within the constraints of the existing repository design.

A description of the above mechanisms and the rationale for inclusion or exclusion follows.

2. SORPTION

The mechanism of sorption has received much attention from the international community and was one of the first to be evaluated for the WIPP. However, there is a distinct difference between the WIPP and most other repository programs. The U.S. Environmental Protection Agency (EPA), the regulator for the WIPP, has required that the WIPP demonstrate that it can still meet the containment criteria even when subjected to numerous human intrusion (i.e., drilling) events. That, coupled with the possible existence of pressurized brine in the lower lying formations, leads to the WIPP potentially being exposed to large volumes of water equilibrating with the actinides in the emplaced waste. Unless a quantity of sorbing material sufficient to sorb all of the actinide inventory is capable of being emplaced, the sorption sites will become saturated with actinides and the dissolved actinide concentration will return to the same level as though the sorbent were not present. The design of the repository was already fixed at the time of this backfill study, and there was insufficient space available to place sufficient sorbent to tie up the entire actinide inventory. Therefore, in the case of the WIPP, sorbents were determined not to be a viable chemical intervention capable of controlling the actinide source term.

3. REDOX CONTROLLERS

Another mechanism for controlling the actinide source term is through the control of the oxidation-reduction (redox) environment. The actinides have a varied and interesting chemistry, partially due to their ability to exist in multiple oxidation states, sometimes simultaneously. Each oxidation state of an individual actinide shows dramatic differences in chemistry. There is a general trend in actinide chemistry whereby the lower oxidation states exhibit significantly lower solubilities than the higher oxidation states, sometimes by many orders of magnitude. Maintaining a highly reducing atmosphere and thus keeping the actinides in the lower oxidation states can have a profound effect on the actinide source term and repository performance.

To achieve the redox benefit to repository performance, a large quantity of an effective reductant would have to be added to the repository to ensure highly reducing conditions. As part of the waste materials and the containers holding the waste, there will be at least 1×10^9 moles of iron placed into the WIPP repository (US DOE, 1996). To put this quantity of iron into perspective, this equates to an approximately 2800:1 molar ratio of iron to plutonium (which is one of the elements of most concern with respect to demonstrating compliance for the WIPP). Metallic iron does not always exhibit sufficiently fast reduction kinetics to provide confidence that under all conditions the actinides will be in a reduced state. Fortunately, iron also undergoes corrosion, which serves as a source of iron ions. In an anoxic environment, Telander and Westerman (1996) have shown that metallic iron undergoes corrosion according to the following reaction:

$$Fe^0 + 2H_2O \rightarrow Fe(OH)_2 + H_2 \qquad \text{(Eq. 4)}$$

As shown above, anoxic corrosion produces Fe^{2+} ions, which are a very good reductant with acceptable kinetics (Clark et al., 1997). Given the large excess of available reductant, there was no justification for adding additional material, in the form of a backfill, to control the redox environment. No further evaluation of added reductants as a backfill material was performed.

The evaluations described above narrowed the range of mechanisms to two: precipitants and pH control. Both of these mechanisms were determined to be able to effect the desired impact on repository performance: the reduction of the actinide source term. To further narrow the field of potential mechanisms, an assessment was performed of the ability to have the desired effect. This assessment was made utilizing existing performance assessment codes and readily available data.

4. PRECIPITANTS

Actinides are known to form many relatively insoluble compounds (Cotton and Wilkinson, 1988). Prominent among these insoluble compounds are the oxides, hydroxides, and phosphates. The existence of the actinide oxides and hydroxides is essentially a function of the pH of the system and is fully reflected in the existing Pitzer thermodynamic databases (Novak *et al.*, 1996) for actinides in high ionic strength solutions. The effect of precipitation of oxides or hydroxides was included in the actinide solubility models that utilize these databases, and the benefit realized via the control of the pH to a basic region. The actinide phosphates are also known to exhibit low solubilities. However, sufficient Pitzer parameters were not readily available to fully implement the beneficial effects of adding phosphate to the system. Limited Pitzer parameters for phosphates were available for actinides tin the +3 oxidation state, but are not available for the other oxidation states of interest (principally the +4 oxidation state). Therefore, due to the inability to readily and fully reflect the effects of adding phosphate to the system, precipitants, except those resulting from the control of pH, were eliminated from further consideration.

5. pH AND fCO$_2$ CONTROLLERS

Materials that can effect control over the pH and fCO$_2$ were then selected as the backfill of choice. There are numerous materials capable of controlling or buffering the pH in the repository system. Over 15 materials were screened for their ability to control the pH in the basic region. Several of these materials, in addition to their ability to control pH, are also capable of reducing the carbonate concentration through the formation of relatively insoluble carbonates. These materials include:

- CaO;
- $Ca(OH)_2$;
- MgO; and
- $Mg(OH)_2$.

As noted previously, the alkaline earth oxides readily react with water to form the corresponding hydroxides. The removal of free water from the disposal area by the reaction with the oxides to form the hydroxides was viewed as yet another benefit, which allowed the list of candidate materials to be narrowed to two: CaO and MgO.

Being in the same chemical group, CaO and MgO oxides are expected to have similar chemistries, and that is generally true. However, CaO is more reactive than MgO, which results in significant differences when considering a material to be used as a chemical control for a nuclear waste repository. One of these differences is the equilibrium pH yielded by these materials. In the WIPP brines, CaO yields a pH as high as 13 or greater, whereas MgO buffers the system at a more moderate pH of approximately 9–10. This may not seem significant, but there is not a consensus in the actinide chemistry community on the ability of the actinides to exhibit amphoteric behavior. An amphoteric material, due to its ability to exhibit both acidic and basic properties, typically has a solubility which decreases as a function of pH to a minimus, but which then increases with further increase in pH. Because the ability of the actinides to exhibit this behavior cannot conclusively be ruled out, and to avoid having to engage this debate, it was determined to take the more moderate route and utilize the weaker base, MgO. At the pH obtained via an $Mg(OH)_2$ buffer, the benefits of a slightly basic solution on the actinide solubility are realized without entering a region where amphoteric behavior could be manifested. The decision to utilize MgO as opposed to CaO also yielded operational benefits. MgO has a higher allowable airborne concentration before the use of respiratory protection is required. CaO, due to its more caustic nature, requires the use of a respirator. Spills of MgO thus cause less of an operational impact.

Once the decision was made to utilize MgO as a backfill, efforts focused on the emplacement design and demonstrating the efficacy of the system.

6. SYSTEM DESIGN

The MgO backfill will be purchased and received in two different containers: (1) a supersack typically holding several thousand pounds, and (2) a minisack typically holding 25 pounds (11.3 kg). MgO is available from several suppliers in a range of grain sizes and purities. Typical purities range from 93% MgO for calcined dolomite to 98% for MgO extracted from brines. Chemical grade product (100% MgO) is also available. MgO is available in a variety of milled and screened grain sizes ranging from a powder (minus 325 mesh) to granular (1.3 cm by 6 mesh). The filled containers will be delivered underground using current shaft and material handling procedures and processes.

The minisack will be 34 inches (86.4 cm) long, 6 inches (15 cm) in diameter, and will be fabricated from a single layer of polyethylene or other suitable material. It will have an integral handle and hook attached into the sack closure. Six sacks will be manually placed in the external voids of each seven-pack unit containing waste drums just before the seven-pack is positioned on the waste stack. The minisack will be lifted up behind the shrink wrap around the top of the seven-pack and slid into place. Once the sacks are in place, the seven-pack will be positioned on the waste stack in the normal manner. A similar process will be used for standard waste boxes (SWB) except that the sacks will be hung from the lift clips on these units.

Supersacks, which may weigh up to 4,000 pounds (1,814 kg), will be handled and placed using normal waste handling techniques. Once each row of waste units is in place, a layer of super sacks will be placed on top of them. The supersack will have an integral slip sheet or base attachment so that it can be handled and placed in a manner that is identical to how waste units are emplaced. Typically, the space above a stack of containers will be 36 to 48 inches (90 to 122 cm), of which about 18 inches (45 cm) will contain the backfill material.

Finally, minisacks will be manually stacked on the floor in the space between the waste stacks. These sacks can be placed horizontally or vertically as convenient, and loading rates up to 100 pounds per linear foot (148.8 kg per linear meter) can be achieved simply and quickly.

A total of about 8,560 short tons (7,764 metric tons) MgO will be emplaced per panel or approximately 85,600 short tons (77,640 metric tons) for the repository.

Backfill placed in this manner is protected until exposed when sacks are broken during creep closure of the room and compaction of the backfill and waste.

7. SYSTEM EFFICACY

The ability of the MgO to function as expected is subject to several assumptions. Among those assumptions are:

- the MgO will control the pH to a region dominated by the brucite/magnesite (or hydromagnesite) equilibrium;
- the MgO will react with the CO_2 generated, if any; and

- the solid phase formed upon reaction of MgO with the brine and subsequently with CO_2 will be brucite/magnesium oxychloride and magnesite/hydromagnesite, respectively.

These assumptions are discussed elsewhere in this volume (Papenguth *et al.*, 1998).

8. CONCLUSION

Chemical intervention through the implementation of a backfill material has shown large benefits to the ability to predict long-term performance and compliance of the WIPP with the applicable disposal regulations. MgO has been selected as the most appropriate material, and its ability to control the pH and remove solubility enhancing carbonate from the system has been demonstrated experimentally.

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APPENDIX 3 TOPICAL PAPERS

CONTENTS

THE PERFORMANCE OF BACKFILLS BASED ON $Ca(OH)_2$ AND CEMENT

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ABSTRACT

Portland cement, $Ca(OH)_2$ and its mixtures with fly ash, slag, silica fume, and other components are used as backfills in nuclear waste repositories. The cement constituents gradually dissolve in percolating water. Dissolution of cement components creates a high pH in the near field, thereby reducing the solubility of many radionuclides. Chemical control over the source term is therefore an important benefit. Other benefits include sorption, operative at concentrations below the solubility threshold, and possible reaction with organic and inorganic complexing agents, e.g., carbonate in groundwater, which mitigates the ability of potential complexants to solubilize radionuclides. The impacts on cement performance of elevated temperature and radiation are discussed, as are some of the potential disadvantages of using alkaline cements.

1. INTRODUCTION

1.1 What is a Backfill?

The concept of backfill originates with mining. Backfill is a solid material that is packed into mine voids to stabilize them against collapse. The backfill material may be of natural origin (e.g., reject fines from ore extraction) or a mixture of natural and manmade materials (e.g., fines bound with slag-cement or $Ca(OH)_2$). The main criteria for material selection are to achieve appropriate mechanical properties at low cost.

In a nuclear waste repository, backfill may fulfill a structural role, e.g., to ensure physical filling of space between oddly shaped packages and the walls of the excavated vault. But backfill has also come to acquire a special role in nuclear waste conditioning: to retard the return of radioisotopes to the environment. This retardation may be physical, but is more usually chemical. In this application, backfill is part of a multibarrier system, and its chemical retardation is an important parameter in performance assessment.

1.2 Why use cement?

Cement - and this usage implies Portland cement and its mixtures with $Ca(OH)_2$ and other blending agents - has many useful properties. Cement is:

- inexpensive and widely available;
- made to standard specifications;
- requires water for reaction and is therefore tolerant of wet wastes;

- continues to floculate and gain strength under water (i.e., it is “hydraulic”);
- is non-flammable and non-toxic;
- is readily processed by remote or automated equipment;
- is dense, and so affords some biological shielding;
- is persistent in the natural environment, where natural analogues demonstrate its persistence; and
- conditions a high pH, which reduces the solubility of many (but not all) nuclides and inhibits microbiological activity.

Cement has emerged high on the list of candidate backfill materials because of these characteristics. Technological experience with cement has enabled control over such physical parameters as strength and permeability. For this reason, it is relatively easy to devise barriers with quite specific present-day properties. Table 1 summarizes some of the design options that are available.

2. NATURE OF PORTLAND CEMENTS

2.1 Production

The Portland cements known today gradually evolved in the period between ca 1800 and 1850 (Blezard 1998). Hence, we have over 150 years experience of their use. Table 2 shows a bulk chemical composition. A mix of raw materials (limestone, shale, sand, etc.) appropriate to form this composition is heated to ~1450°C to achieve the approximate phase composition, also shown in Table 2.

The indurated product of calcination, termed “clinker,” is ground to high specific surface (ca 3000 to 4000 cm^2/g) with added gypsum ($CaSO4 \bullet 2H_2O$) to control hydration properties. The resulting powder is mixed with water to initiate hydration. The hydration reactions produce a product that is like a chemically bonded ceramic, except that bonding is achieved without heat. The hydration is, however, strongly exothermic. The hydrated solids typically shrink, even during isothermal set, although self-heating exacerbates volume changes. To reduce shrinkage and provide a heat sink, sand may be added, giving mortar; or sand and coarser aggregate may be added, giving concrete. Because cement bonds strongly to silicate mineral aggregates, it can be considerably diluted without significant loss of strength. For example, typical construction concretes (density ~2400 kg/m^3) may contain 275 to 450 kg/m^3 of cement.

2.2 Properties

Cement bonds to many other materials, either by surface reaction or, in some cases, with assimilation. Table 3 gives examples. The distinction between surface reaction and assimilation is often dependent on time and temperature: Reactions that occur initially at the surface may gradually progress to bulk reaction. Temperature increases in the range 20 to 50°C often markedly accelerate reaction with embedded materials.

2.3 Mineralogy

Figure 1 (after Taylor 1997) depicts the solid hydrate mineralogy of a fully hydrated Portland cement. $Ca(OH)_2$ is a mineral of essentially constant composition and well-defined properties. It is chemically compatible with a gel-like phase, designated C-S-H (calcium-silicate-hydrate). The Ca:Si molar ratio of gel coexisting with $Ca(OH)_2$ is ~1.8, but single-phase C-S-H gels have been obtained to Ca:Si ratios as low as ~0.8. It is, therefore, a phase whose composition, hence its properties, can vary. In common with other materials of low crystallinity, its gel structure is not well known, although modern instrumental methods (e.g., NMR) disclose some details of the bonding. The role of the minor phases, mainly calcium aluminate hydrates, will be discussed subsequently.

2.4 Chemistry

To ensure plasticity in the fresh mix, excess water must be added than is strictly necessary to achieve complete hydration of the clinker. Moreover, although much of the cement hydrates in the first few weeks, unreacted clinker can persist even in 10- to 100-year-old materials, thus tending somewhat to increase the free water content relative to predictions based on complete hydration. As the solid mass sets, residual free water is increasingly trapped in small pores (Powers and Brownyard 1948).

Cements do not set by drying. Even apparently 'dry' concretes may contain much trapped water, the quantity of which depends on maturity and on the original water to cement (w:c) mix ratio. There is some doubt about the critical minimum w:c ratio required for full hydration. Values derived from bound water measurements lie in the range of 0.28 to 0.41 (Köster and Odler 1986). Typical constructional concretes have w:c ratios in the range of 0.45 to 0.60. The excess water is not pure; it dissolves and concentrates Na and K from the cement. Because anions other than OH^- are relatively insoluble, alkali in pore fluid is effectively present as NaOH and KOH, with the result that pore fluid pHs are in the range of 13.5 to 14.0. $Ca(OH)_2$ is capable of conditioning pH only to ~12.6 at 18°C (Glasser and Marr 1983).

2.5 Physics

Set cements contain a wide range of pore sizes. Nanoporosity is a characteristic feature of C-S-H gel, with the result that it has a high specific surface. The measured values - unlike those for carbon-based sorbents - are very sensitive to the nature of the sorbate, lying in the range of 10 to 20 m^2/g for N_2, but they are much higher for water: 20 to 50 m^2/g. Mesoporosity is defined by pores having entry diameters approximately in the range of 0.01 to 1mm. The total volume of mesoporosity is thus highly dependent on the amount of excess water in the mix (i.e., water not required for chemical hydration) and is a complex function of original mix w:c ratio and degree of maturity.

The relationships between porosity and permeability are not straightforward. At low mesoporosity, water permeabilities of the paste are on the order of 10^{-12}m/s. Increasing porosity initially leads to only slow increases in permeabilities, but beyond a certain critical range of values (ca 20% mesoporosity) permeability increases rapidly. Percolation theory confirms the general validity of these empirical relationships, as shown by Garboczi and Benz (1993). High permeability materials may be required for particular applications, in which case chemically reactive cement powder may be partially replaced by cement-sized but chemically unreactive particles (e.g., ground limestone).

Because hardened cement is intrinsically brittle, dense barriers may be subject to cracking. Normal constructional concrete has expansion joints to allow for movement, but this may not be desirable for impermeable barriers. Reinforcement can be used to restrain cracking. Steel is the preferred reinforcement material; although subject to corrosion, concrete provides reasonable protection for embedded steel on account of its high pH and apparently low-permeability to oxygen (Popovics *et al.* 1983). The elastic properties of steel are intrinsically more suited to restraining tensile stresses than materials with a lower elastic modulus, e.g., polymer fibre or mesh.

3. IMPACTS OF TIME AND TEMPERATURE ON THE INTERNAL CHEMICAL PROPERTIES

3.1 Introduction

This discussion assumes initial closed-system behaviour before broadening the scope of the interactions. Likewise, the simplest chemistry will be assumed before broadening its scope. The pH values are referenced to 25°C.

3.2 Oxidation-reduction

Cement systems contain mainly ions in a fixed oxidation state. Possible exceptions include S, present as SO_4^{2-}, and Fe, present as Fe(III). As might be expected, cements are therefore neutral to oxidizing but are not well poised and do not much affect the oxidation state of radionuclide species. The most important electroactive species that may be added as part of the cement system is sulfide (S^{2-}) sulfur, present in blast furnace slag, high loadings of which reduce E_h to as low as -400 mV (Luke and Glasser 1988, Glasser, *et al.* 1988). Because of the poor poising in cement, other electroactive materials undergoing corrosion, such as steel, may effectively control the E_h. Sulfate in cement will not spontaneously reduce but could potentially act as a host for S-reducing bacteria. The impact of radiolysis on redox properties is discussed in section 6.6.

3.3 pH

Alkalis present in cement are readily leached and cannot be considered to control pH except in the short term. Considering $Ca(OH)_2$ to be the main control, its solubility decreases with rising temperatures, up to ~180°C, with the result that the pH decreases to ~12.0 at 180°C. Its crystalline state is otherwise unaffected and its properties are time-invariant. The behaviour of C-S-H is somewhat more complex. At 25°C, C-S-H persistence is probably assured for 10^3 to 10^4 years, but the beginnings of crystallization are apparent at 55°C and 85°C in experiments of several months to several years duration (Lachowski *et al.* 1997). However, as long as C-S-H (amorphous) remains, the equilibrium pH will remain high.

The nature of the products obtained from C-S-H crystallization depends on composition and temperature. Some 20 synthetic CaO-SiO_2-H_2O phases are known. Several of these crystalline solids may themselves be metastable. We still do not have a clear understanding of the true pattern of stability of the crystalline hydrates, and we also lack thermodynamic data for the solid phases. From incomplete data, we tentatively conclude that:

- There are probably no stable crystalline C-S-H phases in the range of 0 to 100°C with Ca:Si ratios greater than 1.5. But the pH conditioning ability of $Ca(OH)_2$ is not affected by crystallization, nor is the equilibrium amount of $Ca(OH)_2$ in cement likely to be reduced significantly as a consequence of crystallization.

- If crystalline C-S-H phases develop, they are likely to constitute a secondary pH buffering source, with pHs in the range of 9.5 to 11, approximately. This buffer system would become active mainly when the primary buffer, $Ca(OH)_2$, was exhausted.

3.4 Impact of other cement constituents

Alumina, and in part iron oxide, influence formation of the "minor phases" noted earlier. Their role will be discussed subsequently. Magnesium forms $Mg(OH)_2$ in the presence of $Ca(OH)_2$ but, as Al and Si activities increase, magnesium instead forms hydrotalcite and sepiolite (Gollop and Taylor 1992). In Al-rich formulations, hydrogarnet, a solid solution between $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and grossularite, $3CaO \cdot Al_2O_3 \cdot 3SiO_2$, develops (Jappy and Glasser 1991). These phases are typically not abundant and, in any event, do not significantly affect the pH of plain cements, although they do reduce the high-pH (>10.5) buffering reserves.

3.5 Impact of cement additives

Table 4 lists some common additives to cement; the table is restricted to those additives that are intended eventually to form part of the cementitious matrix. The impacts of these materials are roughly proportional to the percentage of cement replaced, although the full impact on chemical properties may not be apparent for some time - years or decades at 0 to 25°C - because of slow reaction kinetics. It is therefore unwise to judge the impact of major additions on the basis of short-term laboratory experiments. To set these percentages in context, while civil engineers are accustomed to using 20 to 65% slag replacement, some suggested formulations for waste matrices may use considerably more, up to 90% replacement.

Cements may also contain organics, both intrinsic and extrinsic. The intrinsic organic content arises mainly during clinker grinding. Table 5 lists some sources of organics, including those optionally added to control rheology and shrinkage of wet mixes. The long-term behaviour of these poorly characterized organics in cement is not well known.

4. WASTE-CEMENT INTERACTION

4.1 Physical

Cement concretes can be used in the formation of physical barriers to control the release of radionuclides. Monoliths in the 200 to 500 l range can be made using existing technology, which will provide significant retardation for radioisotopes with half-lives in the 30 to 50 year range (e.g., Cs, Sr). Moreover, cement barriers may be used in other ways: for example, to restrict the percolation of water through a repository. Such applications, however, lie outside the scope of this presentation. Nonetheless the reader should be aware of the desirability, perhaps the inevitability, of introducing engineering concrete during construction. This includes concrete in the form of rock anchors, grout curtains, spraycrete, or precast sections to maintain the integrity of vaults or to form shaft seals, etc. Even repositories not deliberately cement-conditioned may contain significant amounts of cement, which inevitably will affect repository performance. Therefore, the use of cement to maintain physical integrity will have chemical consequences.

4.2 Chemical

The chemical behaviour of cements is central to their selection and future performance. One can distinguish chemical reactions with materials from those with species, i.e., ions or complexes in aqueous solution. Reactions with materials are largely outside the scope of this review, and it will be assumed that the relevant species is present in solution or can react via the aqueous phase. General reviews are available to provide background, e.g., Barret and Glasser (1992).

Three types of reaction leading to insolubilization of radioactive species are possible, namely:

- sorption onto cement surfaces;
- precipitation by OH^- ions, furnished by dissolution of cement components; and
- reaction with cement solids to form "salts". These may be discrete compounds, e.g., precipitation of Sn(IV) to form $CaSn(OH)_6$ or solid solutions, in which the active species substitutes for some essential (and usually more abundant) species within the structure of one or more cement minerals.

Many radionuclides are present in the wasteform at high dilutions, and it is not always possible to distinguish the binding mechanism. For many species, the binding mechanism is concentration-dependant: sorption dominates at low concentrations while at higher concentrations a solubility limit may be set by formation of a solubility-limiting phase.

The principle of a solubility-limiting phase is illustrated by the behaviour of calcium sulfate, a sparingly soluble salt, in water. As calcium sulfate is added to initially pure water, it dissolves until the solution becomes saturated. Thereafter, further additions will increase the amount of precipitate but, at constant temperature and pressure, the aqueous composition will remain constant. Therefore, when saturation is reached, the flux of $CaSO_4$ transported per unit volume of the aqueous phase becomes independent of loading. This general principle, of solubility-imposed limits on transport flux, is applicable to cement systems.

However, the choice of a solubility-limiting phase for a radionuclide may not be obvious. Compiled data on the maximum solubility of selected species incorporated in a cement matrix in cement pore fluids are given in Table 6 (from Glasser *et al.* 1998). These data must be regarded as provisional because, in the majority of cases, the nature of the solubility-limiting phase is not known. Until it is characterized, reported solubilities may be artifacts of the experiment. Minimal verification steps to establish the existence of a solubility-limiting phase and determine its impact on performance include the following:

- for elements having multiple oxidation states, verification that the desired speciation has been conserved in the course of experiment;
- determination of the chemical nature of the solubility-limiting phase, i.e., its formula and structure type or other characterization parameters; and
- synthesis of the solubility-limiting phase, followed by determination of its solubility and stability in response to changing pH, Eh, temperature, and the impact of ground waters.

Nevertheless the overall impact of cement imposes solubility limits on many species and is an important justification for using cement as a chemical barrier.

5. THERMAL FACTORS

5.1 Overview

Portland cements and concretes are not normally used in environments where the temperature exceeds 40 to 45°C. During initial set, large masses may occasionally exceed 50 to 55°C but, to avoid subsequent thermal contraction, this excursion is usually controlled by design. Cements have been used for prolonged service in "warm" environments: e.g., in oil wells (40 to 120°C) or at even higher temperatures in geothermal wells. Experience shows that the cement must be specially proportioned to have a high silica content (ca 50 mol%) in order to maintain strength over reasonable performance lifetimes (Bensted 1998).

5.2 Stability of cement minerals

Even in a dry environment (no liquid water, but humid) the decomposition temperature of $Ca(OH)_2$ is high, ca 400°C. Its solubility decreases slowly with rising temperatures in the range of 0 to 200°C, approximately. Table 7 shows the data to 100°C.

The silicate and aluminate content of Portland and blended Portland cements complicates the phase changes that are observed. The most important single phase of these cements is cement gel, C-S-H. Because gels are unstable at all temperatures, crystallization can be expected to occur, although at ~85°C reactions do not proceed to completion within 1 to 2 years. But at higher temperatures, 160 to 180°C, using suitably prepared reactants, complete crystallization can often be obtained in 10 to 100 days. Table 8 shows the nature of the products obtained. This is a mode-of-occurrence compilation: The stable equilibria are not known. If comparison is restricted to

~25 °C, crystallization generally reduces the pH by 1 to 2 units, relative to a gel of the same composition. However, if $Ca(OH)_2$ is present, it will continue to act as a high-pH buffer.

Several other important points concerning the impact of temperature are as follows:

- The impact of siliceous blending agents and temperature lowers the pH of cement. However, if free $Ca(OH)_2$ persists, the pH decrease is slight relative to 25 °C.
- Reduction of pH implies a reduction of solubility and, other factors being equal, a longer pH conditioning lifetime.
- The solubility of Ca, which at ~25 °C is much greater than Si, becomes much more nearly congruent at 160 to 180 °C. Indeed, Si may in some instances dissolve faster than Ca, especially at compositions with Ca/Si <1.0 and above 180 °C.
- The crystalline structures that result from crystallization of gel contain a range of silicate anion types, but those with layered or sheet-like structures may have useful ion exchange and sorptive properties.
- The crystalline phases are deliberately designated by their mineralogical names to emphasize that they occur and persist in nature.
- Once temperature returns to ambient, the crystalline phases will not spontaneously revert to gel; crystallization is an irreversible process.
- Phase relations in the $CaO-SiO_2-H_2O$ system are not well known, and few reliable data are available except for $Ca(OH)_2$.

6. INTERACTIONS WITH NEAR-FIELD COMPONENTS

6.1 Overview

In the preceding section, the "closed system" aspect of cement behaviour was described. However, as time increases, or as temperature increases, or both, cements increasingly react with components in the near field. These reactions may be either extrinsic or intrinsic, i.e., if the potentially reactive material is embedded in or is in direct contact with cement. In the case of extrinsic reactions, the presence of liquid water greatly facilitates mass transport necessary for reaction.

6.2 Reactions with species in the near field

Key reactions and their consequences are summarized in Table 9. Intrinsic reactions arising from solid waste components have been studied in most national programs. However, rock excavated from vaults may not be suitable for aggregates. Engineering experience shows that rocks containing glass, tridymite, cristobalite, and various forms of cryptocrystalline and strained silica are unsuitable for use in humid environments. Physical expansion, resulting in disruption, may occur as a consequence of aggregate-cement incompatibility (Shayan 1996).

Extrinsic reactions may affect both the repository host rock and the concrete barriers. On the other hand, processes such as complexation of actinides as soluble carbonate are virtually ruled out because cement so effectively removes carbonate. Carbonate reaction at <160°C results in formation of $CaCO_3$ and silica gel, while at higher temperatures scawtite, $Ca_6Si_6O_{18}{\cdot}CaCO_3{\cdot}2H_2O$, becomes stable. Mg replaces Ca in a $Ca(OH)_2$ backfill, and degradation will occur as a consequence of reactions of the type:

$$Ca(OH)_{2\,(s)} + Mg^{2+}{}_{(aq)} = Mg(OH)_{2\,(s)} + Ca^{2+}$$

Replacement is also accompanied by continuing dissolution of Ca in the same manner, but not necessarily to the same extent, as in pure water.

Chloride is not particularly harmful to cement performance; $Ca(OH)_2$ and C-S-H are capable of conditioning the pH of NaCl solutions, at least up to ~8 M, almost as well as in initially pure water. Solubilities of the cement phases, especially $Ca(OH)_2$, are increased only slightly by the presence of chloride. Chloride enhances the corrosion rates of steel; Leeming (1989) summarizes the present state of knowledge. Sulfate is likely to have an impact on physical barrier performance, and the minor components of cement often control these reactions. For example, the Al_2O_3 component in cement reacts with infiltrated sulfate to form ettringite at <100°C. Owing to accumulation of low-density ettringite in subsurface zones of cement paste, expansion with cracking often occurs. The phenomenon is well known in the oil industry, where special cements, low in Al_2O_3, have been developed to resist sulfate attack. Such cements are widely used in the oil industry and have standard API specifications (Nelson 1990).

Destructive reactions with groundwater components do not necessarily accumulate. For example, if a well-made sulfate-resistant concrete is exposed to sea water, it develops a semi-protective skin of brucite ($Mg(OH)_2$), calcite ($CaCO_3$), and silica gel. Experience shows that this skin can be established over a wide range of salinities and will reheal if broken. Consequently, the initial rapid permeation of sea water components most damaging to embedded steel (oxygen, chloride) slows quite rapidly once this semi-protective layer is established.

Progress is being made in assessing these and other reactions with geochemically abundant constituents, and we now have the data to predict, for most components of groundwater:

- which reactions will occur, and over what ranges of concentrations, in the temperature range up to ~85°C;
- the mass balances between precipitation and dissolution reactions;
- the pH conditioning potential and saturation concentrations of percolating solutions; and
- the confidence that predictions can be made using equilibrium codes because the reaction direction of field examples is sufficient to move the system toward the predicted equilibrium.

Cements also have the potential to denature some organic substances. For example, humic acids are precipitated in alkaline, Ca-rich environments. Some potential complexants (e.g., citric and oxalic acid, or oxalate) are neutralized; citrate probably by rearrangement to carbonate and oxalate precipitated as its calcium salt (see Smillie and Glasser 1998). Phosphate is also very effectively removed by precipitation.

However, a number of aspects of deterioration cannot presently be predicted with confidence:

- physical consequences of dissolution and precipitation: porosification, expansion with cracking, etc.;
- the tendency of reaction products to inhibit equilibrium attainment between fresh cement solids and percolating water;
- reaction kinetics between cement and waste species and/or embedded materials.

6.3 Impact of cement on rocks and minerals in the near field

The pore fluid of a cement, pH at least 12.4, is so rarely encountered in nature that it is almost certain to react with rocks and minerals in the near field. Broadly, three process might be surmised:

- surface hydroxylation of minerals, with changes to their sorptive properties;
- ion exchange, initially with alteration to the surface and perhaps also to bulk mineral properties in the longer term;
- outright destabilization of one mineral with respect to others; this might simply speed a process already occurring (e.g., conversion of feldspars to clays).

Dilution of cement pore water will of course diminish the impact of the high pH “footprint” on the properties of the far field. But if flow is two-dimensional, e.g., if flow occurs through cracks, dilution may not be too important a factor. Thus the high alkaline plume may have substantial impact on:

- sorption characteristics of rocks and minerals;
- the stability of near-field minerals, including secondary barriers such as bentonite, which is destabilized by cement;
- precipitation and dissolution processes which could, in turn, influence permeation properties.

The concept of an alkaline plume impacting rock properties is relatively recent. Nevertheless, natural analogue studies, such as those at Maquarin, demonstrate that springs and seeps that permeate natural rocks akin to cements can emerge somewhat distant from the cement rock source and still have high pH (Savage 1997).

6.4 Microbiological degradation

Although concretes have been used in a wide range of environments, actual examples of attack by microbiological systems are either rare, poorly documented, or anecdotal. Warm crude oil inoculated with sulfate-reducing bacteria is said to attack cement. But cements free from organic substances do not offer a supply of nutrients other than S, and moreover their high pH is inimical to favourable growth. Concretes in outdoor environments are occasionally attacked by complex colonization, but at least some of the species involved require light for photosynthesis. Indirect attack may also occur, as in silage pits and fermentations, where sugars and organic acids are generated.

6.5 Colloid generation

The initial stages of cement hydration generate colloids as the aqueous phase, which quickly supersaturates. Supersaturation is discharged by precipitation. The gel phase in cements is strongly flocculent, and mature cement and concretes appear not to form colloids, as evidenced from long experience with concrete pipes used to transport potable water. Therefore, persistent colloid generation from cements appears unlikely. The main possibilities for colloid generation are likely to arise when a high-pH plume is diluted and/or neutralized, or by action of the high-pH plume on rocks, minerals, and other components in the near field.

6.6 Radiological stability

The main impact of radiation on cements is radiolysis of water. Rates of radiolysis are not significantly different than in pure water. Extremely high fluxes inhibit cement from setting, but it is unlikely that fresh cement will ever be used in this application. Many reactors for power production have concrete containments, which are exposed to prolonged and moderately high levels of radiation. No instances of strength loss or other detrimental features have to our knowledge been reported.

One factor that should be noted is the oxygen storage capacity of cement. During radiolysis of water, H_2 and O_2 are normally evolved in stoichiometric ratio, i.e., 2:1. But in practice oxygen is scarce (Wilding 1992). It is speculated that evolved O_2 is converted to peroxides (O_2^{2-}) in the alkaline environment and thereafter sorbed by cement phases. If correct, the E_h could rise substantially, with consequences for enhanced corrosion of metal and stabilization of more highly oxidized radwaste species.

7. DISCUSSION

Analysis of cement performance has been made on a phenomenological basis. Although much progress has been made in understanding the long-term performance of cement and concrete, some features and processes remain incompletely defined. If chemical processes are envisioned as occurring at the atomic level, we can scale these features and processes. At the nanometer level, the pertinent questions are:

- What are the binding forces between cement and radionuclides? Can we distinguish sorption (surface, bulk) from solid solution and true precipitation as a solubility-limiting phase?

- Can these binding forces, once characterized, be isolated for separate study and the results incorporated into static thermodynamic models as well as dynamic models involving migration?

- What features of cement behaviour relevant to performance are as yet incompletely documented: for example, oxygen storage by cement hydrates and its impact on E_h, on corrosion, etc.?

- Will prolonged warm conditions result in crystallization of the cement gel phase and, if so, what will be the consequences?

Proceeding to a larger scale (micrometer to mm), the relevant questions are:

- Will barrier layers formed on cements as a consequence of reaction with groundwaters inhibit cement performance in terms of the ability of barriers to condition percolating water?

- Where concrete (as distinct from cement) is used, will "inert" fillers and aggregates remain inert in the long term? If not, what will be the consequences?

At a still larger scale (mm to m) the relevant questions are:

- When concrete is used as a construction material, even if not in immediate contact with waste, do we need to take account of its pH conditioning impact? If so, how do we assess the impact for performance assessments?

These questions cannot at present be answered conclusively. But research on cement properties has given us the confidence to assert that answers to these questions are important and, moreover, that we have the methodologies and capabilities to provide answers. In formulating experimental and theoretical approaches, it is also important to realize that modellers often work in terms of specific time frames. Although kinetics are difficult to quantify, progress is also essential to link kinetics with equilibria in order to provide data in suitable form for the modeller to evaluate cement barrier performance over a series of time frames.

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Table 1. Backfill design options.

Primary Consideration	Response
Good physical retention combined with chemical retardation.	Use dense and impermeable concretes, developed, for example, for water-retaining structures.
Good chemical retardation but permeable to gas.	Dilute cement with inert material, choosing particle size distributions to obtain less than optimum packing.
Retrievability, but ensuring good chemical conditioning.	Soft backfills having low cement content and possibly high $Ca(OH)_2$ contents.

Table 2. Range of compositions of cement available in the UK (1987).

Oxide	**wt. %**
SiO_2	19-22.2
Al_2O_3	4.1-6.2
Fe_2O_3	2.0-3.3
CaO	63.2-64.0
MgO	0.8-2.2
SO_3	2.5-3.0
K_2O	0.43-0.8
Na_2O	0.13-0.24
Phases	**wt. %**
Ca_3SiO_5	46-66
Ca_2SiO_4	8-29
$Ca_3Al_2O_6$	5-13
$Ca_2(Fe,Al)_2O5$	6-10

Table 3. Physical bonding of cement to other materials.

Material	Bond Characteristics
Steel	Passivates steel, the oxide coating of which bonds physically to cement.
Glass	Bonds well initially but glass is broken down by high pH.
Mineral aggregates	Good bonds with quartz and limestone. Some minerals, e.g., tridymite, cristobalite, opal, react strongly, with expansion.
Organic fibres	Bonding largely frictional, but adequate. Synthetic fibres (nylon, polythene, polypropylene) not degraded in 10-20 years.

Table 4. Chemical and mineralogical aspects of some matrix-forming additives to Portland cement.

Additive	Purpose and Long-Term Impact
Coal combustion, fly ash (class F)*.	Improve fluidity of wet cement. Reacts with and reduces potentially available $Ca(OH)_2$.
Glassy blast furnace slag and class C* fly ash.	Slag lowers Eh. Both react with and produce potentially available $Ca(OH)_2$ but not as rapidly as class F ash.
$CaCO_3$ (ground limestone):	Added to enhance permeability. Above 160°-180°C, reacts strongly with calcium silicate hydrate forming scawtite. Major reduction in potential $Ca(OH)_2$.

* ASTM classification

Table 5. Organic content of Portland cement.

5a. Intrinsic organics

Organic	Comment
Oil, grease, ethanol amines, stearates, miscellaneous.	Contamination from grinding mills and so-called grinding aids; also, organic content contained in gypsum, 2-5% of which is interground.

5b. Extrinsic organics

Organic	Comment
Water reducing additives and plasticizers.	Lignosulfonates, sulfonated melamine, and naphthalene formaldehyde condensates.
Proprietary anti-bleed, anti-foaming, anti rebound and shrinkage control additives.	Wide class of organics formulations, mostly commercially confidential compositions.

Table 6. Solubility of selected radionuclides in cement-conditioned water or in cement pore fluid.

Species	25°C Solubility (Molar)	Species	25°C Solubility (Molar)
Am (III)	3×10^{-11}	Ra (II)	1×10^{-6}
Pu (III)	7×10^{-11}	Pb (II)	4×10^{-4}
Np (IV)	8×10^{-9}	Sn (IV)	1×10^{-7}
Pa (V)	5×10^{-10}	Pd (II)	10^{-4} to 10^{-6}
Th (IV)	4×10^{-9}	Zr (IV)	$\sim 1 \times 10^{-8}$
U (VI)	2×10^{-7}	Te (IV)	5×10^{-8}

Table 7. Solubility of portlandite, $Ca(OH)_2$.

Temperature °C	Solubility g/ℓ	Temperature °C	Solubility g/ℓ
0	1.30	30	1.09
5	1.28	40	1.00
10	1.25	50	0.92
15	1.21*	60*	0.83
20	1.17*	80*	0.66
25	1.13	99	0.52

*Interpolated values

Table 8. Crystallization products of C-S-H gel.

Ca:Si Molar Ratio of Gel	Characteristic Product Obtained at ~160-180°C
0.85-1.0	tobermorite
1.0-1.4	xonotlite, foshagite
1.4-1.8	hillebrandite

Table 9. Environmentally conditioned reactions.

9a. Intrinsic

Reaction	**Consequences***
Cement plus unsuitable aggregate	Expansion, which if continued is disruptive.

9b. Extrinsic

Reaction	**Consequences***
Carbonate, $CO_{2\ (aq)}$	Formation of $CaCO_3$; reduction of pH.
Chloride, Cl^-	Not damaging to cement.
Sulfate	**Can disrupt dense concrete.**
Na, K	Not harmful.
Mg	Replaces Ca; lowering of pH.

*At concentrations typical of potable groundwaters: brines and high salinities require special treatment.

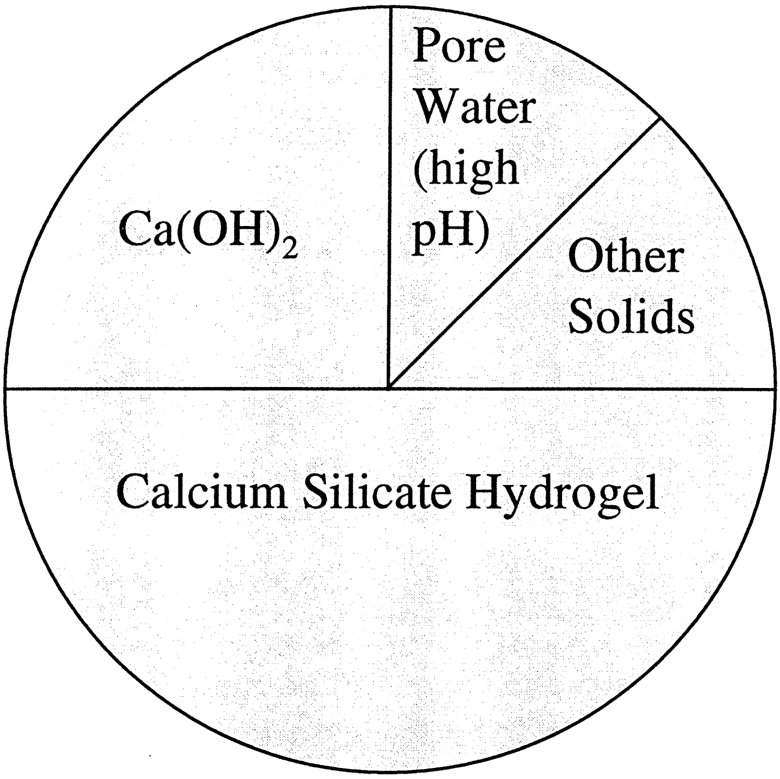

Figure 1. Schematic showing the phase composition of a fully hydrated (25°C) Portland cement.

BACKFILL AND SEALING MATERIALS AS GEOCHEMICAL BARRIERS FOR RADIONUCLIDE CONTAINMENT IN GERMAN SALT FORMATIONS

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1. INTRODUCTION

The safety of geologic disposal relies on multibarrier containment of radionuclides by both engineered and natural systems, with some inherent redundancy. The engineered/geoengineered barrier systems comprise the waste form, packaging materials, potential overpacks, backfill and sealing materials. The natural geologic barrier is provided by emplacement in deep rocks with minimal groundwater flow. Backfill and sealing materials are considered both as physical and (geo)chemical barriers against radionuclide release. Long-term safety provided by physical barriers is based on minimizing groundwater access to the waste package (isolation) and retardation of transport of contaminated groundwater. Geochemical barriers contribute to long-term safety by limiting radionuclide mobility even in presence of water.

In Germany, underground investigation of the Gorleben salt dome as a repository site for high level waste is proceeding rapidly. A concept for sealing and backfilling void volumes is not yet finalized. Important materials proposed include crushed salt, apatite and bentonite. However, other options are also considered. Physical barrier effects, including thermomechanical properties and porosity/permeability properties, are discussed by Brewitz (1998; this volume). This paper discusses investigations of backfill and sealing materials as (geo)chemical barrier in salt formations.

2. GEOCHEMICAL APPROACH TO BACKFILL AND SEALING MATERIAL PERFORMANCE

Geochemical assessment of backfill and sealing materials performance under repository-relevant conditions involves five topics: (i) the long-term geochemical stability of the backfill and sealing materials and their beneficial physical and chemical properties in case of brine access; (ii) the geochemical conditioning of the groundwater chemistry (Eh, pH, pCO_2) by solid/liquid interaction providing reduced radionuclide mobility; (iii) the retention of radionuclides by sorption and by coprecipitation within secondary alteration products; (iv) the role of the geochemical barriers as potential secondary sources for radionuclide release; and (v) the potential detrimental role of backfill materials by potential acceleration of waste form dissolution rates or by release of nonradioactive toxic chemicals.

2.1 Long-term geochemical stability of the backfill and sealing materials

Various geochemical processes could alter the beneficial physical and chemical characteristics of backfill and sealing materials by alteration of the material itself. For example, smectite may alter to illites, and concretes/cements to $Mg(OH)_2$-type materials etc. Geochemical stability may be based on establishment of thermodynamic equilibria, mass transfer limitations (e.g., limitation of supply or transport of potassium for smectite/illite transformation) and on slow chemical surface reaction kinetics. Alteration sequences of primary backfill and sealing materials can in part be predicted by geochemical reaction path modeling. Paragenetic alteration sequences may be significantly altered by the formation of metastable phases. It is important to know whether secondary alteration phases will keep some of their beneficial properties. An empirical approach to assessing the long-term stability of backfill materials is by studying natural analogue materials in salt formations. Certain minerals suggested as backfill materials in salt are also found in many million-year-old salt deposits: crushed salt, clays, apatite; while others (e.g., magnetite, apatite) are known from other geologic locations to persist for hundreds of millions of years.

2.2 Geochemical conditioning of the groundwater (brine) chemistry

Radionuclide release from the waste forms, solubility, formation of solid phases (precipitation), migration, sorption, and colloid formation depend on the geochemical environment.

Because of the various geochemical interactions between backfill, sealing, containers, and waste materials, the geochemistry of brines in the near field of disposed nuclear waste will be significantly altered when compared to brines existing in undisturbed salt formations. Three geochemical parameters are of utmost significance for radionuclide mobility: pH, Eh, and pCO_2.

The pH: Natural saline solutions, including the solutions in Table 1, generally have a low buffering capacity for pH. Consequently, the pH can vary significantly because of waste/water interactions. Fixed pH conditions require solid/liquid phase equilibria-based buffer systems (e.g., cementitous materials, $Mg(OH)_2$). The large range of potential pH values (3-10, even higher with cement) in a disposal location is a major source in uncertainty in expected radionuclide solubilities. It has been reported that many long-lived fission products and actinides exhibit high solubility and a low tendency for sorption in Mg-rich brines. Maximum concentrations found for Pu and Am in the presence of dissolved spent fuel and high level waste glass were on the order of 10^{-4} to 10^{-5} mol/l. In particular, in the glass/Mg-rich brine/H_2O system, pH values as low as 3 were obtained, resulting from the formation of Mg-rich smectitic minerals. In the absence of silica sources (e.g., in the presence of spent nuclear fuel), a pH around 5 to 6 is expected in Mg-rich brines. Solution concentrations of many radiotoxic elements can decrease by orders of magnitude if pH increases to values >8. High pH values can be obtained by cement, MgO, or fly ash addition.

The Eh: Under reducing conditions, important redox-sensitive radioelements such as Np, U, Pu, Tc, or Se are transferred in their sparingly soluble tetravalent oxidation state. Most deep repositories, such as the Gorleben salt dome, are planned in rock formations with anoxic or even reducing geochemical environments. For example, in Gorleben, reducing brines were found with up to 1000 mg/l Fe^{++}. Often methane, and sometimes H_2S, are found as compounds of gas inclusions in salt, clearly indicating reducing conditions. However, oxidizing conditions may occur in close vicinity to disposed wastes. These may result from air intrusion during repository operation, from oxidizing waste contents, or from post-emplacement oxidant generation by radiolysis. Conditioning of a reducing near field can be achieved in particular by the anoxic corrosion of Fe available as container material. From a geochemical point of view, large quantities of iron are beneficial; however, this beneficial effect must be balanced against the potentially detrimental effect of the generation of large quantities of hydrogen gas upon contact with brines.

Main element solution composition: For a salt dome like that of Gorleben, the typical salt brines are summarized in Table 1. These are reference solutions in the German research program on high level waste disposal.

Compositions of naturally occurring saline solutions are controlled by temperature and are dependent on salt/solution equilibria, the six-component Na-K-Ca-Mg-Cl-SO_4 system of oceanic salts. Most salt brines are saturated with halite (NaCl). The relation between the stability fields of various salt minerals in the composition range of saturated solutions at 25°C is described in Figure 1. Halite is not shown because of its omnipresence.

The partial pressure of CO_2: It is well known that radionuclide mobility (increased solubility, decreased tendency for sorption) is strongly increased by carbonate complexation. This is true particularly for the tri- and hexavalent, but also for the tetra- and pentavalent actinides. Carbonate sources include carbonates in the emplacement horizons, CO_2-rich gas inclusions, and the biodegradation products of organic wastes. The carbonate content of salt brines is significantly lower than that of typical groundwaters in hard rock formations. The main reasons for this are the large concentrations of Ca and Mg found in most brines, leading to calcite or magnesite control of carbonate concentrations. Systematic calculations of carbonate equilibria were performed, covering the main salt brine compositions in Figure 1. At each position of this diagram, the activity of Ca^{2+} and Mg^{2+} is known. This allows calculation of the stability field boundaries between calcite and magnesite as well as the of activity of CO_3^{2-}. The smaller triangle in Figure 1 shows that carbonate concentrations are mainly controlled by magnesite. Calcite is dominant only in the KCl-rich corner and in $CaCl_2$-rich solutions, which are relevant in cement/brine systems. High CO_3^- activities can only be expected in Na_2SO_4-rich NaCl solutions with very low Mg contents. Based on these calculations, it seems that the natural salt/water system already has a strong capacity to maintain low carbonate concentrations. The addition of special backfill additives like MgO may only be useful for chemical conditioning of carbonate activities in the case of expected intruding Na_2SO_4-rich NaCl solutions.

2.3 Retention of radionuclides by sorption and coprecipitation

The mobility of radionuclides depends strongly on (i) the chemical nature and stability of the species in groundwater and (ii) the characteristics of the various surfaces of geoengineered barrier materials.

(i) Chemical nature of dissolved radioelements. Typical mobile species are complex ions or colloids. Key factors controlling radionuclide mobility are charge differences between surfaces and solution species, and specific chemical interaction affinities. In contact with groundwaters, most surfaces of backfill and sealing materials are negatively charged. Radionuclide mobility is highest if the solution species have the same negative charge as the surfaces. Consequently, all cations tend toward surface sorption.

The geochemical stability of positively charged species decreases with increasing charge. The charge of the bare ion depends strongly on the oxidation state. Positive ions can decrease their charge and increase their mobility by complexation or colloid formation. Elements in higher oxidation states form oxo-ions with lower charges. Complexation increases with pH and carbonate concentration because of the formation of hydroxo- and carbonato- complexes.

The oxidation state of many radiolements depends on the redox state of the geochemical environment. At the low redox potentials expected in the near field, elements such as Np, U, Pu, and Tc will be reduced to their tetravalent state. They become then rather low in solubility but show a high tendency for colloid formation. Systematic experimental and modeling investigations of the thermodynamic behavior of actinides and long-lived fission products in natural saline environments are in progress. Work is focused on heptavalent Tc, hexavalent U and Pu, pentavalent Np, and tetravalent U, Pu, Np, and Tc. The work also considers complexation with hydroxide, chloride and carbonate ions, the effects of ionic strength, pH and redox potential. Considerable research is still necessary, particularly for understanding the behavior of tetravalent elements.

(ii) Nature of backfill and sealing materials surfaces: With respect to radionuclide retention, the specific surface area, sorption site density, and retention mechanism must be considered. It is important to distinguish between reversible and irreversible retention processes as well as between sorption and coprecipitation. The various reactions are illustrated in Figure 2.

The reversible binding of radionuclides by ion exchange mechanisms (e.g., in clay interlayers) provides retardation of potential radionuclide fluxes to the environment. In the case of an intrusion of a limited brine volume to the waste forms, followed by flow across the backfill for a limited time period, the potential maximum flux of radionuclides to the far field may be significantly reduced by (in principal reversible, yet permanent) entrapment of radionuclides. However, for long-term lasting water flux across the backfill barrier in the case of very long-lived radionuclides, the total release from the repository and the resulting maximum concentrations in the environment may not be reduced but may be retarded by reversible sorption. A different situation arises if radionuclides are irreversibly sorbed on the surfaces of backfill materials or are fixed in the structure of the secondary phases by coprecipitation. For example, it was observed that trivalent actinide sorption on silica surfaces occurs by incorporation (diffusion? surface site restructuring?) in the silica structure. Similarly, An(III) may be retained from solution by diffusion into the apatite crystal structure. Future remobilization would have to involve the dissolution of the host phase, and maximum radionuclide flux to the far field would depend on brine flux volumes, on the saturation index of the brines with respect to the host phase, and on host phase solubility. Potential secondary host phases for coprecipitation are alteration products from cementitious materials, apatite, or container degradation products, etc.

2.4 Secondary sources for radionuclide release

Source terms must be developed not only for primary waste forms (source term I) but also for radionuclides bound to backfill or sealing materials and their alteration products. Radionuclides may become remobilized if the secondary phases are redissolved (source term II). This is important particularly if the geochemical conditions change with time. For example, initial interaction can occur in NaCl-rich brines, leading to the formation of secondary radionuclides containing phases that may be unstable in the presence of a later intrusion of $MgCl_2$ solutions.

2.5 Potential detrimental role of backfill materials

(i) Potential acceleration of waste form dissolution rates: It is important to consider synergistic effects among the various components of the repository near field. For example, it has been reported that under certain conditions the presence of carbon steel may lead to accelerated dissolutions rates of nuclear waste glass. This results from the formation of Fe-silicates, which control saturation of silica. The importance of these effects is governed both by thermodynamic driving forces and by the relative rates of waste-form and backfill dissolution.

(ii) Release of nonradioactive toxic chemicals: Safety assessments of repositories may need to prove both long-term radiological safety and the absence of groundwater pollution by nonradioactive toxic chemicals. Components like fly ash, with some beneficial properties for radionuclide immobilization but high contents of toxic elements, may thus be found detrimental to overall repository safety.

(iii) Release of backfill colloids. Backfill barriers such as bentonite were shown to filter radiocolloids generated during waste form dissolution. The overall efficiency of this effect has not yet been assessed. On the other hand, at the backfill/host rock boundary the backfill material may release some colloidal material by dispersion processes. Examples are smectitic clay particles, which may become detached from the bentonite surface. If the bentonite has sorbed certain radionuclides, these may also become dispersed.

3. GEOCHEMICAL PROPERTIES OF INDIVIDUAL BACKFILL MATERIALS FOR SALT FORMATIONS

Various backfill and sealing materials have been studied for use in repositories designed for salt formations. Studies of radionuclide retention of apatite were performed at the Free University of Berlin and studies of magnetite were conducted at INE-FZK. For modeling radionuclide migration, empirical sorption data for the long-lived radionuclides Np, Pu, U, and Th were generated for different backfill and sealing materials proposed for the German radioactive waste disposal site in Morsleben (ERAM). The work was conducted by INE-FZK for the Bundesamt für Strahlenschutz (BfS). The materials studied were crushed salt from Morsleben, fly ash, and Na- and Ca-bentonite. Solutions included a Mg-rich quinary salt brine (Solution 1) and a NaCl-rich solution, (Solution 3). The effect of complexing waste constituents (EDTA, citric acid, and isosachcharinic acid) and of colloid formation has also been investigated. The experimental conditions are batch sorption tests in preconditioned solid/liquid systems, continuously shaken at room temperature, in Ar with 1%CO_2. A brief description of some principal materials follows.

3.1 Apatite

Potentially important backfill additives are phosphate minerals such as Hydroxyapatite (HAP), $Ca_5OH(PO_4)_3$. The adsorption of Sr on synthetic HAP can be described by a Langmuir adsorption isotherm and follows an ion exchange mechanism (Lazic and Vukovic, 1991). For Mg and NaCl-rich salt brines the kinetics and mass balance for retention of the radionuclides U(VI), Th, Np, and Pu influenced by HAP have been studied in the temperature range between 25 and 120°C by FU Berlin (Gauglitz et al., 1992a; 1992b; 1992c; Gauglitz, 1994). The experiments were performed with a high initial concentration of 0.01 mol/l dissolved actinide ions per 0.1 mol/l of HAP. Under these conditions new actinide phases precipitate by dissolution of HAP, and sorption was not important as a retention mechanism.

With U(VI) at all temperatures, uranyl micas were formed (i.e., layered minerals with U/P ratios of 1 in the layers and divalent cations and water molecules in the interlayers): Saléeite $Mg(UO_2)_2(PO_4)_2{\cdot}9H_2O$ is formed in Mg-rich Solution 2 at 25°C while Meta-Autunite $Ca(UO_2)_2(PO_4)_2{\cdot}6H_2O$ is formed in the NaCl-rich Solution 3 and Meta-Autunite II $Ca(UO_2)_2(PO_4)_2{\cdot}0\text{-}2H_2O$ in solution 2 at higher temperatures. The uranyl micas are solid solutions. In contrast to saturated salt brines, in distilled water uranylphosphates $(UO_2)_3(PO_4)_2{\cdot}4H_2O$ were formed. There are indications that Np also can be incorporated in the structure of the mica, leading to almost 100% reduction of Np concentrations in NaCl-rich brines. In the case of Th, amorphous phases were formed. Solution concentrations of U(VI) were between 10^{-7} and $8{\cdot}10^{-6}$ M, and concentrations of Th were between $5{\cdot}10^{-7}$ and $2{\cdot}10^{-5}$ M.

The reaction path of HAP with salt brines has been calculated using the geochemical code EQ3/6 (Wolery, 1983; Wolery and Daveler, 1990), applying the specific ion interaction model of Pitzer and a database applicable to actinide chemistry in high ionic strength solutions. Missing were ion interaction coefficients for the various uranyl phosphate complexes. Solubility constants of uranyl micas were taken from the compilation of Phillips et al. (1988). The calculations simulate a stepwise dissolution of HAP in the salt brine. The speciation in solution and the degree of saturation of potentially oversaturated phases were calculated. This allows predictions of the kinds of secondary phases that can precipitate in a given solution and how much HAP needs to be dissolved before equilibrium is reached. Also important is the evolution in solution pH and the corresponding equilibrium concentration of U(VI).

The calculations of HAP dissolution in Solution 1 indicate that a stable equilibrium system is expected. The calculations showed that 0.1698 M HAP can be dissolved incongruently in 1 kg H_2O of solution 1 before equilibrium is reached. The release of Ca from HAP leads to the precipitation of anhydrite. Formation of brucite ($Mg(OH)_2$) buffers the pH at a value of about 7.4. This resulting pH is independent of the starting pH. A concentration of 0.0001 M uranyl-ion leads to the formation of either $CaUO_4$ or, in the case of slow precipitation kinetics, to the formation of becquerelite. In this case an equilibrium concentration of U(VI) of about $2.3{\cdot}10^{-6}$ mol/kg is computed.

In the NaCl-rich Solution 3, the pH is not buffered by the addition of HAP. Depending on the starting pH, different amounts of HAP will need to be dissolved to reach equilibrium (between 0.003 M at pH 1 and 10^{-10} M at pH 9). In the presence of 0.0001 M U(VI), Na-Autunite formation is predicted in the pH range 2 – 4 with equilibrium U(VI) concentrations lower than 10^{-7} M. With increasing pH, the existence of $CaUO_4$ or becquerellite was computed. U concentrations increase to about 10^{-6} M because of the predominance of U(VI) hydroxo species at the computed pH.

Only in the acid pH range (Solution 3) were the experimental observations in agreement with the computed results. In the experiments, the starting conditions were acidic because of the large quantity of added actinide nitrate solution. One may thus infer from the modeling exercise that the experimentally formed phases may not in all cases remain stable under repository-relevant neutral-to-alkaline pH conditions. More experimental work is necessary to confirm the positive effect of apatite as a backfill additive.

3.2 Magnetite

Magnetite is the dominant iron corrosion product expected to form in repository-relevant salt brines during container corrosion. Magnetite is known for its sorption capacity as well as for its ability to control Eh conditions. Figure 3 presents an Eh/pH diagram showing magnetite stability in the $MgCl_2$-rich saturated salt brines.

If metallic iron is present, the Eh is given by the water stability boundary (i.e. by the hydrogen pressure of the system). However, hydrogen evolution is a potentially detrimental property of the iron/magnetite brine system. Hydrogen evolution is impeded if magnetite is added directly as backfill material. In this case the Eh would be at the oxidizing boundary of the stability field of magnetite, because small traces of oxidants would lead to the formation of traces of ferric oxides, and consequently the Eh is controlled by the coexistence of magnetite and ferric oxide.

As an example for radionuclide retention, sorption and reduction mechanisms for U(VI) on real carbon steel-based container corrosion products were studied in an $Ar/8\%H_2$ flushed glove box. Most experiments were performed in two steps: (1) a fine-grained carbon steel was corroded in $MgCl_2$-rich brines at elevated temperatures (90–150°C) for a few months and, (2) U(VI) was added to the system at room temperature. After one day, already more than 98% of initially dissolved uranium was found associated with immobile phases. A reciprocal relationship was found with solution concentrations of uranium and the nominal mass of magnetite. Reduction of hexavalent to tetravalent uranium was observed, but to a much less pronounced extent than expected from thermodynamic considerations. A significant quantity of uranium was found irreversibly bound to magnetite. Even in strong acids, uranium could not be remobilized prior to complete magnetite dissolution. This indicates a coprecipitation mechanism controlling U retention by magnetite in the presence of corroding iron. However, this mechanism may not be active if magnetite is added directly as backfill material (without metallic iron). Here, sorption processes may be more important.

3.3 $MgO/Mg(OH)_2$

MgO has been proposed as a backfill material because of its capacity to control pH and CO_2 concentrations. MgO reacts with potentially intruding brines and forms $Mg(OH)_2$ or Mg oxychlorides (e.g., $Mg_2Cl(OH)_3 \cdot H_2O$). If CO_2 is present, magnesite or hydromagnesite will be formed. The hydration reaction is associated with an increase in pH, volumetric expansion, and the production of heat. Positive and negative effects of void volume evolution and thermal problems are not yet sufficiently clear (NEA/IAEA, 1997). On the other hand, $Mg(OH)_2$ can easily be formed by various geochemical reactions of Mg-rich salt brines with other backfill materials. Examples are apatite/brine and cement/brine interactions. By corrosion of low grade steel, $Mg(OH)_2$ containing phases will be formed as iron corrosion products in Mg-rich brines.

The main advantage of MgO addition would be the pH effect. Magnesite controls the maximum CO_3^{2-} concentrations in most brines of the hexary system of oceanic salts. With MgO addition, alkaline pH values >8 can only be established if no additional chloride- or sulfate-based Mg-minerals can be dissolved (either absent in the mineral assemblage of the disposal horizon or entirely dissolved).

3.4 Clay

Clays are considered a component for a backfill barrier because of their dual properties: a marked swelling and a high cation exchange capacity (CEC). Swelling will limit access of water to the waste packages and accordingly reduce corrosion, while a high CEC helps to retain radioactive nuclides that have escaped the metal container. Any change in either of the two clay properties will retard the functioning of the backfill barrier. In the presence of salt brines, both properties are somewhat reduced. High concentrations of K^+ in salt brines may lead to faster ilitization than in groundwaters of granite formations. Similarly, cation exchange equilibria are shifted by high contents of alkali earth ions. This leads to lower sorption capacities for multivalent radionuclides. On the other hand, clays formed as alteration products of nuclear waste glass corrosion (e.g., saponite) are well known to retain significant quantities of trivalent rare earth and actinide elements, and tetravalent and hexavalent elements, in $MgCl_2$ and in NaCl-rich solutions. Typical sorption coefficients (Rs) on glass corrosion products in $MgCl_2$ solutions at pH>4 were in the range of 10^5 ml/g for Th and $>10^3$ ml/g for Eu and U(VI). Results of recent studies at INE-FZK for the ERAM (Morleben) waste disposal site show strong radionuclide sorption from brines on Na and Ca-bentonites. Sorption coefficients were at about 2000 - 5000 ml/g for Th and Pu and were significantly lower for U(VI) and Np(V). Sorption is only slightly reduced by the addition of complexing agents. The addition of Na- and Ca-bentonite to neutral saturated salt solutions had little effect on solution pH (variation smaller than 1 pH unit).

3.5 Cement

Concrete and cement have been proposed as waste matrix material, backfill material, and as structural components of radioactive waste repositories (Bath et al., 1987). The amount of concrete and cement associated with these repositories, especially in low-level waste facilities, is often quite large (e.g., 8.2×10^5 m^3: Karlson et al., 1986). Solidification or desegregation of concrete in natural environments will produce high pH solutions. The pore fluids in hydraulic cement range in pH from 12.5 to 13.5, have high ionic strengths, and are dominated by Na and K in concentrations ranging from 300 - 4200 ppm and from 100 - 7500 ppm, respectively (Andersson et al., 1989; Lunden and Andersson, 1989). Ca concentrations in these pore fluids are much lower and range in concentration from 20–130 ppm. The release of this alkaline, high-pH plume to the surrounding media has been modelled (Haworth et al., 1989; Reardon, 1990; Jeffries et al., 1988; Berner, 1990; Vieillard and Rassineux, 1992) showing first a period of NaOH and KOH release (pH > 13), followed by a solution composition controlled by portlandite $Ca(OH)_2$ and subsequently a solution composition controlled by calcium-silicate-hydrate (CSH) gels (pH to 9–10) (Figure 2).

3.5.1 *Interactions between cementitious material and brines*

The reaction path between cementitious materials and salt brines was calculated for Solution 2 (Table 1) and a saturated NaCl solution using the EQ3/6 code and the HMW Pitzer database (Phillips et al., 1988). In a first step, only portlandite dissolution is considered. The computed results differ significantly for the two brines:

NaCl solution: Dissolution of about 0.5 g portlandite/kg water increases the pH to 12.3. At a Ca concentration of 685 mg/kg water, the system reaches equilibrium related to the saturation of halite and portlandite. These results correspond to experimental findings (Vejmelka et al., 1990).

Magnesium-rich brine: The computed pH rises to 7.7 after dissolution of a small quantity of portlandite. After dissolution of about 1 M portlandite/kg water, the SO_4^{2-} concentration drops by a factor of 1000 (to 11 mg/kg water). Solution pH increases steadily with the portlandite dissolution up to a value of 9.1. At this pH, the Ca concentration reaches 4.3 mol/kg water and the Mg concentration is reduced from initially 4.7 mol/kg to 0.055 mol/kg. This level corresponds to the dissolution of the amount of portlandite present in 1 kg of hydrated cement (OPC). The computed results correspond to the experiments.

Solid phases controlling the composition of the solution are anhydrite ($CaSO_4$) and Mg-oxychloride ($Mg_2Cl(OH)_3 \cdot H_2O$). Additional dissolution of portlandite increases the Ca concentration. After nearly complete removal of Mg from solution, the pH increases to 12. The dominating solid phase will be $Mg(OH)_2$. Figure 4 shows the dissolved species in comparison with experimental findings. The correspondence between experiments and model computation depends on initial concentration of portlandite in the samples. Data concerning the initial composition are not available. A portlandite concentration of about 28% was assumed.

In a second step, calcium-silicate-hydrate (CSH) phases are considered. Published CSH dissolution data are fitted to describe the CSH solubility. Modelling the dissolution of the main cement phases as portlandite and CSH phases by means of EQ3/6 and using extended databases allows prediction of the geochemical environment in the case of brine penetration into a repository. Solid solution models are developed in to order to describe the dissolution of CSH phases of cement. Initial brine composition and the evolution of pH, brine composition, and solid phases can be computed as a function of corrosion progress. Aluminum-containing phases form an important mass of solid phases in cement. Pitzer parameters of aluminate ions are given by Reardon (1990), but dissolution of CAH (calcium aluminate hydrate) phases are not yet modeled.

3.5.2 *Radionuclide retention in cement*

Chapman and Flowers (1986) compiled solubility data of all the relevant radionuclides in intermediate level waste types under the high pH conditions relevant to cement waste forms. The solubilities of most of the significant long-lived radionuclides are low, with the exception of ^{226}Ra, ^{14}C, ^{135}Cs, and ^{129}I. During the last 20 years, numerous experimental studies on the leaching of various low and intermediate level wastes types have been performed. In Germany, corrosion and leaching studies of cemented waste forms have concentrated on salt brines (Rudolph and Köster, 1977; 1979; Rudolph. et al., 1982; Vejmelka et al., 1982; Bechthold et al., 1983; Köster et al., 1985; Vejmelka et al., 1990; Marx and Keiling, 1989; Vejmelka et al., 1990; and Glasser et al.,1996).

A high mobilization rate of Cs in ordinary Portland Cement matrices was observed, with diffusion through the cement pore structure being one of the controlling mechanisms. The production of secondary phases was seen to have a marked effect on the mobilization of some elements. The precipitation of new phases may influence the mechanical properties of the waste forms.

For the reaction path between cementitious materials and brines described above, calculations for the solubility of U(VI) were performed as a function of solution pH and the evolution of solution composition. Coprecipitation was ignored for simplicity.

U(VI) concentration between 10^{-4} and 10^{-5} mol/l is modelled close to the initial state of the brines. With increasing pH, the maximum U(VI) concentrations decreases by several orders of magnitude (Figure 5). The solid phase controlling the concentration in the high pH range may be $CaUO_4$. If pH increases into the alkaline range, U(VI) concentration is computed below measured data by several orders of magnitude. The reason for this discrepancy may be attributed to kinetically retarded precipitation of the $CaUO_4$ phase. In the literature, a dependence of the solubility product of this phase on the degree of crystallization is reported; however, this effect should not affect the solubility by orders of magnitude. In the high pH range, U(VI) concentrations are expected from experiments with cemented waste forms (Marx and Keiling, 1989) and from experiments with pure cement phases (Moroni and Glasser, 1988; Glasser et al., 1996) to be in the range of 10^{-8} to 10^{-9} mol/l.

Cement is not only important in reducing the solubility of radionuclides by alkaline pH conditions; sorption effects are also significant. An overview of the sorption coefficients (given as Rs) measured for various cement phases in saline brines is given in Table 2. The table shows the rather high sorption of some elements. For performance assessment, however, long-term stability of these phases is not evident. In particular, ettringite will be dissolved in some brines.

Sorption of all elements in the systems under investigation decreases in the sequence Th > U > Np > Pu.

3.6 Fly ash

Due to its alkali content, large effects were observed with fly ash addition: in Mg-rich solutions, the pH increased by 1.3 units, in NaCl solutions by 4 units. Fly ash leads to strongly reducing conditions, caused by the presence of sulfide minerals in the fly ash. The resulting redox potentials are in the range of –150 mV to –250 mV.

The results of the sorption experiments for ERAM (Morsleben) show in general for Pu and Th the highest sorption coefficients in the following order: fly ash > Ca-bentonite ≈ Na-bentonite >> rock salt. The sorption coefficients are in the range between 5700 ml/g for Pu on fly ash and 20 ml/g for Pu on rock salt. Np and U show strong sorption only, with fly ash resulting in sorption coefficients of 2750 ml/g for Np and 1200 ml/g for U. The high sorption is caused by the high sulphide contents and the concomitant establishment of reducing geochemical conditions. Under these conditions, Np and U are probably in their tetravalent state and consequently exhibit similar properties to Th. The similarity of Pu and Th may indicate for the anoxic conditions of the experiments that Pu is always in the tetravalent state.

3.7 Crushed salt

Crushed salt is the principal backfill material considered in Germany, mainly for is ability to compact and seal during the heat-driven convergence of the disposal locations. Nevertheless, its function as geochemical barrier has not yet been taken into account. In this regard it is interesting to note that even crushed rock salt has shown some sorption capacity for radionuclides (study for ERAM, Morsleben). From the complexing agents, only EDTA and citric acid showed some influence on the sorption of the radionuclides in the systems with rock salt (Pu, Th). Moreover, a certain retention mechanism for ^{135}Cs may become operative in case of thermal gradients. Certain fractions of Cs dissolved from heat-generating waste forms will coprecipitate at cooler sites together with chloride salt minerals such as halite. However, geochemical scoping calculations based on ideal solid-solution models seem to indicate that this effect is not very effective in reducing the overall flux of Cs to the far field.

4. SYNERGYSTIC EFFECTS

In the design of (geo)engineered barrier systems, various materials may coexist simultaneously and synergistic effects must thus be considered. Examples are clay backfill in the vicinity of cementitious materials, and clay backfill in the vicinity of a corroding container.

4.1 Clay/cement interface

Previous experimental studies conducted to understand the alteration of clays under high pH conditions using different starting materials over a range of temperatures, pHs, and solution compositions have produced zeolites, K-feldspar, and clays (Barrer, 1982). Focussing on the K-dominant system, varying types of zeolites have been observed to grow and precipitate (Hawkins, 1981; Donahoe et al., 1984; Donahoe and Liou, 1985). These studies indicate that it is important to follow the paths of reaction to understand reaction rates at low temperatures.

Bauer et al. (in press), Bauer and Berger (in press) and Bauer (1997) worked out the dissolution and transformation behavior of kaolinite in high-molar KOH solutions. The reaction of kaolinite with KOH can be analyzed in two parts, one of dissolution and a second phase where the Si-Al concentration in solution is determined by the growth and redissolution of new phases. During the congruent dissolution period, the aqueous concentrations of Si and Al increased linearly with log(t) regardless of temperature and the KOH concentration. The sudden change of the silica and aluminum concentration (decreasing concentration) in solution with log(t) reflects the beginning of precipitation of a secondary phase. At this point, precipitation and crystal growth control the solution concentration and the dissolution of kaolinite. As for other aluminosilicates, the preliminary thermodynamic calculations show that the measured kaolinite dissolution rates cannot be easily related to the chemical affinity of the overall reaction. The speciation calculations showed that the solutions were always largely undersaturated with respect to kaolinite. There was no unique relation between the rate decrease and the calculated saturation index either. On the other hand, a single relation between r/r_0 and the $Al(OH)_4^-/OH^-$ activity ratio seems to fit all our data except for the rates at lower pH (0.1 m KOH).

The degree of oversaturation of the solution is controlled by the crystallization and growth dynamics of the illite and zeolite phases. The higher the temperature, the faster the crystallization reaction progresses. The length of time that the pure dissolution situation pertains to 35°C is roughly ten times that at 80°C. Thus, if alkaline solutions percolate through a kaolinite barrier, they will remain aggressive to a higher degree for a longer period of time at lower temperatures.

Bauer and Velde (in press) studied the alteration behavior of different smectites in alkaline solutions. A first dissolution stage reacts smectite with KOH, changing the crystal shape and hence the coherent diffracting domain for XRD. In contrast to kaolinite, the concentrations of Si and Al in solution increased linearly with time. For a given temperature and KOH concentration, the calculated dissolution rates are constant with time and independent of the solid-solution ratio, suggesting no chemical affinity effect. When plotting log(rate) versus log $a(_{OH^-})$, the same proportionality of the smectite dissolution rate constant to $a_{OH^-}{}^{0,15\pm0,06}$ is found at 35° and 80°C. The activation energy of smectite dissolution appears independent of pH and is found to be 65 ±4 kJ/mol at pH 12.5 or 52 ±4 kJ/mol at a given OH^- activity.

The general sequence of reaction products observed during dissolution of either kaolinite or smectite in highly alkaline solutions is:

kaolinite ▸ illite ▸ KI-zeolite ▸ phillipsite ▸ feldspar-K
smectite ▸ I/S ▸ illite ▸ KI-zeolite ▸ phillipsite ▸ feldspar-K + quartz

I/S, Illite, KI-zeolite and phillipsite are metastable phases. This evolution can also be compared with Ostwald's rule of successive transformations.

The experimental results of Savage et al. (1992) may be applicable to the engineering of radioactive waste disposal sites that use smectite in combination with cement barriers in their design. According to these results, smectite barriers may lose some of their desirable properties, which include high sorptivity, longevity, and low permeability (Lee and Tank, 1985) by reaction with alkaline waters to form I/S of low expandability and/or new phases. The I/S minerals are, however, only an intermediate step in a series of dissolution and recrystallisation phases that eventually produce feldspar.

The compaction of clays foreseen as hydraulic barriers (hydraulic conductivities of $10^{-9}{}_{m}$/sec or less) would reduce convective flow to minimal values and hence the interaction effect (dissolution of clays) would be minimal. Under these alkaline conditions, kaolinite or smectite dissolution will occur, but new phases will be produced to replace the clays and the system will not lose volume or much mass. However, should pathways be opened by fractures or other effects that increase permeability, the dissolution of the clays under alkaline conditions could be important to the stability of a clay barrier.

4.2 Iron/iron oxide/clay interface

Iron is being evaluated as a reactive barrier material to mitigate the transport of a wide array of highly mobile contaminants. Preliminary results in our laboratory showed that smectite and kaolinite in contact with metallic iron can be transformed under reducing conditions into chlorite. The study of two systems of clay-iron-glass and salt-iron-glass, which represent the frame of the German and French repository concepts, under oxic and reductive conditions is the topic of present research in our institute.

5. CONCLUSIONS

A large suite of geochemically stable backfill materials are available for disposal concepts in salt formations. Many of these materials could act as potentially efficient geochemical barriers for radionuclide retention. Sorption coefficients were highest for cement phases and glass corrosion products, followed by fly ash and Ca- and Na-bentonite. Crushed salt showed comparatively low but still significant sorption. The barrier effect can either be based on sorption (clays, cement, magnetite) or coprecipitation (apatite, magnetite) or on conditioning of the near field geochemical environment (pH, pCO_2, Eh) in a way that radionuclide mobility becomes low (magnetite, cement, MgO). Potentially positive effects must be balanced against potentially detrimental effects (release of radionuclide-containing colloidal backfill components, release of chemical toxic elements, e.g., from fly ash, pumping effects for waste form dissolution by sorption of matrix components on backfill components). Integrated geochemical modeling of the various materials interactions in the repository near field is an important tool for predicting the geochemical stability of various backfill candidates and degradation processes, and for the determination of the geochemical conditioning reactions for the near-field chemistry. Examples were discussed in which, according to geochemical modeling, the expected effect of backfill additives would also be operative in the absence of these components (MgO). In another case (apatite) geochemical modeling showed that the experimentally observed formation of specific secondary radionuclide containing phases (uranyl mica) may not be expected under realistic conditions. Finally, it appears very important to confirm the relevance and validity of laboratory findings of barrier effects for realistic natural conditions.

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Table 1. Molal element concentration in typical salt brines

	Mg^{++}	Ca^{++}	Na^{+}	K^{+}	SO_4^{--}	Cl^{-}
Solution 1	3.691	—	0.453	0.517	0.266	7.821
Solution 2	*5.587*	*0.327*	*0.086*	*0.021*	*6.06E–4*	*11.94*
Solution 3	0.018	0.022	6.107	0.036	0.058	6.107

Table 2. Sorption coefficients of different elements at solid cement phases

		Hydrotalcite	Ettringite	Tobermorite	CSH-gel
Element	solution	$R_s / l \cdot g^{-1}$	$R_s / l \cdot g^{-1}$	$R_s / l \cdot g^{-1}$	$R_s / l \cdot g^{-1}$
Th	NaCl sol.	18-33	39-61	77-150	55-100
	Q brine	6.3-8.1	7.1-16	24-58	27-99
U	NaCl sol.	9-27	5-6	10-16	8.1-23
	Q brine	22-55	6.7-18	4-10	5.2-28
Np	NaCl sol.	0.7-5.6	5.8-130	440-920	
	Q brine	0.03-0.09			
Pu	NaCl sol.	4.6-34	80-160		
	Q brine	0.01-0.18			

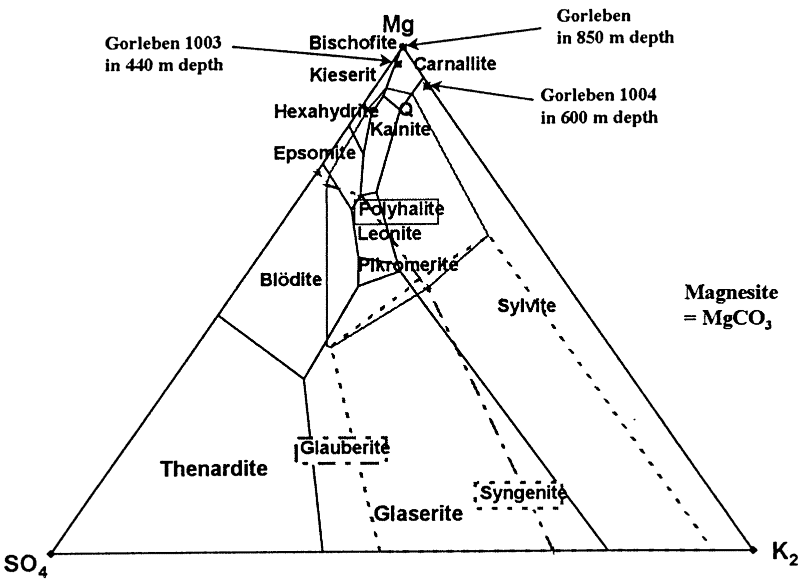

Figure 1. Stability fields of various salt minerals and compositional range of saturated solutions in the 6 component Na-K-Ca-Mg-Cl-SO_4 system of oceanic salts at 25°C and corresponding stability fields of carbonate minerals Magnesite and Calcite (=Ca).

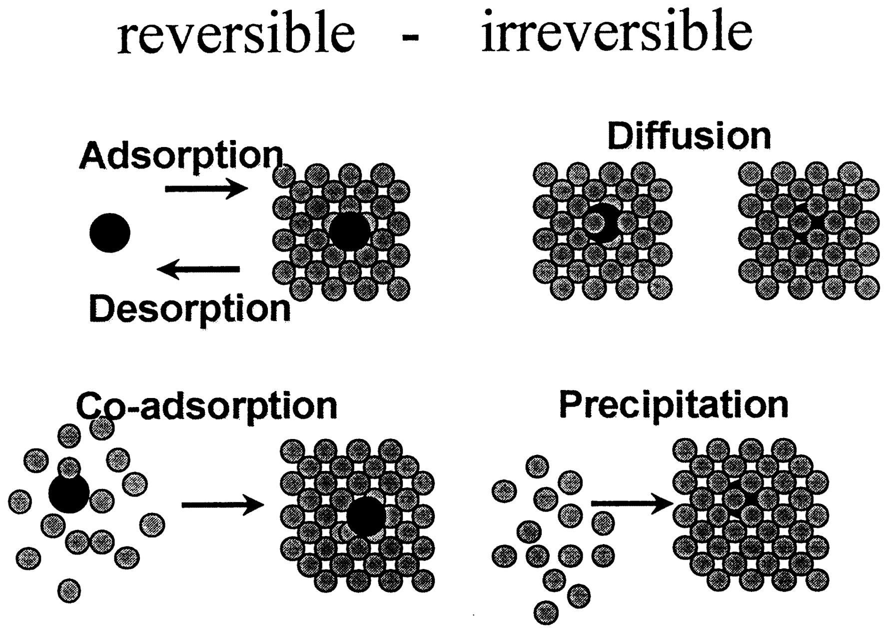

Figure 2. Schematics of radionuclide retention mechanism.

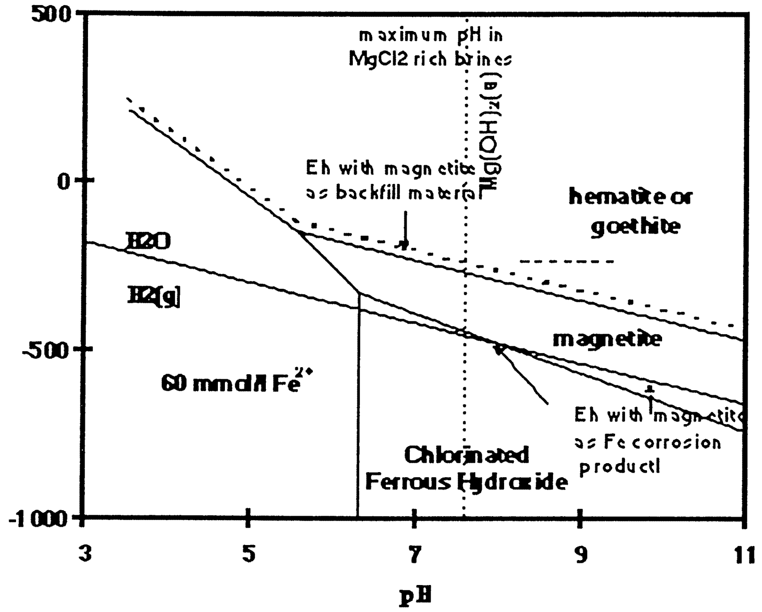

Figure 3. Eh/pH diagram showing magnetite stability in $MgCl_2$ rich saturated salt brines.

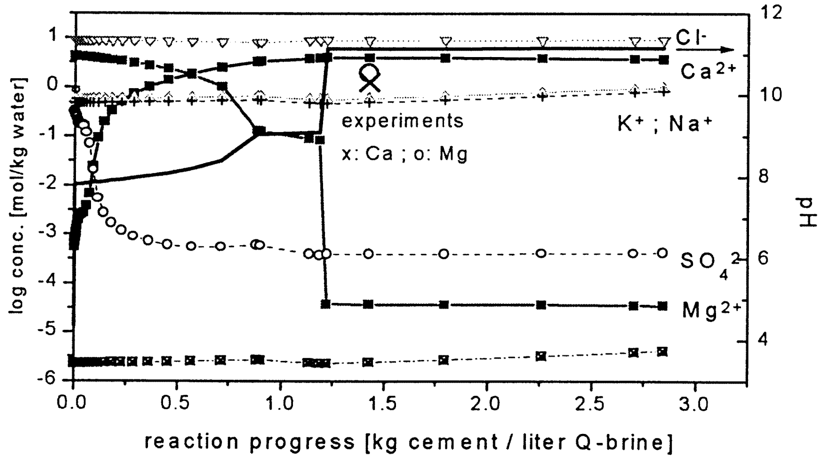

Figure 4. Dissolved phases in the system portlandite/Qbrine and atmospheric CO_2 partial pressure.

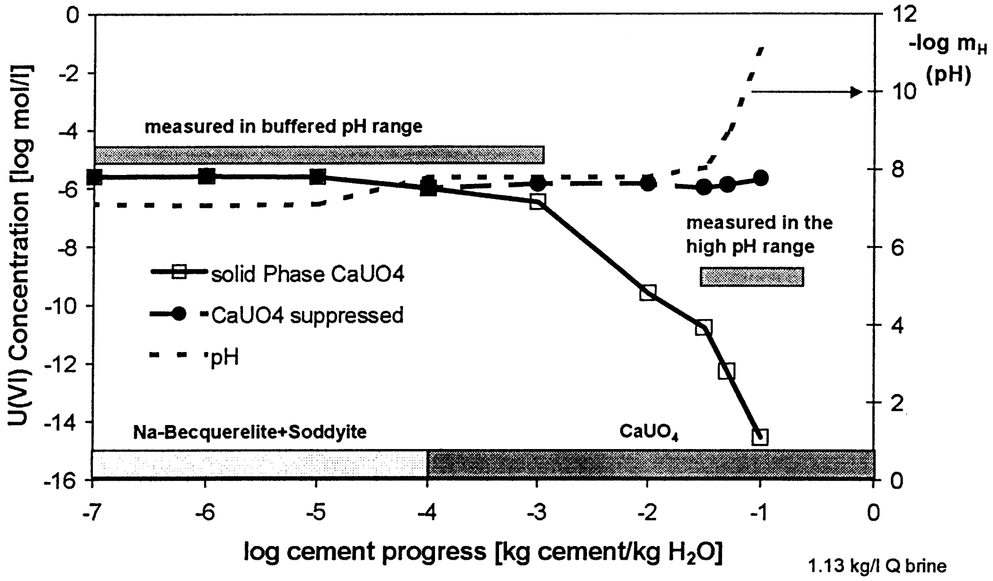

Figure 5. Cement progress vs. U(VI) concentration.

STATUS OF RESEARCH ON MAGNESIUM OXIDE BACKFILL

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1. INTRODUCTION

In contrast to cementitious and phosphatic materials, bentonite, and crushed salt, relatively little attention in the international waste disposal community has been given to MgO as a potential backfill or backfill additive. In fact, as far as we know, only two major research efforts have focused on MgO: (1) an investigation in the early 1980s to identify an appropriate desiccant for a high-level waste (HLW) repository in salt; and (2) recent investigations to identify an appropriate chemically controlling backfill for the Waste Isolation Pilot Plant (WIPP).

In the early 1980s, MgO was investigated as a backfill material for the United States' concept for HLW disposal in a hypothetical "salt" repository. Simpson (1980; 1983) considered a variety of materials, including cements, clay minerals, oxides and hydroxides (e.g., $Ca(OH)_2$, CaO, MgO), chlorides, borates, carbonates, phosphates, zeolites, fly ash, and synthetic materials, primarily for their desiccation capacities. Important secondary criteria included compatibility with hypersaline environments, thermal conductivity and stability at 200°C, low solubility, solid form, good sorptive properties, long-term geologic stability, limited reaction with CO_2 in air, chemical simplicity, availability of large volumes (or easily synthesized), inexpensive, and ready availability (Simpson, 1980). On the basis of those criteria, Simpson narrowed his focus to MgO, CaO, MgO-CaO mixtures, Ca_2SiO_4, and bentonite. Laboratory work that followed focused on quantifying dehydration and thermal properties. Simpson (1983, p. 47) concluded that MgO was " superior to bentonite and dicalcium silicate in regard to desiccant capacity, thermal stability of the hydrous product, and thermal conductivity." MgO has little ability to sorb radionuclides and so early studies focused on a salt-bentonite mixture at temperatures relevant to HLW disposal.

Evolving programmatic needs and relatively recent performance assessment (PA) sensitivity calculations showed that the primary performance issue at the WIPP was uncertainty in actinide solubilities, primarily with Am^{3+}, Pu^{3+}, and Pu^{4+}. The transuranic (TRU) waste destined for the WIPP contains a significant amount of cellulosic, plastic, and rubber material (US DOE, 1996b), which may be attacked by microbes in the repository to produce methane and carbon dioxide. Consequently, a concerted effort was initiated to decrease the concentration of carbonate ion, which is a strong actinide-complexing ligand (Bynum et al., 1998). MgO backfill was selected for this purpose and the consequences of the selection were included in the PA calculations conducted for the Compliance Certification Application (CCA; US DOE, 1996a), submitted to the US Environmental Protection Agency as part of the WIPP licensing process.

To assess the behaviour of MgO at the WIPP, there have been three phases of research. As part of the effort to confirm that MgO was a suitable carbonate-ion controlling backfill for the WIPP, scoping experiments were conducted in late 1996. The second phase, conducted in early 1997, was prompted as part of the mandated independent review of the CCA. Essentially, the concern was that MgO would develop a low-permeability "reaction rim" that would inhibit further reaction with carbonate. After addressing further this concern successfully, a third phase was initiated that is focusing on understanding the chemical behaviour of MgO, and on exploiting the geomechanical and hydrological attributes of MgO backfill.

We have found that MgO has merit not only in the geochemical arena, but may also help improve the structural and hydrological performance of the repository. As a "broad spectrum" backfill or backfill additive, it may be useful for the international community to consider MgO. In this paper, we present overviews of the work of Simpson (1980; 1983) and the second and third phases of MgO research conducted for the WIPP.

2. PROPERTIES OF MAGNESIUM OXIDE

MgO, known also as periclase or magnesia, is manufactured commercially for use as a pH-controlling agent, a smokestack gas scrubbing agent, a ceramic material, and as an animal feed supplement. It is typically mined or is produced by precipitation from seawater, after addition of calcined limestone or dolomite. MgO is manufactured in several different grades, primarily to provide a range of reaction rates for the consumer (e.g., low-burned, hard-burned, and dead-burned). By controlling the processing temperature and milling, the grain size, porosity of pellets, and crystallinity are manipulated to create materials that react with water and carbon dioxide at different rates. For the WIPP, the hard-burned material provides an acceptable compromise between sufficiently high emplacement density, long-term reactivity, and resistance to reaction with atmospheric CO_2. This material consists of approximately 10-µm periclase crystallites, sintered together to form pellets about 0.5 to 4 mm in diameter, possessing about 50% pellet porosity, and about 95% or better MgO purity. The pelleted form allows easy emplacement as bagged material, or perhaps even as loose air-blown material. MgO is not as caustic as CaO, so worker safety is less of an issue. In the United States, MgO is readily available and reasonably priced.

3. CHEMICAL BEHAVIOUR

In the presence of water, MgO reacts to form brucite ($Mg(OH)_2$). At the WIPP, cellulosic, plastic, and rubber materials in the waste may be degraded by microbes, yielding carbon dioxide and possibly methane, and with water, yielding carbonic acid. Although relatively weak, carbonic acid is capable of driving the pH of the repository into the acidic range. More important, however, is the combination of carbonate with actinides to form stable carbonate complexes, which increase actinide solubility. To buffer, and ultimately limit, the carbonate ion concentration, the brucite formed can react with carbonic acid to form magnesium carbonate:

$$Mg(OH)_2(s) + H_2CO_3 \leftrightarrow MgCO_3(s) + 2\,H_2O \qquad (1)$$

Depending on the groundwater chemistry, a Mg-OH-Cl hydrate (Sorel cement) may form in place of, or in addition to, brucite. Although the chemical changes involving MgO are simple, understanding the kinetics of the reactions under repository-relevant conditions presents a significant challenge.

Several brine simulants have been used in WIPP investigations of MgO to represent brines present in the Salado Formation (repository horizon) and the Castile Formation (an underlying brine source). The Castile brine simulant is based on samples collected from the ERDA-6 well, and is referred to as "ERDA-6" brine. Salado brine was simulated using two different formulations. The Salado Primary Constituent (SPC) brine, has relatively high magnesium and low sulphate concentrations (Novak, 1993) and represents a simplification of "Brine-A", originally described by Molecke (1983). A more realistic Salado Formation Brine, called "generic weep" or "GW brine", has been developed based on chemical analysis of several dozen brine samples collected from three areas of the WIPP repository (Krumhansl et al., 1991). GW brine contains about 0.8 M Mg, or about one-half the concentration in SPC brine.

3.1 CO_2 buffering by MgO

Experiments were conducted during the second phase of the WIPP MgO research to demonstrate that MgO would continue to react with CO_2 even after significant portions of MgO converted to magnesium carbonate. Aliquots of MgO pellets in two pellet-size fractions were placed in small polyethylene bottles and covered with WIPP brine. Pure CO_2 gas was bubbled into the bottles for periods of up to four weeks. Periodically, pellets in triplicate sets of bottles were decanted, rinsed in ethanol, and processed to determine mineralogy, textural characteristics, and weight-fraction carbon. The extents of conversion were observed to be as high as 33 mol% in four weeks. Such high uptake rates suggest that the planned MgO backfill will be capable of consuming all WIPP CO_2 production. The fundamental difference between the MgO carbon uptake experiments described here and MgO carbon uptake in the WIPP repository is the pCO_2 under which the reaction will occur. Our initial scoping experiments used an artificially high pCO_2 (1 atm) to obtain measurable carbon uptake results in several weeks. In contrast, the pCO_2 in the repository will be many orders of magnitude less. To better simulate actual repository conditions, experiments are currently being conducted to investigate CO_2 uptake at much lower partial pressures of CO_2 and over much longer time periods (Figure 1).

Autoclave experiments using as input 10 atm of CO_2 provide additional information about the reaction mechanism, particularly on the direction of movement and exchange of the reaction-rate-controlling ions through the surface precipitates on MgO pellets. The outward growth of crystals suggests that rate-controlling ions are diffusing out, but morphological arguments are weak in such applications. If inward diffusion of carbon-bearing species was the dominant reaction, then a ten-fold increase in the CO_2 pressure should accelerate the reaction rate by a similar amount. In fact, the carbon uptake curves for the 1 atm and 10 atm tests are strikingly similar. It follows that the diffusion gradient responsible for transferring mass during the CO_2 titration process is unchanged. Hence the rate-determining step must be the release and transport of ions from the pellet to the exterior of the sample, where they interact with the $CO_{2(aq)}$ to precipitate a solid carbonate mineral.

To evaluate long-term MgO performance, the morphology of magnesium carbonate precipitates must also be considered. A wide variety of magnesium carbonate minerals have been identified and described in the published literature. The formation of magnesite, anhydrous $MgCO_3$, is kinetically inhibited at ambient temperatures. However, analog information suggests that magnesite will begin to form after several centuries (see Section 3.2). Magnesite is likely to exist as discrete hexagonal plates similar to the magnesite found in the Salado Formation (Krumhansl et al., 1990, their Figure 8). In our initial experiments, conducted with 1 atm pCO_2, nesquehonite ($MgCO_3 \cdot 3H_2O$) was the dominant magnesium carbonate phase, having an acicular morphology. At lower pCO_2, however, phase diagrams suggest that the likely mineral phase will be hydromagnesite ($4MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$), which has a loose platy habit. Given the extremely low CO_2 fugacity arising from the very slow pCO_2 generation in the actual WIPP system, we expect that nesquehonite will not form and that the favored metastable phase will be hydromagnesite. This hypothesis is consistent with published phase diagrams (Figure 2; Lippmann, 1973). Laboratory experiments conducted at relatively high pCO_2 provide a maximum bounding case for assessing the impact of coatings because the nesquehonite crusts observed in the laboratory restrict diffusion more than the loose platy hydromagnesite precipitates expected under actual WIPP conditions.

The occurrence of various magnesium carbonate minerals is important for the WIPP system because the different mineral phases will buffer CO_2 fugacity at different levels. Field and laboratory analogs provide some insight into the development of the hydrated and anhydrous magnesium carbonate minerals.

3.2 Analog evidence for magnesium-carbonate mineral formation

Analog studies of magnesium carbonate minerals provide insight into expected mineral assemblages in our experiments and in the WIPP repository. In contrast to the ready formation and common occurrence of hydrous magnesium carbonates at 25°C, magnesite (as well as dolomite) has not been formed in short-term laboratory experiments at 25°C (e.g., Lippmann, 1973; Bathurst, 1971). Evidence accumulated over the past four decades attributes this to the hydration behaviour of the magnesium cation (Langmuir, 1997; Lippmann, 1973; Reeder, 1983; Usdowski, 1994; Purser et al., 1994; Brady et al., 1996). Magnesium has a high charge-to-ionic-radius ratio and very tightly held waters of hydration. To form magnesite at low temperatures (e.g., 25–35°C) in relatively short periods of time requires that conditions that facilitate dehydration of the magnesium cation must be present. Only hydrothermal synthesis techniques can produce artificial magnesite in a restricted time frame (days to months).

3.2.1 Natural analogs

Magnesite has been identified in sediments in locations around the world, including southern Australia (Aldermann, 1965; Peterson et al., 1966; von der Borch, 1965; De Dekker and Last, 1989; Alderman and Skinner, 1957; Skinner, 1963), Saudi Arabia (Butler, 1969; De Groot, 1973), Turkey (Irion and Müller, 1968), and Utah (Graf et al., 1961). The sedimentary record also contains evidence that magnesite has formed at low temperatures (Garber et al., 1990). The common conditions exhibited in all those occurrences are the presence of high ionic strength solutions, moderate to high pH values, and high Mg^{2+} to Ca^{2+} ratios in solutions. Particularly the first condition, high ionic strength, facilitates stripping the waters of hydration from the magnesium cation (Lippmann, 1973).

Usdowski (1994) compiled results from many of the studies from Saudi Arabia and southern Australia that were mentioned in the previous paragraph (Figures 3 and 4). The most extensive work on recent magnesite was conducted in the Coorong area of southern Australia (Figure 3), where a series of ephemeral lakes has developed inside a restricted lagoon near the coast. The source of the magnesium and calcium is seawater, which becomes concentrated in the arid environment. Evaporation of seawater also results in a high ionic strength. Because hydromagnesite also occurs in different ponds in the same complex, it is speculated that the magnesite may have originated in a hydromagnesite-aragonite assemblage that has since dehydrated and reacted with the aragonite to produce a (disordered) dolomite plus the magnesite. Usdowski (1994) superimposed his best estimate of the stability fields of dolomite and magnesite and of dolomite and calcite, which he compiled from several published works (Figure 4). The phase boundaries for dolomite and magnesite formation are consistent with the observed natural occurrences. Moreover, the total ionic concentrations (proportional to ionic strength) and the Mg to Ca ratios of the Salado and Castile brines fall within the range of observed occurrences of magnesite (Figure 3). The environmental conditions in Saudi Arabia are similar to those in the southern Australia locations. In Saudi Arabia, however, the setting is a sabkha in which a shallow sloping coastal area in an arid environment is periodically inundated with seawater. The arid environment results in evaporation, again increasing the ionic strength but sustaining a high Mg-to-Ca ratio. As with the examples from southern Australia, the compositions of brines under WIPP repository conditions are within the range of conditions where magnesite is observed to form (in fact, magnesite is observed in the Salado Formation: Stein and Krumhansl, 1988; Krumhansl et al., 1990, their Figure 8).

In addition to Saudi Arabia and southern Australia, magnesite has also been observed forming in Recent-age sedimentary environments. Irion and Müller (1968) identified magnesite and the double carbonates dolomite and huntite ($Mg_3Ca(CO_3)_4$) in sediments in a hypersaline ephemeral lake in Turkey. Rather than hydromagnesite being the source for magnesite, huntite may have served as a precursor. Radiocarbon (^{14}C) age dating showed a date of formation of 6,000 ±140 years before present for carbon extracted from dolomite, which brackets dolomite precipitation to some time during the past 6,000 years. In a study of the sediments associated with Glacial Lake Bonneville in Utah, Graf et al. (1961) found dolomite and a protomagnesite with an enlarged unit cell volume ("proto" is used here to indicate precursor; protomagnesite is thus an immature precursor form of magnesite). Once again, the environment of deposition was interpreted to contain high ionic strength brines resulting from an arid environment. Radiocarbon age dating of carbon in a dolomite sample indicated an age of 11,150 years. The climate at Glacial Lake Bonneville was estimated to have changed from arid to wet about 10,000 to 11,000 years before present (Graf et al., 1961). The radiocarbon age date, coupled with the climate change, suggests that the dolomite precipitated between about 150 and 1,150 years.

3.2.2 *Laboratory analogs*

Sayles and Fyfe (1973) conducted perhaps the most extensive experiments to investigate magnesite growth. Their experiments were conducted in variety of solutions, although all were at relatively low ionic strengths. Experiments conducted at 126°C show that the run products consisted completely of magnesite after reaction times of 3 to 8 days. A variety of researchers have conducted experiments at temperatures exceeding 200°C. The most relevant series of experiments, in terms of temperature and ionic strength, were conducted at 60°C for seven years (Usdowski, 1994), where magnesite was found in reaction products.

To extrapolate the exceedingly slow reactions to lower temperatures relevant to the WIPP, an Arrhenius expression was used. Data from experiments described by Usdowski (1994; 1989) and Sayles and Fyfe (1973) were used to provide an estimate of the time required for formation of magnesite. Extrapolation of those data suggests that, at a WIPP-relevant temperature of about 28°C, magnesite may form within several hundred years. That result is consistent with comments in Usdowski (1994), in which he speculated that dolomite ($MgCa(CO_3)$, another carbonate mineral requiring full dehydration of the Mg ion) will form in 600 years at low temperatures.

4. HYDROLOGICAL AND GEOMECHANICAL PROPERTIES

As discussed in the introduction to this paper, MgO was selected only recently for use as backfill in the WIPP. For the CCA, the stated purpose of the MgO backfill was to decrease actinide solubilities by controlling the carbonate ion concentration. However, we are currently developing more comprehensive conceptual models for the WIPP as a system, in recognition of the fact that a large portion of the repository contents will be MgO.

For the "undisturbed scenario" (see Bynum et al., 1998), in which the only source of brine is seepage from the Salado Formation, we are evaluating the potential for a dry repository in which MgO acts as a desiccant. In a dry or even slightly humid repository, gas generation from iron corrosion and microbial degradation of organic carbon is significantly reduced and no dissolved- or colloidal-actinide source term exists. In the absence of free water, degradation of the waste would be reduced, preserving large particles that are less likely to be mobilized. In a spallings-type release, in which the repository is penetrated by drilling, gas pressures would be reduced to a level where the performance impact is substantially diminished. In addition, formation of Sorel cement would severly limit contaminant particle release in response to drilling penetration of the repository ("disturbed scenario").

4.1 Desiccation properties

Simpson (1980, 1983) investigated MgO hydration in water vapor at temperatures from 20 to 150°C. In his earlier work, Simpson (1980) used powdered reagent MgO and various brine simulants and found that at 100°C hydration was nearly complete after only a few days. MgO hydration results in uptake of 31 wt% water (a weight gain of about 45%). At 20°C, Simpson (1980) found that hydration, after periods of up to 70 days, reached only one-half of completion. In Simpson (1983), additional hydration work was conducted on pelleted MgO, crushed to various size fractions and reacted with water vapor (Figure 5). That work shows that, at 20°C and over reaction times up to about 80 days, the extent of hydration reached was only one-half completed. At 60°C, the impact of the size fractions becomes noticeable, and complete hydration was observed in the 31–62.5 µm-sized fraction. Simpson noted that the vapor pressure of the brine has a significant effect on hydration rates, although thermodynamic calculations show that

$Mg(OH)_2$ will always be the stable phase with any brine. Brines rich in very soluble salts, such as $MgCl_2$, require an especially effective desiccant.

In our more recent experiments with completely immersed MgO, we also observed kinetic inhibition of MgO hydration at a WIPP-relevant temperature of 28 °C. In fact, in a one-year experiment in Salado (SPC) and Castile Formation brine simulants, brucite was not detected with powder X-ray diffraction (detection limit approximately 2 wt%). Results of MgO hydration experiments conducted at 40, 60, and 90°C under completely immersed conditions using Salado (GW) brine show a pronounced incubation period during which conversion to brucite is negligible, particularly at lower temperatures (Figure 6). Plotting the time required for the onset of hydration using an Arrhenius plot indicates a large activation energy, probably caused by nucleation of seed crystals (Figure 7). Activation energies resulting from diffusion through a surface coating would be much smaller. Moreover, the linear nature of the plot suggests that the reaction inhibition is not caused by diffusion, because the surface precipitates formed on pellets at different temperatures varies, and would have different diffusion characteristics. Extrapolating rates to the WIPP temperature of 28°C suggest that the incubation period prior to onset of hydration will be on the order of one to two months. The decrease in hydration rates after significant extents of hydration may result from reductions in reactive surface area as hydration proceeds, or from limitations in reactants diffusing into the MgO pellet mass. In systems with high magnesium concentration and an excess of brine, precipitation of Sorel cement may shield pellets sufficiently to reduce hydration rates.

4.2 Porosity and permeability reduction

Porosity occlusion and reductions in permeability may result primarily from: (1) MgO hydration to form brucite; and (2) MgO reaction with brines containing sufficient concentrations of $MgCl_2$ to produce Sorel cement (see Section 4.3). In a scenario where the MgO is rigidly constrained, such as between drums in the WIPP repository (or in the laboratory in heavy aluminum cylinders), MgO hydration produces a hard mass with low permeability. Experiments are in progress to quantify porosity and measure permeability in such samples.

In systems containing greater than about 0.8 M $MgCl_2$, Sorel cement will precipitate under basic pH conditions imposed by MgO (Figure 8). Essentially, the brine contributes $MgCl_2$ and the MgO pellets contribute hydroxide to form a magnesium-chloride-hydroxide hydrate mineral. The morphology of precipitates at the surfaces of MgO pellets changes as Mg concentrations increase. Sorel cement has a wispy fibrous morphology and will occlude porosity, reduce permeability, and also imparts substantial strength in MgO samples. The tabular crystals, which may be brucite, provide some compressive strength, particularly if the MgO is physically constrained as it hydrates. In the WIPP, if the repository becomes sufficiently humid for microbial production of CO_2, hydrated MgO will react with carbonate to form hydrated magnesium carbonates. As a consequence, porosity might increase as magnesium-carbonate hydrate minerals mature and release water (Figure 9).

Results of capillary-wicking experiments show that MgO pellets have the ability to lift brine a significant distance against gravity, on the order of at least one meter. We attribute this phenomenon to the combination of several factors: the range of pellet sizes (from about 0.5 to

4 mm diameter) resulting in reduced porosity in loosely packed masses, the presence of grain to grain contacts in loosely packed masses, and the appreciable porosity in the pellets themselves (they consist of approximately 10-µm crystallites fused together as pellets). Experiments to better characterize and model this behaviour are in progress.

4.3 Strength enhancement

At the WIPP, strength enhancement is particularly important to minimize performance impacts from a spallings release. It would also be advantageous to be able to demonstrate that waste is not degraded to very small, easily entrained particles, but instead consists of larger waste aggregates held together by cementitious materials.

Several chemical reactions involving MgO will result in strength enhancement. Hydration reactions, if the MgO is physically constrained, produce hard masses with some compressive and tensile strength. Formation of Sorel cement, when MgO is exposed to systems with sufficient $MgCl_2$, produces considerable strength (Figure 8). Finally, in systems where carbon dioxide is generated, magnesium carbonate cements will form. Experiments are in progress to evaluate magnesium carbonate cements also. Other aspects of the program are currently working on improving models of brine flow into the repository from the Salado Formation to assess the possibility that wetting the backfill, which is prerequisite to all strength enhancement reactions, could in fact occur.

5. CONCLUSIONS AND FUTURE DIRECTIONS

For the WIPP, chemical and physical characteristics of MgO suggest it to be the most beneficial backfill choice, particularly because it has the ability to buffer the aqueous chemical conditions to control actinide solubility. In the current experimental program, we are developing a technical basis for taking credit for the complete set of attributes of MgO in geochemical, hydrogeological, and geomechanical technical areas, resulting in an improved conceptual model for the WIPP such as the following. Water uptake by MgO will delay the development of mobile actinides and gas generation by microbes and corrosion. Reduced gas generation will reduce or even eliminate spallings releases. As MgO hydrates, it swells, reducing porosity and permeability, which will inhibit gas flow in the repository, in turn reducing spallings releases. Hydration will also result in a self-sealing mechanism by which water uptake and swelling of MgO adjacent to a groundwater seep cuts off further seepage. Reaction with some groundwaters will produce cementitious materials, which will help to cement waste particles or produce a cohesive solid mass. Larger particles are less likely to be entrained in a spallings release. If sufficient water eventually accumulates in a repository to support microbial gas generation, magnesium carbonate cements will form; also producing good cohesion and strength.

ACKNOWLEDGMENTS

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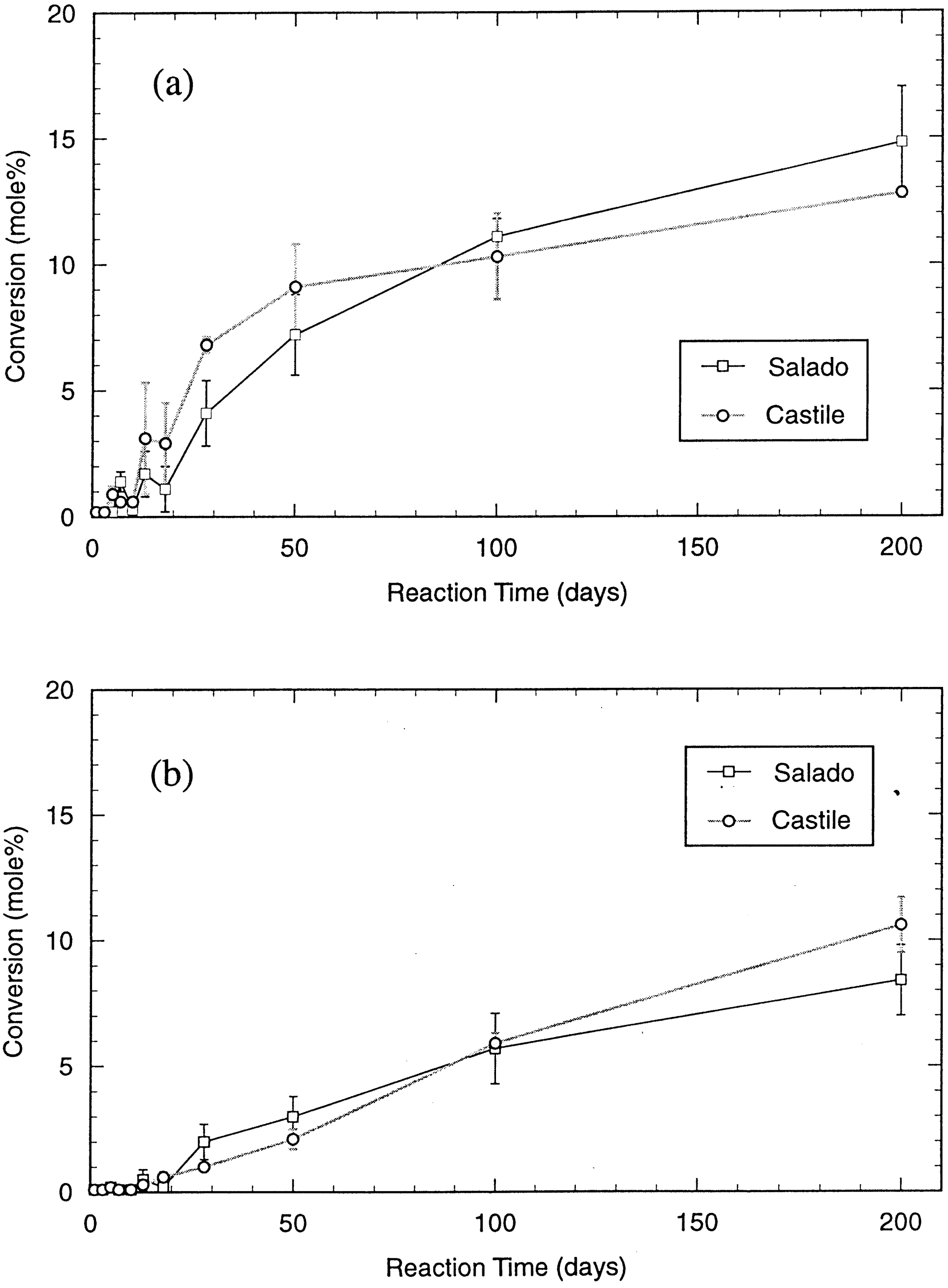

Figure 1. **Carbon uptake by MgO pellets (mostly 0.5 to 4 mm diameter) in Castile (ERDA-6) and Salado (SPC) brine at relatively low pCO_2 conditions: (a) 5% CO_2; and (b) 0.5% CO_2. Points represent averages of three carbon measurements for each of the three parallel experiments for each sample day. Error bars denote one standard deviation of the experiment replicates.**

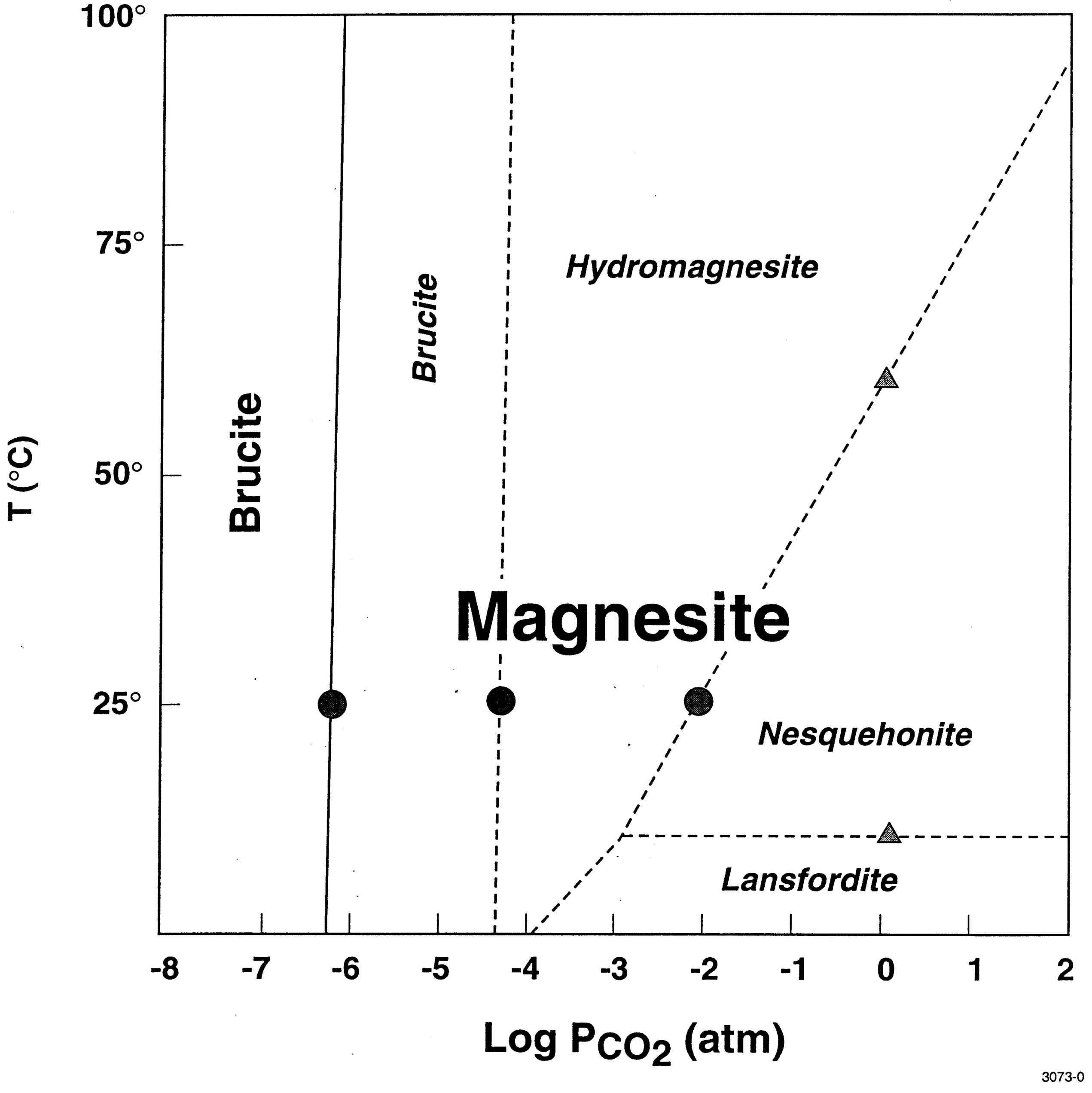

Figure 2. Phase diagram for the magnesium carbonate system; dashed lines indicate boundaries for metastable phases and solid lines represent stable phase boundaries. This diagram, like most equilibrium phase diagrams for magnesium carbonate minerals, represents metastable mineral phases at steady state; the only stable phase in the right side of the diagram is magnesite. The WIPP repository temperature is about 28°C (modified from Lippmann, 1973).

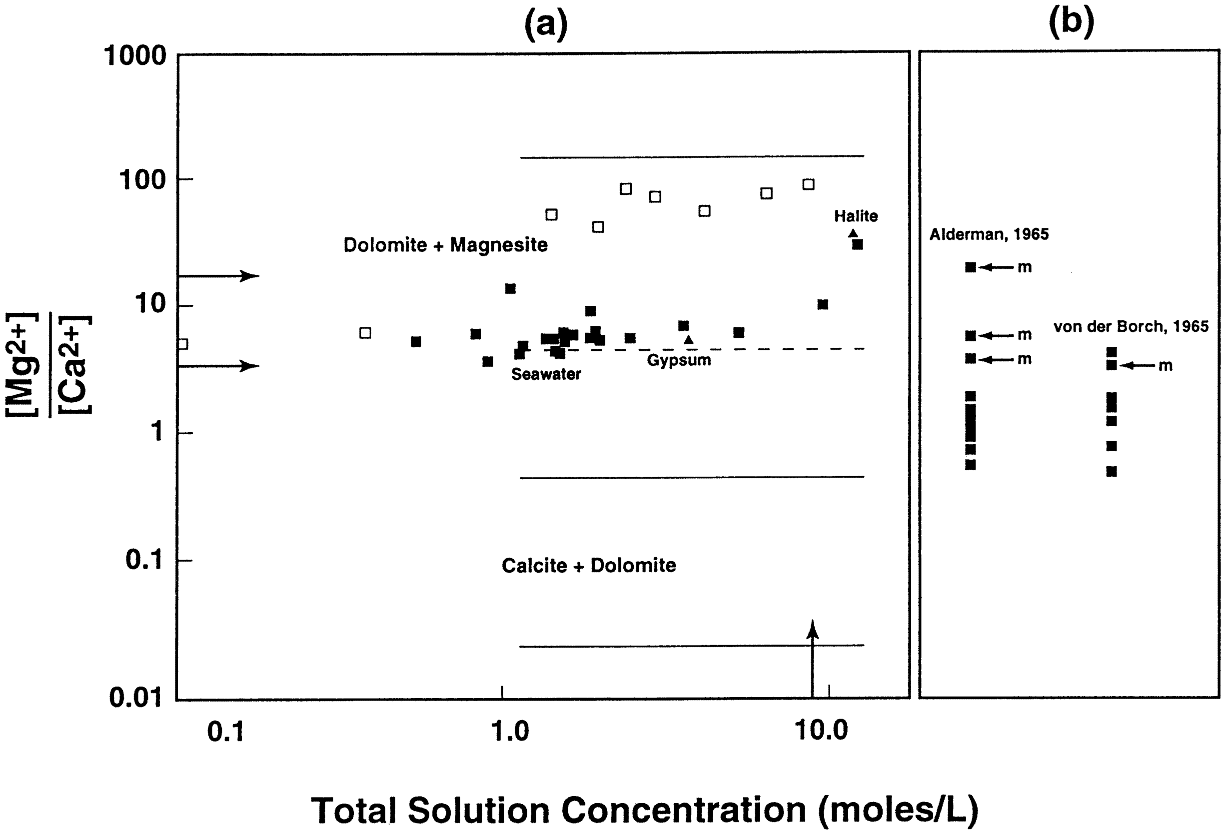

Figure 3. Conditions of formation of magnesite in southern Australia(modified from Usdowski, 1994). In this figure, Usdowski has plotted data he compiled from several key papers together with his best estimate of stability fields of dolomite, magnesite, and calcite. Arrows mark WIPP brine conditions. Note that in both (a) and (b), brine compositions are in the dolomite and magnesite stability range. (a) Compiled by Usdowski from data on the Coorong area, described in Alderman and Skinner (1957), Skinner (1963), and De Dekker and Last (1989). (b) Compiled by Usdowski from data on South Australia, described in Alderman (1965) and von der Borch (1965).

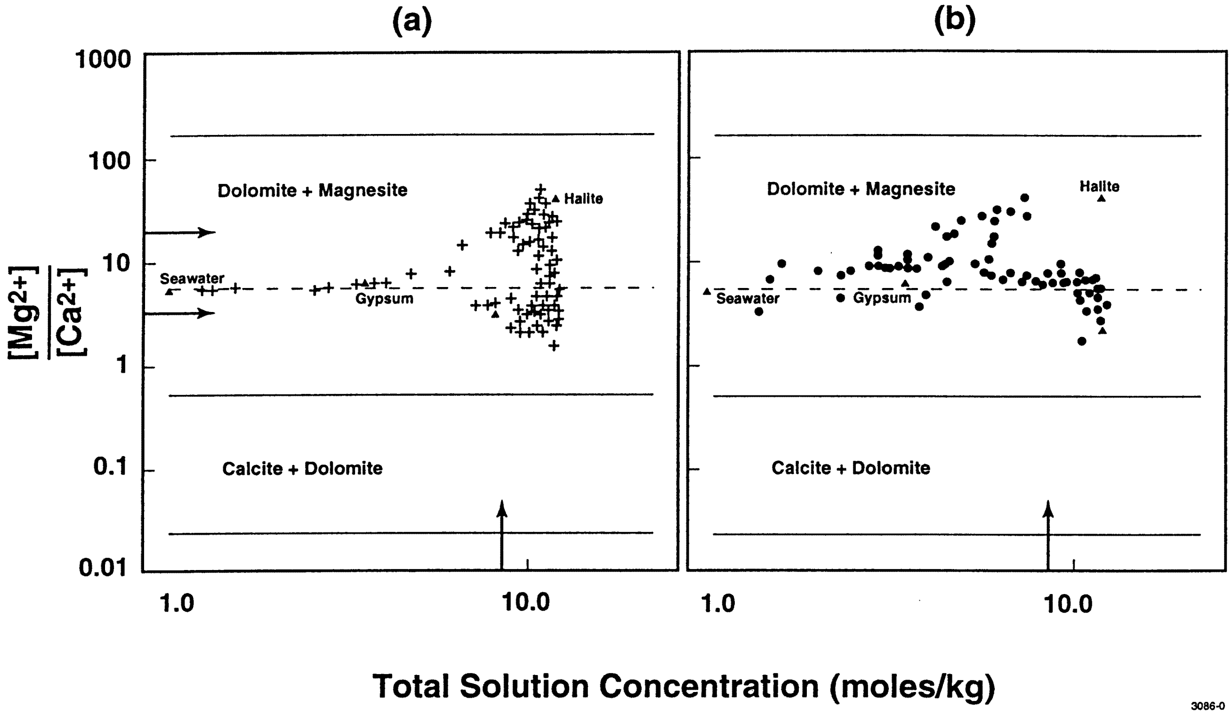

Figure 4. Conditions of formation of magnesite in Saudi Arabia (modifiedfrom Usdowski, 1994). In this figure, Usdowski has plotted data he compiled from several key papers together with his best estimate of stability fields of dolomite, magnesite, and calcite. Arrows mark WIPP brine conditions. Note that in both (a) and (b), brine compositions are in the dolomite and magnesite stability range. (a) Compiled by Usdowski (1994) from data on Abu Dhabi, Saudi Arabia, described in Butler (1969). (b) Compiled by Usdowski (1994) from data on Umm Said, Persian Gulf, described in De Groot (1973).

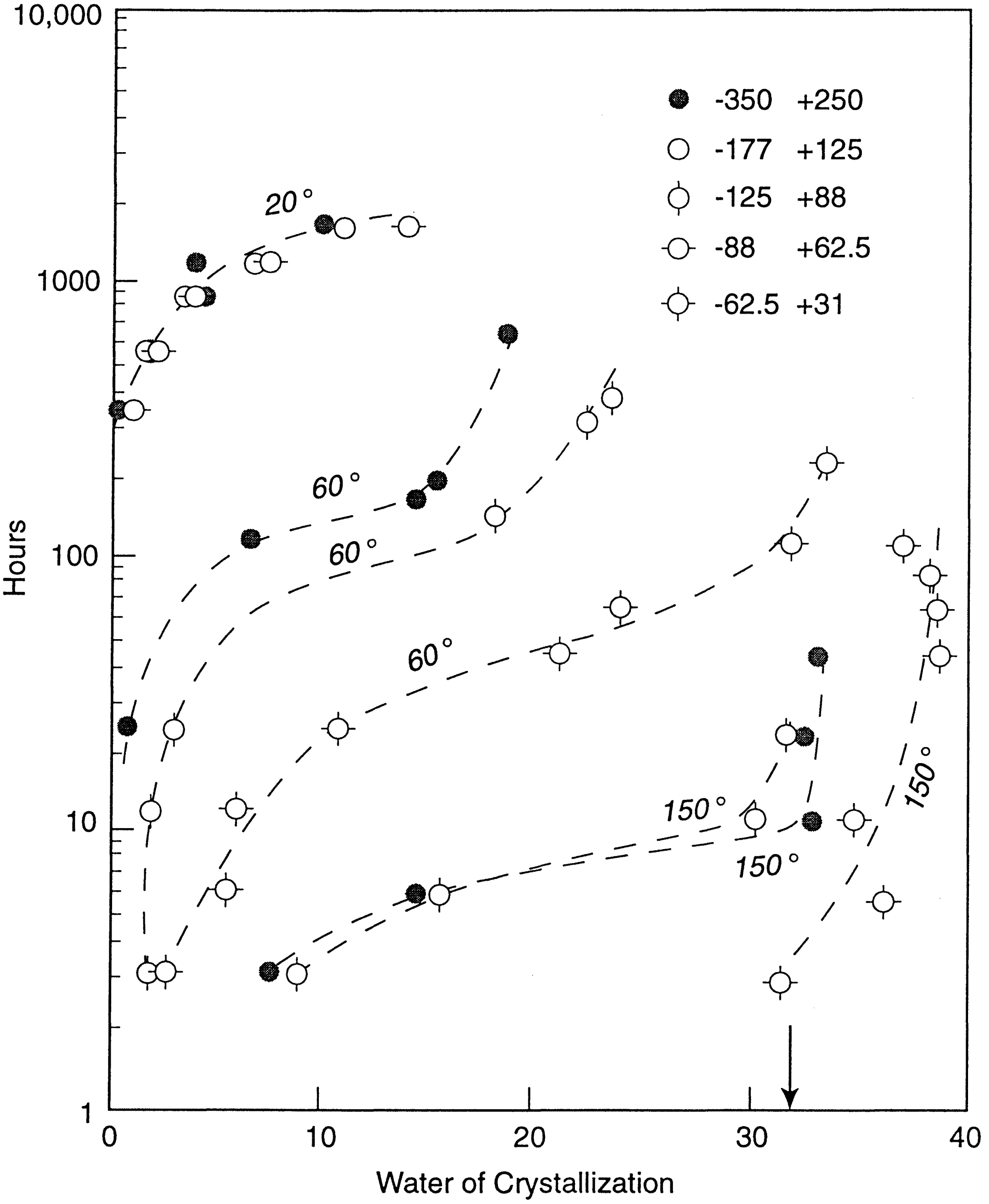

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Figure 5. MgO hydration in water vapor as a function of grain size and reaction temperature. Completely hydrated MgO contains 31 wt% water, as indicated by the arrow. Figure and modified caption from Simpson (1983).

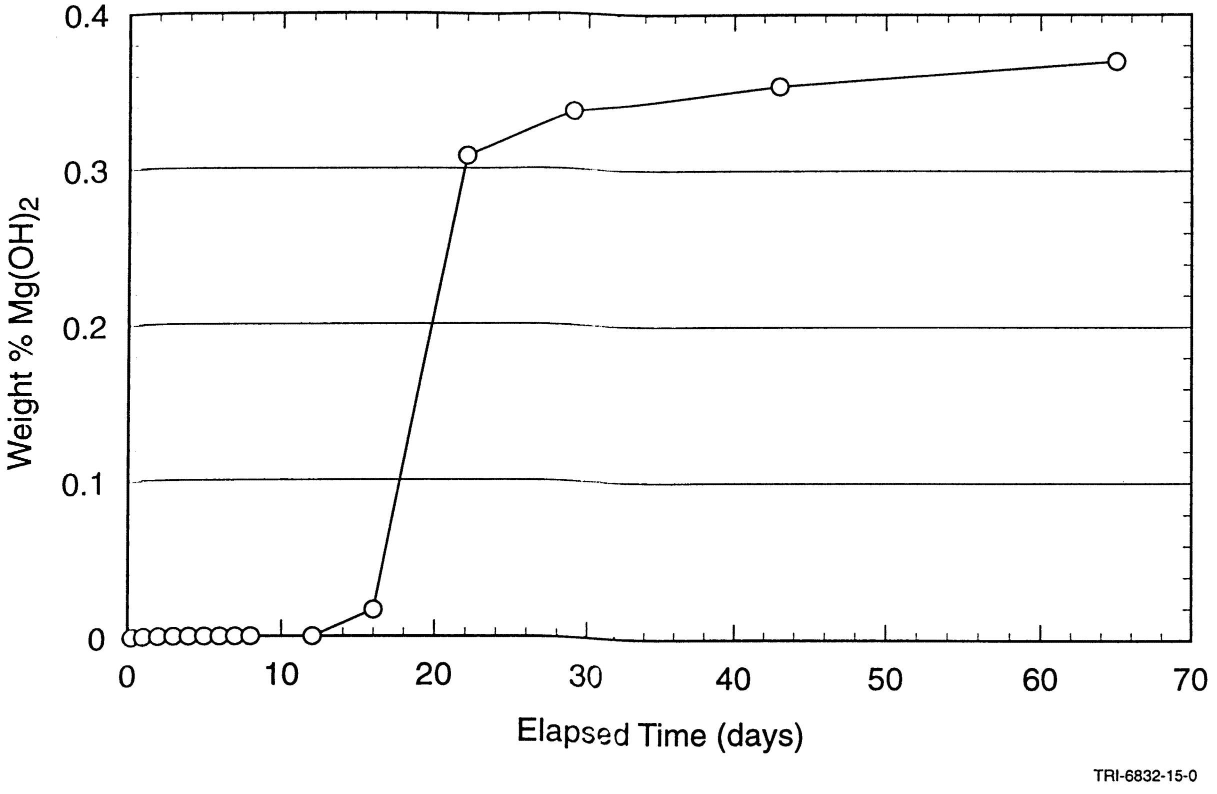

Figure 6. MgO hydration under complete immersion in Salado (GW) brine at 40°C. Note the characteristic "S"-shaped reaction curve, defined in this case by a 12-day incubation period, rapid hydration to about 35 wt% brucite, followed by a decrease in hydration rate. The incubation period is probably related to nucleation; the asymptote is probably related to limitations in reactant diffusion into partially hydrated MgO pellets.

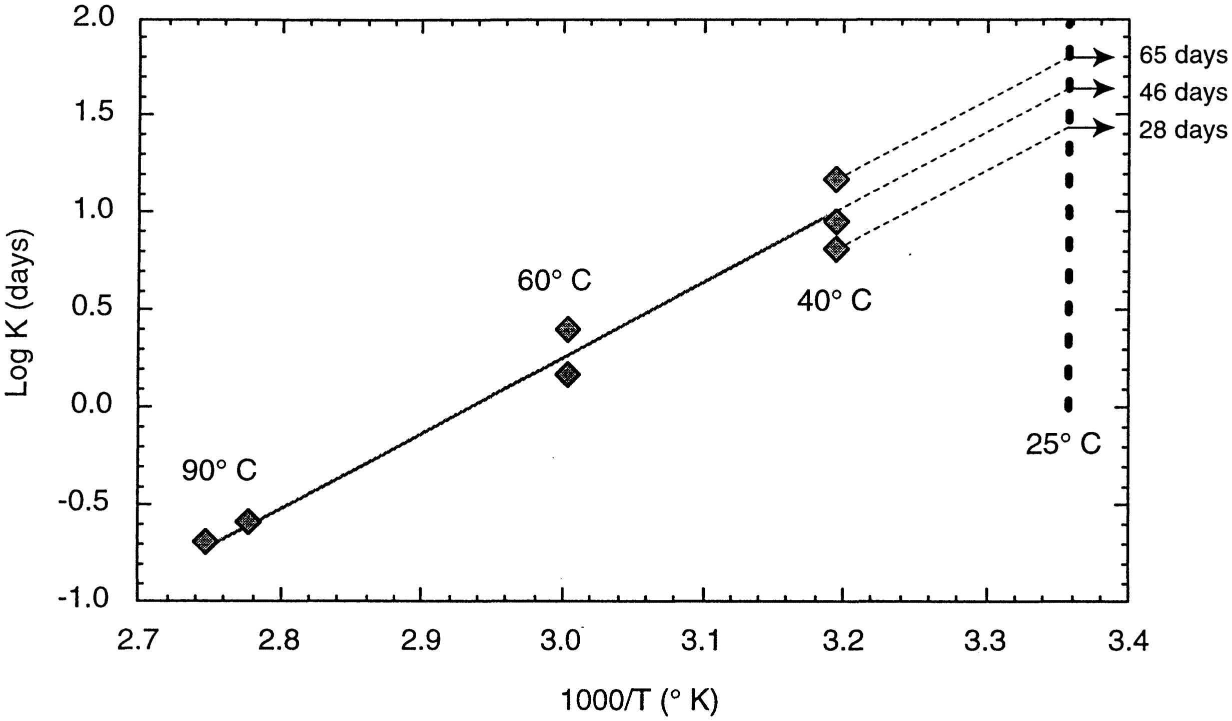

Figure 7. Arrhenius plot of the MgO hydration incubation period, based on hydration under complete immersion in deionized water at 40°C, 60°C and 90°C. Extrapolation to WIPP repository-relevant temperature of 28°C suggests that hydration will begin in a period of one to two months. The relatively large activation suggests that the incubation period is due to nucleation rather than diffusion.

Surface Textures Developed On MgO In A 5 M NaCl Matrix

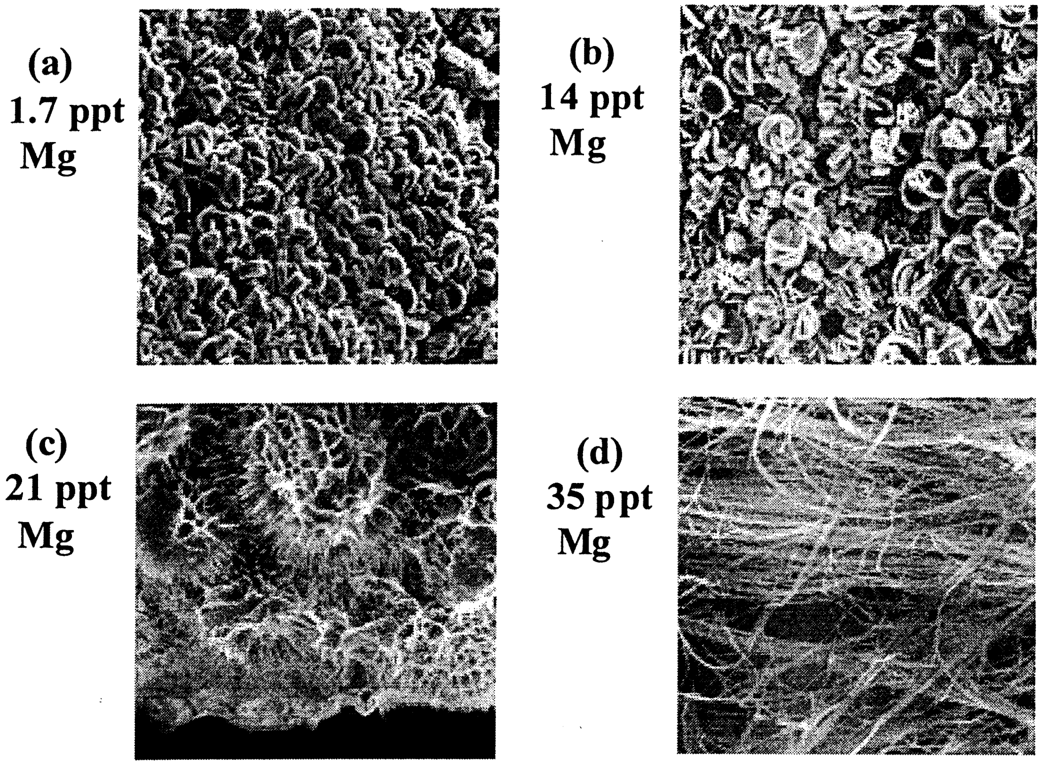

Figure 8. Surface textures developed on MgO pellets at different magnesium concentrations at room temperature. Background electrolyte was 5 M NaCl. Mg concentrations ranged from: (a) 0.08 M (1.7 parts per thousand; ppt); (b) 0.7 M (14 ppt); (c) 1.0 M (21 ppt); and (d) 1.7 M (35 ppt). The tabular crystals formed at Mg concentrations less than about 0.8M are brucite. At greater Mg concentrations, Sorle cement forms, which has a wispy fibrous habit.

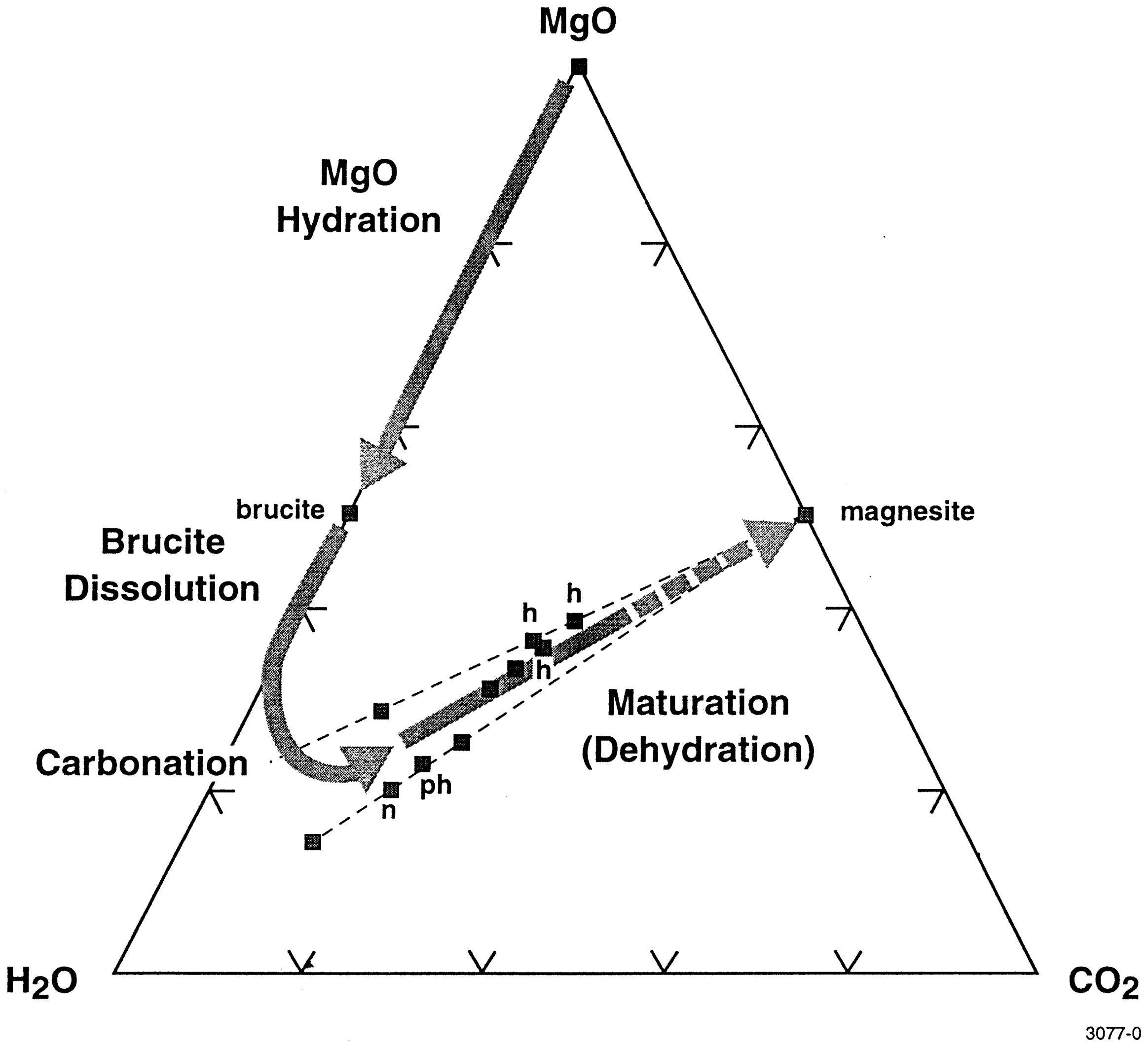

Figure 9. Ternary diagram in $MgO-CO_2-H_2O$ space, showing a schematic reaction path for the periclase to brucite to magnesite transformation. Hydrated magnesium carbonate minerals occupying the interior of the diagram are metastable with respect to magnesite. The upper dashed line is defined by minerals containing two hydroxide anions per formula unit. The lower dashed line is defined by minerals containing waters of hydration but no hydroxide anions. The reaction path arrow designated as "maturation" does not imply that the entire sequence of hydrated magnesium carbonate minerals must be transgressed. In our experiments, nesquehonite ("n") formed under high pCO_2 conditions, but converts to hydromagnesite ("h"), probably through a protohydromagnesite ("ph") intermediary. Under lower pCO_2 conditions, hydromagnesite will form. The stable phase, given sufficient time for reaction, is magnesite. Sorel cement, a magnesium-chloride-hydroxide hydrate, would plot toward a fourth apex of this diagram, defined by chloride. (Mineral compositions compiled primarily from information in Lippmann, 1973).

THE REPRESENTATION OF BACKFILLS IN PERFORMANCE ASSESSMENT FOR RADIOACTIVE WASTES

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1. INTRODUCTION

Engineered components, including seals and backfill, are included in the near field of most radioactive waste repositories. Engineered components can be designed to improve performance, can be built to specification, and their long-term performance may be subject to less uncertainty than that associated with the natural system. This reduces uncertainty in performance assessment (PA) and provides added assurance in the performance of the disposal system.

The principal objectives of this paper are to:

- describe the way in which PA studies are undertaken and, in particular, discuss the way in which backfills are considered in PA studies;
- identify key scenarios and processes relevant to the use and assessment of backfills;
- identify areas of remaining uncertainty related to backfill representation in PA; and
- make suggestions regarding the need for future research and assessment in this area.

2. PERFORMANCE ASSESSMENT

A PA is an analysis to evaluate the performance of a system or subsystem, followed by comparison of the results of such analysis with appropriate standards or criteria (NEA 1991). A PA becomes a safety assessment when the system is the overall waste disposal system and the performance measure is radiological impact or safety. The aims of performance and safety assessments include developing sufficient understanding of the physical and chemical behaviour of the disposal system, quantification and prediction of future system behaviour, assessment of uncertainties in system behaviour predictions, and demonstration of the adequacy of the assessment to a range of audiences. The typical components that comprise PA and the interactions among them are illustrated in Figure 1.

The first stage in PA involves the development of scenarios for analysis within the overall context of the site of interest and applicable regulations. Typically, four basic steps are involved in scenario development:

(i) identify and classify all phenomena (i.e., features, events, and processes or FEPs) potentially relevant to the performance of the disposal system;

(ii) eliminate FEPs according to well-defined screening criteria;

(iii) form scenarios from the remaining FEPs in the context of regulatory performance criteria; and

(iv) specify scenarios for consequence analysis.

The identification and classification of all FEPs potentially relevant to the performance of a disposal system is an inherently subjective process. Scenario construction is typically preceded by a systematic screening procedure to identify those FEPs to be included in PA modelling. FEPs may be excluded because they are beyond the scope of the PA, are physically unreasonable in the context of the particular disposal site, have a low probability of occurrence, or are of low consequence to the performance of the disposal system.

The next stage in PA is the development of a conceptual model. The conceptual model represents a broad understanding of the FEPs that are included in the scenario under consideration and the couplings between FEPs, and incorporates a set of qualitative assumptions used to describe a system or subsystem for a given purpose. The next stage in PA modelling involves transcription of the conceptual model into computationally tractable mathematical models. The conceptual model provides the context within which these mathematical models operate and defines which processes they must include. The implementation of mathematical models in computer codes leads to the calculational models used in PA consequence analyses. Specific parameter values are then used with the PA codes to undertake the consequence analyses. All stages of model development inevitably involve a process of model simplification, and it is important that decisions and assumptions are documented and justified.

A series or hierarchy of models may be established at varying levels of complexity. The simplest representations are often used in safety assessment. More complex model treatments may be employed in the assessment of subsystem performance, and these treatments may extend to detailed research-level models of particular processes. The establishment and use of such a modelling hierarchy allows an appropriately detailed analysis of individual FEPs of particular importance.

Deterministic and/or probabilistic calculations may be made in order to quantify the future evolution of the disposal system. Deterministic analyses may be established on the basis of conservative and/or best estimate assumptions and parameter values. Probabilistic analyses provide an understanding of the range of possible future disposal system behaviour by making many simulations using different parameter values. Nonetheless, conservatism may also enter into probabilistic analyses of poorly quantifiable FEPs.

3. BACKFILL OBJECTIVES, FUNCTIONS, AND SELECTION

Three main classes of sealing or backfilling material have been proposed for use in repositories for radioactive waste: cementitious materials, swelling clays, and materials excavated during repository construction (e.g., salt). The conceptual basis for the use of engineered components in radioactive waste disposal facilities varies depending on programmatic requirements. Different materials offer a range of potential performance benefits depending on their chemical, hydrological, and structural (mechanical) properties.

We are unable in this short paper to present a comprehensive review of the treatment of backfills in the relatively large number of PA studies that have been performed for the different waste disposal systems. Instead, we illustrate the range of treatments by focusing on the following three areas, distinguished according to the primary function of the materials considered:

(i) components with a primarily chemical function;

(ii) components with a primarily hydrological function; and

(iii) cementitious components with a primarily structural (mechanical) function.

The major design objectives influencing the choice of materials for engineered components are as follows:

- Chemical components used to condition the repository near-field environment should promote conditions that reduce radionuclide solubilities and/or canister corrosion rates. Ideally they should also have high adsorption characteristics for relevant radionuclides, contain few complexing agents that could enhance release and transport of radionuclides, undergo only limited volume changes, and evolve only small amounts of heat resulting from reactions after emplacement.

- Hydrogeological components should possess long-term low hydraulic conductivity in order to retard migration of radionuclides in groundwaters. In some cases there may be a competing objective, namely that gas permeability be high enough to avoid the generation of high gas pressures within the repository. It is desirable that any cracks will self-heal.

- Structural components should possess long-term mechanical stability, bond strength and low shrinkage. When used near heat-generating wastes, these components should also exhibit similar thermal expansivity to the surrounding rock mass in order to minimize cracking caused by differential expansion.

Certain other factors and considerations may apply in the selection of materials:

- ease of emplacement within the repository, particularly with regard to worker safety;

- ease of retrieval of disposed waste; and
- availability, low cost, and adequate quality control.

3.1 Backfills with a primarily chemical function

Applications and material characteristics

The potential range of chemical backfill materials is large. Many different materials may be used to buffer pH and control radionuclide solubilities and/or to sequester radionuclides by chemical sorption and (co)precipitation processes.

Notable examples of specific relevance to deep disposal include:

- The UK Nirex Reference Vault Backfill (NRVB): a mixture of 40% OPC, 15% lime, and 45% crushed limestone. This backfill is used to maintain a high-pH aqueous environment in the repository. The high pH lowers the solubility of key radionuclides and promotes radionuclide sorption.
- Magnesium oxide: This backfill is to be used at the US WIPP facility (US DOE 1996) to buffer the pH of the repository to moderately basic conditions in order to reduce the solubility of key radionuclides. In addition, magnesium oxide will also act to consume carbon dioxide gas by the formation of relatively insoluble carbonate solids.

PA scenarios

For deep disposal, chemical backfills are considered within two broad types of scenarios:

- undisturbed performance scenarios involving releases via a groundwater pathway, and
- disturbed performance scenarios involving future human intrusion events.

Chemical backfills buffer the pH of the near-field groundwaters and therefore control radionuclide solubility. The range of chemical backfill formulations partly reflects a range of views on desirable pH conditions in radioactive waste repositories. For example, on hydration the NRVB is likely to contain ≈40 mole% $Ca(OH)_2$ (Tyrer *et al.* 1995) and so will condition a high porewater pH (>12). The use of magnesium oxide as backfill at the WIPP will have a less marked influence on pH (~9–10). MgO is discussed in detail in a companion paper in this appendix and is not described further here. The chemistry of the near field will also influence radionuclide sorption within the repository, and the backfill itself may act as an important substrate onto which radionuclides may be sorbed.

PA modelling

Backfill dissolution processes may be represented using thermodynamic models to describe the behaviour and evolution of the solid phases present in the backfill. However, such models are rarely incorporated directly in PA, and it is more usual to represent the chemical action of the backfill by assuming radionuclide solubilities and K_d values appropriate to the expected chemical conditions. Key assumptions usually made in this approach are that the backfill conditions the entire repository and that this conditioning effect persists over the long term.

The PA for the deep disposal of LLW/ILW at the UK Sellafield site included the treatment of a chemical backfill (Nirex 1995a). This PA considered only the groundwater pathway, and the near field of the repository was represented as a homogeneous system. Supporting studies were made to investigate some of the potential effects of spatial heterogeneity in the near field (Nirex 1995b, Askarieh *et al.* 1997). The cementitious backfill was assumed to be sufficiently porous and permeable to allow the development of uniform chemical conditions and radionuclide concentrations throughout the repository, and to enable gases to migrate readily out of the near field and thus prevent pressurization. It was assumed that incoming groundwaters and the repository porewater would be fully conditioned by the cementitious backfill in the vaults to high pH (>12). Steel corrosion was assumed to buffer Eh to low values. These chemical conditions were assumed to remain constant throughout the period assessed (10^6 years). The aqueous behaviour of each radionuclide was characterized by a solubility limit and a distribution coefficient appropriate to these conditions. Thus, the backfill material was assumed to limit solubilities and to sorb radionuclides and retard their transport out of the repository.

Outstanding PA uncertainties

In the Nirex PA (Nirex 1995a) a number of uncertainties associated with near-field features and processes were identified that could adversely affect backfill and repository performance. These included the reduction of backfill buffering capacity due to chemical interactions with incoming groundwaters and degradation products of organic wastes, gas generation by metal corrosion and microbial activity, and complexation of radionuclides by degradation products of organic wastes. These processes were not quantified during the PA calculations.

Other uncertainties associated with the performance of chemical backfills include:

- The thermodynamic models for describing the dissolution behaviour and buffering capacity of blended cementitious materials (e.g., Atkins *et al.* 1992a, 1992b, Glasser *et al.* 1998) have mostly been derived from the study of simple chemical systems in the laboratory, and their application to real repository conditions is uncertain. For example, the effects of elevated temperatures and complex saline groundwaters on the chemical evolution of cements remain poorly constrained.

- PAs commonly assume that homogeneous chemical conditions will prevail in the repository and that no preferred flow pathways through the backfill will form, potentially allowing waters to move through the repository without becoming chemically conditioned by the backfill. Such assumptions remain to be evaluated thoroughly.

3.2 Backfills with a primarily hydrological function

3.2.1 Clay backfills

Applications and material characteristics

Bentonite clay is the principal component of the backfill in many deep repository concepts hosted in crystalline rock or clay. It has two main uses:

- Bentonite clay is used as a material to surround the canisters of waste within vertical or horizontal deposition holes. In disposal concepts hosted in crystalline rock, the bentonite is sometimes referred to as the 'buffer', and fills the gap between the canisters and the host rock. Bentonite is used in this way in the Canadian, Finnish and Swedish disposal concepts (Figure 4).

- Bentonite clay is used as a material to fill the void space within the tunnels and shafts. For disposal concepts in which the waste canisters are emplaced within disposal rooms and tunnels, the bentonite surrounds the canisters and separates them from the host rock. Bentonite is used in this way in the Canadian, French, Japanese, Spanish and Swiss disposal concepts hosted in crystalline rock, and in the Belgian disposal concept hosted in clay.

Repositories hosted in clay may make use of the local host rock as the backfill. Repositories hosted in crystalline rock may also use the local host rock as ballast, which is mixed with bentonite clay to form the backfill.

In the Canadian disposal concept, both clay- and cement-based material have been considered for use as backfill. Clay is currently favoured for the disposal rooms because of a desire to maintain a near-neutral pH adjacent to the waste containers. Mixtures of ballast and clay, including 90:10 sand to bentonite, and 75:25 crushed granite to clay, have been evaluated. Such mixtures have considerably lower swelling pressures than pure bentonite, thereby reducing complexity in their emplacement. However, at sufficiently high densities, the hydraulic conductivity of the mixtures will remain low, thereby maintaining their hydrological function. Such densities can be achieved by compaction, either *in situ* or prior to emplacement. Mixing ballast with the bentonite can also improve other performance characteristics of the backfill, such as resistance to erosion, thermal behaviour, and sorption capacity.

In the Canadian and Swedish disposal concepts, the backfill is to be emplaced within the disposal rooms and tunnels in two layers (Figure 4). For example, the Canadian concept (AECL 1994b) includes a lower backfill of a 25:75 mixture of clay to granite, with a dry density of 2.1×10^3 kg m^{-3}, and an upper backfill of a 50:50 mixture of sodium bentonite and silica sand, with a dry density of 1.4×10^3 kg m^{-3}. In later studies, crushed granite was considered as an alternative to the silica sand in the upper backfill because the Fe(II) minerals in the granite would promote reducing conditions. This condition is desirable because it will help to ensure that technetium and other redox-sensitive radionuclides occur in their reduced, relatively immobile states.

PA scenarios

Clay backfill may influence these two commonly analyzed types of scenarios:

- normal evolution scenarios, and
- poor sealing scenarios.

Normal evolution scenarios typically consider diffusive transport of radionuclides from the canister, through the clay backfill or buffer, and into the surrounding host rock or excavation disturbed zone (EDZ) (Figure 5) (e.g., SKB 1995, ENRESA 1997). Poor sealing scenarios involve some type of deficiency of the seals (e.g., ENRESA 1997) or a deficiency of the backfill itself (e.g., NAGRA 1994, Marivoet *et al.* 1997).

PA modelling

Both normal evolution and poor sealing scenarios involve analysis of releases via the groundwater pathway and therefore depend on the hydrological and transport properties (permeability/ hydraulic conductivity/porosity) assumed for the clay, and the dimensions of the backfill (effective thickness). The secondary function of the clay in retarding radionuclide transport by sorption is represented in PA using appropriate retardation coefficients. PAs represent material properties such as density and swelling pressure implicitly through the use of appropriate values for permeability and effective diffusivity.

For example, in the normal evolution scenario considered in the Canadian Environmental Impact Statement (EIS), the backfill was assumed to maintain its integrity over the 100,000 years of the PA simulation (AECL 1994a). No distinction was made in the PA between the different materials comprising the upper and lower backfill. The properties assumed for the backfill in the vaults were a hydraulic conductivity of 10^{-10} m/s and an effective thickness of 1.4 m. The backfill was modelled as completely filling the vaults between the buffer and the low-permeability host rock. Transport of radionuclides through the backfill and buffer was primarily by diffusion. Transport of radionuclides along the backfilled disposal rooms, tunnels, and shafts was not modelled because these features were assumed to have a lower permeability than the surrounding host rock.

In the Belgian PA for Mol (Marivoet *et al.* 1997), the normal evolution scenario was based on the assumption that the clay used to seal the tunnels and lower shafts had identical properties to the surrounding host clay. However, in the poor sealing scenario, it was assumed that the permeability of the backfill was higher than that of the surrounding clay and that therefore the repository tunnels and shafts would act as preferential pathways for groundwater flow. The disposal room backfill was assigned a hydraulic conductivity 10^4 times higher than that of the host rock. In the backfilled tunnels and shafts, the hydraulic conductivity was set 10^3 times higher than that of the host rock, and the porosity was increased to 1.5 times that of the host rock. The consequences of this scenario were evaluated by calculating the vertical flux of various radionuclides in the shaft at the interface between the host rock and the overlying aquifer and comparing that with the results from the normal evolution scenario (Marivoet *et al.* 1997).

Outstanding PA uncertainties

PAs generally assume that there is no deterioration of the hydrological properties of clay backfills over time, despite the possibility that such deterioration may occur over the relevant time scales. For clays, concern over long-term durability focuses on the hydrothermal alteration of minerals, especially the transformation of smectite clays to illite or micas, or silicification. Both processes decrease swelling capacity and increase hydraulic conductivity. Several programmes have drawn attention to the long-term preservation of bentonite clays in the geological record, and have used this as supporting evidence for the long-term stability of Na-bentonite in radioactive waste repositories (e.g., SKB 1995). Natural bentonite deposits that are being considered for use in deep repositories have preserved their swelling capacity and low hydraulic conductivity for millions to hundreds of millions of years. Nevertheless, such deposits differ in scale and may have been preserved under different geological conditions, in comparison with the proposed uses of bentonite in repository sealing systems. They therefore do not necessarily provide good natural analogues for the long-term durability of clay backfills in repository environments.

Clay backfills have been assumed by several programmes to act as efficient filters of colloids (e.g., AECL 1994b), thereby allowing transport of radionuclides by repository-derived colloids to be screened out of PAs. Evidence supporting this assumption comes from the Cigar Lake natural analogue, among other studies.

3.2.2 Salt backfills

Applications and material characteristics

Apart from the MgO backfill material proposed to be used at the WIPP (US DOE 1996), the principal backfill material in salt-hosted repositories is crushed salt. Other countries with salt-hosted repository concepts are Germany, the Netherlands and Spain. However, the Netherlands and Spain have yet to select a specific site, and published PAs are entirely generic. In Germany, radioactive waste disposal sites exist at Morsleben and Gorleben.

In the reference design for the Gorleben repository considered by Becker *et al.* (1997), the repository is located 840 m below the surface and 540 m below the top of the salt dome. HLW and heat-producing ILW canisters are emplaced in disposal boreholes, while the remaining waste is emplaced in storage chambers. The disposal boreholes are not backfilled but are sealed at the top with a 10-m plug of salt or salt-concrete. The shafts, disposal tunnels, flank tunnels, and the area between the shafts and the disposal and flank tunnels are backfilled with crushed salt. Disposal tunnels are sealed with salt-concrete. Finally, the shafts are backfilled with crushed salt and sealed to give bulk permeabilities that are assumed to be at least as low as the surrounding salt formation.

PA scenarios

When considering deep disposal in salt with salt backfill at Gorleben, Becker *et al.* (1997) investigated three scenarios:

- a normal evolution scenario;
- a solution mining scenario; and
- an uplift scenario.

In the normal evolution scenario, it was assumed that the repository was backfilled with crushed salt and sealed in the normal manner. Brines were available to flow into the repository, but would only do so only to the extent allowed by convergence of the salt by creep and the resulting disappearance of void space. The behaviour of the backfill and seals was important to the consequences of this scenario, both during the brine inflow phase and during the subsequent phase when the repository brines were subjected to increasingly high pressure resulting from salt convergence.

In the solution mining scenario, it was assumed that a cavern would be created near the repository by solution mining, causing several canisters of waste to fall into the excavated volume and break open. The cavern would then be filled with water and sealed. The subsequent evolution of the system and the transport of radionuclides to the biosphere were modelled.

In the uplift scenario, it was assumed that diapiric ascent of the salt dome uplifted the whole repository over the next few thousand years. Subrosion (underground erosion of salt) at the top of the salt dome would then cause the waste to come into contact with groundwater aquifers, leading to release to the biosphere within approximately 10^6 years.

PA modelling

In the PA calculations conducted by Becker *et al.* (1997), the hydrological performance of the disposal borehole plugs, the crushed salt backfill, and the various types of seal were all directly modelled. Both deterministic and probabilistic analyses of the normal evolution and the solution mining scenarios were made, whereas only a deterministic analysis of the uplift scenario was made. Parameter values for sealing components - including porosity and permeability of borehole plugs, seals, and crushed salt backfill - were all specified. No attempt was made to construct a detailed model of the transport of radionuclides along the shafts to the surface.

Outstanding PA uncertainties

One of the key processes that must be considered within PAs of salt-hosted repositories is the convergence of the salt surrounding the backfilled tunnels, shafts, and disposal rooms. The behaviour of the seals and backfill is important to repository performance during convergence, when the repository brines are subjected to increasingly high pressure. Models for salt convergence contain numerous parameters describing the material properties of salt backfill and host rock, and the stress-strain evolution of the repository environment. Some of the required parameter values are poorly known. Further study of the convergence and compaction behaviour of salt backfill and the relationship between the permeability and porosity of the backfill could reduce uncertainty in these values.

3.3 Cementitious components with a primarily structural (mechanical) function

Applications and material characteristics

Structural cementitious components are commonly used in shallow radioactive waste disposal repositories, such as the Centre de la Manche and the Centre de l'Aube in France, El Cabril in Spain (Figure 2), and Drigg in the UK (Figure 3). In such disposal systems, cements are not used for backfill as such, but they occur in other repository components that may influence PA. Uses include:

- structural components of the repository - for example, as vault walls and floors, roadways, and drains;
- waste containers and conditioning material within waste containers to cement the various waste forms and incorporate any liquid waste.

Underground disposal concepts in many countries also include cementitious materials as structural components. In addition to those uses noted above, cementitious materials may be used in such disposal concepts as:

- structural components of the repository - for example, as tunnel supports, shotcrete, and shaft linings;
- tunnel, shaft, and borehole seals; and
- fracture seals (grouts).

Different material formulations are required for these different roles according to the practicalities of emplacement and performance requirements. These formulations typically include blends of ordinary Portland cement (OPC) with pulverized fly ash (PFA) and/or other pozzolans, with or without superplasticizers.

PA scenarios

Structural cementitious components may influence two broad types of scenario that require consideration:

- undisturbed performance scenarios involving releases via groundwater pathways; and

- disturbed performance scenarios involving future human intrusion events.

For example, at shallow disposal sites the material properties of structural cementitious components such as concrete vault walls may influence rates of subsidence and thereby affect the integrity of the site cap. In both shallow and deep disposal systems, the hydrological properties of structural cementitious components may influence radionuclide transport along specific pathways into the surrounding geosphere. The physical and mechanical properties of cement-conditioned wasteforms will influence the amount of material that could be exhumed during a drilling intrusion. A secondary effect of the presence of structural cementitious components may be that their chemical effects influence radionuclide solubilities and sorption in the near field. These secondary chemical effects are discussed further below for the case of chemical backfills.

PA modelling

The effects of the gradual degradation of structural cementitious components are usually not included explicitly within PA models. For shallow facilities, assumptions are often made regarding the successful elimination of voids beneath the site cap, or that differential subsidence across the facility will not be significant. PA models represent the hydrological properties of structural cementitious components through estimates of material porosity, permeability, and hydraulic conductivity. Radionuclide transport through such features may be represented using diffusion and/or advection models based on effective diffusivities and estimated flow rates. Such models may also include representation of radionuclide retardation effects using appropriate distribution coefficients (K_ds). PAs rarely take account of the effects of structural cementitious components on releases resulting from future human intrusion.

The PA treatment of structural cementitious components for the Spanish El Cabril shallow LLW repository is described by Ulibarri (1993). The assessment of the groundwater pathway was made for two periods: the institutional control period (the first 300 years) and afterwards. In the first 300 years, radionuclide releases from the waste were based on waste-form leaching test results, which were applied to the fraction of the waste containers assumed to have degraded. After the institutional control period, all the structural cementitious components were assumed to be completely degraded and to have the properties of concrete dust. Radionuclide leaching in this phase was represented using appropriate distribution coefficients. In the human intrusion scenario, doses were calculated assuming that workers inhaled a mixture of contaminated dust composed of particulate waste and completely degraded engineered components.

Outstanding PA uncertainties

The main uncertainty relating to the treatment of structural cementitious components in PA concerns their longevity. Without information on degradation processes and rates, and the properties of degraded components, PAs often make quite unrealistic assumptions about their long-term performance (e.g., complete degradation). For deep repositories, the structural components represent only a small fraction of the potential radionuclide transport pathway, and neglecting the performance of such engineered components in PA calculations may be a reasonably conservative approach.

4. DISCUSSION AND CONCLUSIONS

Table 1 presents a summary of the treatment of selected engineered components in PA studies for a number of disposal programmes.

4.1 Chemical properties of backfills

The chemical properties of backfills are generally represented in PAs through just two parameters: radionuclide solubility and solid/fluid distribution coefficient. In some disposal concepts the backfill is designed to buffer and control the chemistry of the repository near field in order to constrain radionuclide solubilities and/or distribution coefficients to favourable ranges (e.g., Nirex, 1995a, US DOE 1996). These concepts rely on maintaining a state of chemical disequilibrium between the repository and the surrounding natural system. A requirement of safety cases for such concepts is a demonstration that the desired buffering effect can be maintained for an adequate period of time. The persistence of the pH buffering capacity of cementitious backfills, particularly in complex saline groundwaters and at elevated temperatures, are remaining uncertainties.

Other disposal concepts (e.g., AECL 1994a, Marivoet *et al.* 1997) attempt to work with the favourable natural characteristics of the host rock by using backfills that are close to chemical equilibrium with the host rock. The range of concepts is illustrated in Table 2, which shows the expected pH of the repository and the host rock porewaters for a range of deep disposal systems.

4.2 Hydrological properties of backfills

The basic hydrological properties of backfills (porosity, permeability, hydraulic conductivity) are used in PA consequence calculations, and it is often assumed that these properties will remain constant over time, even though long-term durability is not well constrained. Several programmes have drawn attention to the long-term preservation of bentonite clays in the geological record, and have used this as supporting evidence for the stability of Na-bentonite in radioactive waste repositories (e.g., SKB 1995). The durability of cements is also uncertain, and there is a notable lack of data pertaining to cement performance on long timescales. The potential effects of cracking on the properties of cementitious backfills is a key remaining uncertainty. Table 3 presents the backfill composition, and the hydraulic conductivities and effective diffusivities used in a number of PA studies.

A key factor determining which flow-pathways are evaluated in PA is the permeability contrast between the backfill or buffer and the host rock. For disposal systems in crystalline rocks where clay is used as backfill, the pathway evaluated is generally the shortest route through the clay from the canister to the host rock (usually the EDZ). For disposal systems where clay backfill is emplaced in clay host rocks or where salt is used to backfill salt formations, it is more likely that the backfills have greater permeabilities than the host formations, at least over the short term, potentially resulting in preferential flow through the repository excavations.

4.3 Mechanical properties of backfills

PA consequence calculations usually exclude explicit representation of the mechanical properties of cementitious structural components. Uncertainties remain with regard to the long-term durability of these components. For clay backfills, mechanical properties such as density and swelling pressure are indirectly accounted for in PA by use of appropriate permeability and diffusivity values. For salt backfills, PA simulations have included explicit modelling of salt creep (e.g., Becker *et al.* 1997).

4.4 Outstanding Issues

Most PAs have assumed that conditions in the repository remain constant over time, and have not included explicit simulation of the temporal evolution of the backfill or other materials present. Attempts have been made in some PA studies to reflect the expected chemical evolution of the repository near field by selecting radionuclide solubilities and distribution coefficients appropriate to different stages in repository history (e.g., Sumerling 1996, ENRESA 1997). However, results from the relatively large number of research studies that have been performed with the aim of quantifying backfill degradation and dissolution rates have generally not been transferred to PA in any quantitative sense. Such studies contribute to safety assessment mainly through developing fundamental process understanding and understanding the limits of PA calculations.

PAs generally assume that conditions in the repository are spatially homogeneous. An understanding of the potential effects of physical or chemical heterogeneity within the near field is often lacking. PAs generally exclude explicit modelling of radiolysis, volume changes, colloidal processes, biological activity, and physical and chemical heterogeneity within the repository. Such features and processes are often eliminated from PA calculations during the development of conceptual models, using reasoned arguments concerning their potential significance to the performance of the disposal system.

This paper has focused on existing plans for backfill materials. However, research into relatively new backfill materials (e.g., apatites) continues. Optimization of the backfill for a particular disposal concept will require consideration of a number of factors beyond material performance, such as repository design, the nature of the waste, the nature of the repository host rock, practicalities and operational safety constraints on backfill emplacement, and the availabilities and cost of component materials for the backfill.

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Table 1. The treatment of selected engineered components (backfill, buffer, and shaft and tunnel seals) in performance assessment (PA), or in supporting calculations, for a range of countries.

<table>
<tr><th>Country and Site or Assessment</th><th>Reference</th><th>Buffer</th><th>Backfill</th><th>Shafts and Tunnel Seals</th><th>Fracture seals</th></tr>
<tr><td colspan="6">CRYSTALLINE HOST ROCK</td></tr>
<tr><td>Canada (EIS)</td><td>AECL (1994a)</td><td>1</td><td>1</td><td>3a</td><td>3a</td></tr>
<tr><td>Finland (TILA-96)</td><td>Vieno and Nordman (1996)</td><td>1</td><td>1</td><td>Tunnels 2
Shafts 3b</td><td>3b</td></tr>
<tr><td>Japan (H-3)</td><td>PNC (1992)</td><td colspan="2">1</td><td>3b</td><td>3b</td></tr>
<tr><td>Spain (Deep disposal in granite)</td><td>ENRESA (1997)</td><td colspan="2">1</td><td>1, 2</td><td>3b</td></tr>
<tr><td>Sweden (SR-95)</td><td>SKB (1995)</td><td>1</td><td>3b</td><td>3b</td><td>3b</td></tr>
<tr><td>Switzerland (Kristallin-I)</td><td>Nagra (1994)</td><td>1</td><td>2</td><td>2</td><td>3a</td></tr>
<tr><td>UK (Nirex 95)</td><td>Nirex (1995b)</td><td>Not present</td><td>1</td><td>3b</td><td>3b</td></tr>
<tr><td>USA (Yucca Mountain TSPA)</td><td>TRW (1995)</td><td>Not present</td><td>1</td><td>3b</td><td>3b</td></tr>
<tr><td colspan="6">CLAY HOST ROCK</td></tr>
<tr><td>Belgium (EVEREST)</td><td>Marivoet et al. (1997)</td><td>Not present</td><td>1</td><td>2</td><td>Not present; assume fractures in clay will reseal</td></tr>
<tr><td>Switzerland (Project Gewahr)</td><td>Nagra (1985)</td><td>1</td><td>2</td><td>3b</td><td>Not present; assume fractures in clay will reseal</td></tr>
<tr><td colspan="6">SALT HOST ROCK</td></tr>
<tr><td>Germany (EVEREST)</td><td>Becker et al. (1997)</td><td>Not present</td><td>1</td><td>1</td><td>Not present; assume fractures in salt will reseal</td></tr>
<tr><td>Netherlands (PROSA)</td><td>Prij et al. (1993)</td><td>Not present</td><td>1</td><td>1</td><td>Not present; assume fractures in salt will reseal</td></tr>
<tr><td>USA (WIPP CCA)</td><td>US DOE (1996)</td><td>Not present</td><td>1</td><td>1</td><td>Present in non-salt units but not modelled in PA (3b)</td></tr>
</table>

Key:	1	Component parameterized and modelled as a distinct geometric element in reference scenario.
	2	Component parameterized and modelled as a distinct geometric element in additional scenarios.
	3a	Component present in repository but not modelled as a distinct geometric element in the PA, based on the results of supporting calculations.
	3b	Component present in repository but not modelled as a distinct geometric element in the PA, and no formal supporting calculations have been reported with the PA.

Table 2. Expected groundwater and backfill pH values for a range of sites and disposal concepts.

Country and Site or Assessment	Reference	Host Rock Groundwater pH	Assumed Near-Field pH	Disequilibrium Measure ΔpH
CRYSTALLINE HOST ROCK				
Canada (EIS)	AECL 1994a	near neutral	7 - 9 for clay, ≈ 10 - 11** for low pH cement	< 2 for clay, ≈ 3 - 4** for low pH cement
Spain (Deep disposal in granite)	ENRESA 1997	7.3*	9.0*	1.7
Sweden (SITE-94)	SKI 1996	6.5 - 8.1	7.7 - 9.3	<2.8
UK (Nirex 95)	Nirex 1995b	6 - 8.5	>12	3.5 - 6
USA (Yucca Mountain)	SNL 1993	6.5 - 9.4	6.5 - 9.4	0
CLAY HOST ROCK				
Belgium (Mol)	Marivoet *et al.* 1997	8.5	8.5 for clay, 12.0 for cement	0 for clay, 3.5 for cement
SALT HOST ROCK				
USA (WIPP CCA)	US DOE 1996	7 - 7.6	9 - 10	1.4 - 3

*These central values were actually considered as functions of time and temperature and were subject to ranges of uncertainty.

**Authors' estimates, not taken directly from AECL 1994.

Table 3. Backfill materials considered in various disposal programmes, and hydraulic conductivities, permeabilities and diffusivities used in PA calculations.

Country and Site or Assessment	Reference	Backfill Materials	Emplacement geometry	Hydraulic conductivity (ms^{-1})	Effective diffusivity, $m^2 y^{-1}$		
					D_I	D_{Sr}	D_U
CRYSTALLINE HOST ROCK							
Canada (EIS)	AECL (1994a)	Upper layer: 50:50 Na-bentonite/sand. Lower layer: 25:75 clay/crushed granite	Upper low-density and lower high-density layers	10^{-10}	2.3×10^{-3}	4×10^{-3}	2.3×10^{-3}
Finland (TILA-96)	Vieno and Nordman (1996)	Upper layer: 80:20 crushed rock/ bentonite. Lower layer: 90:10 crushed rock / bentonite	Upper layer fills last 2 metres of head space	Not specified	3.2×10^{-2}	6.3×10^{-3}	6.3×10^{-3}
Japan (H-3)	PNC (1992)	Bentonite containing ~40% quartz	Mechanically emplaced lower layer; pneumatically emplaced upper layer	Not specified			
Spain (Deep disposal in granite)	ENRESA (1997)	Bentonite	Horizontal tunnels	10^{-11} - 10^{-13}	Distribution function varying between 3×10^{-2} and 3×10^{-3}		
Sweden (SR-95)	SKB (1995)	10-15% bentonite, 80-85% quartz sand, or 30-40% bentonite, 60-70% crushed rock	Deposited in horizontal layers, compacted with vibratory roller	10^{-9} - 10^{-11}	7.9×10^{-5}	7.9×10^{-1}	3.2×10^{-3}
Switzerland (Kristallin-I)	Nagra (1994)	Bentonite (Volclay MX-80) / sand mix	Tunnel and disposal areas	Not specified			
UK (Nirex 95)	Nirex (1995b)	Nirex Reference Vault Backfill (NRVB): OPC, lime and crushed limestone	Around waste	~10^{-8} (includes waste)			
USA (Yucca Mountain TSPA)	TRW (1995)	Crushed rock (tuff)	Not finalised	Permeability 3.9×10^{-14} m^2	Function of the degree of saturation. Single conservative value used: 1.1×10^{-1} at 30%		

Table 3. Backfill materials considered in various disposal programmes, and hydraulic conductivities, permeabilities and diffusivities used in PA calculations.

Country or Project	**Reference**	**Backfill Materials**	**Emplacement geometry**	**Hydraulic conductivity (ms^{-1})**	**Effective diffusivity, $m^2\ y^{-1}$**		
					D_I	D_{Sr}	D_U
CLAY HOST ROCK							
Belgium (EVEREST)	Marivoet *et al.* (1997)	ILW: injected concrete or Boom Clay. HLW: stainless steel shroud, pre-compacted Boom Clay. Tunnels and lower parts of shafts: pre-compacted Boom Clay. Upper parts of shafts backfilled with local sand	ILW: around waste within disposal galleries. HLW: 0.03 m-thick stainless steel shroud around waste, 0.75 m-thick clay around shroud	3.2×10^{-12}	6×10^{-3}	3×10^{-4}	3×10^{-6}
Switzerland (Project Gewahr)	Nagra (1985)	Bentonite (Volclay MX-80)	Disposal areas	Not specified			
SALT HOST ROCK							
Germany (EVEREST)	Becker *et al.* (1997)	Crushed salt	Disposal area, but not deposition boreholes	Permeability ~10^{-10} m^2	Not specified		
Netherlands (PROSA)	Prij *et al.* (1993)	Crushed salt	Disposal area, but not deposition boreholes	Permeability ~10^{-10} m^2	Not specified		
USA (WIPP CCA)	US DOE (1996)	MgO	In sacks, around the waste canisters in the disposal rooms	Permeability of waste region: 1.7×10^{-13} m^2	Not specified		

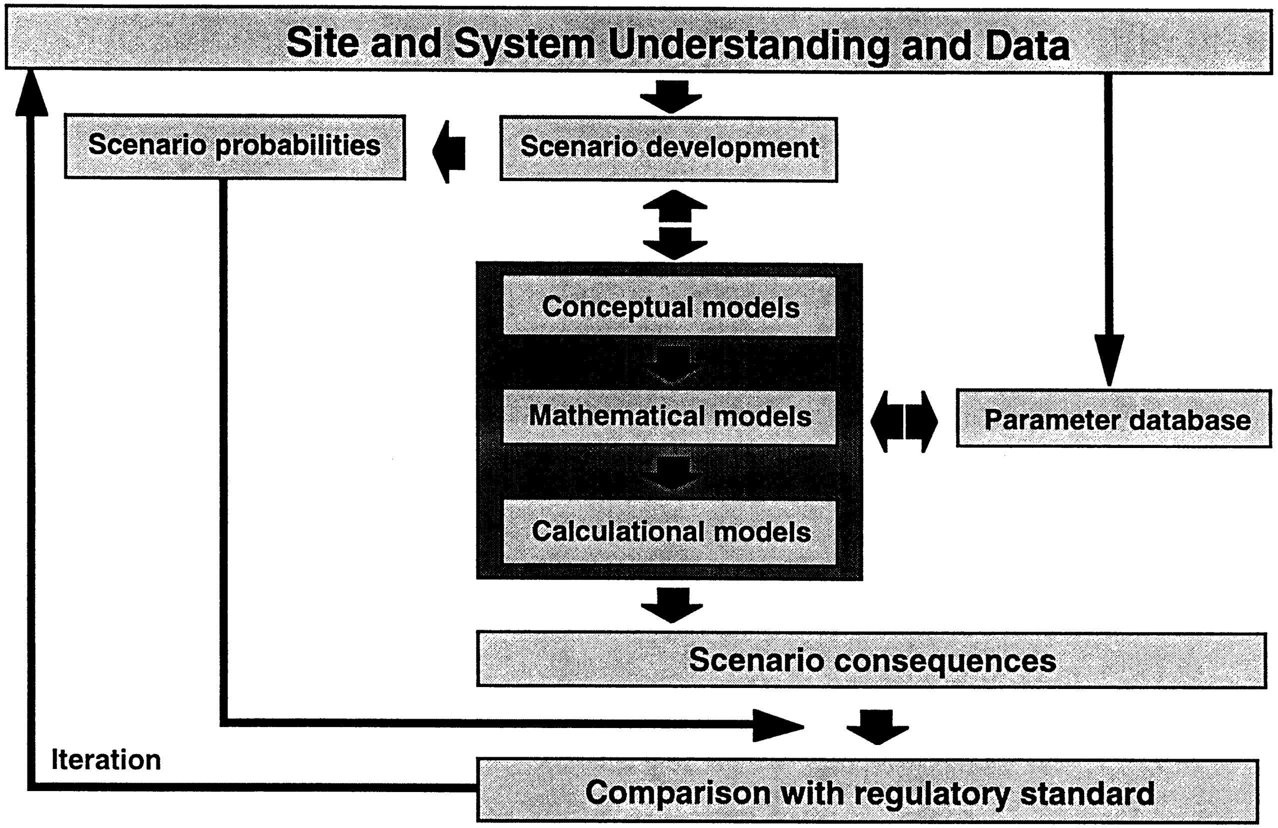

Figure 1. Typical structure of performance assessments of radioactive waste disposal sites.

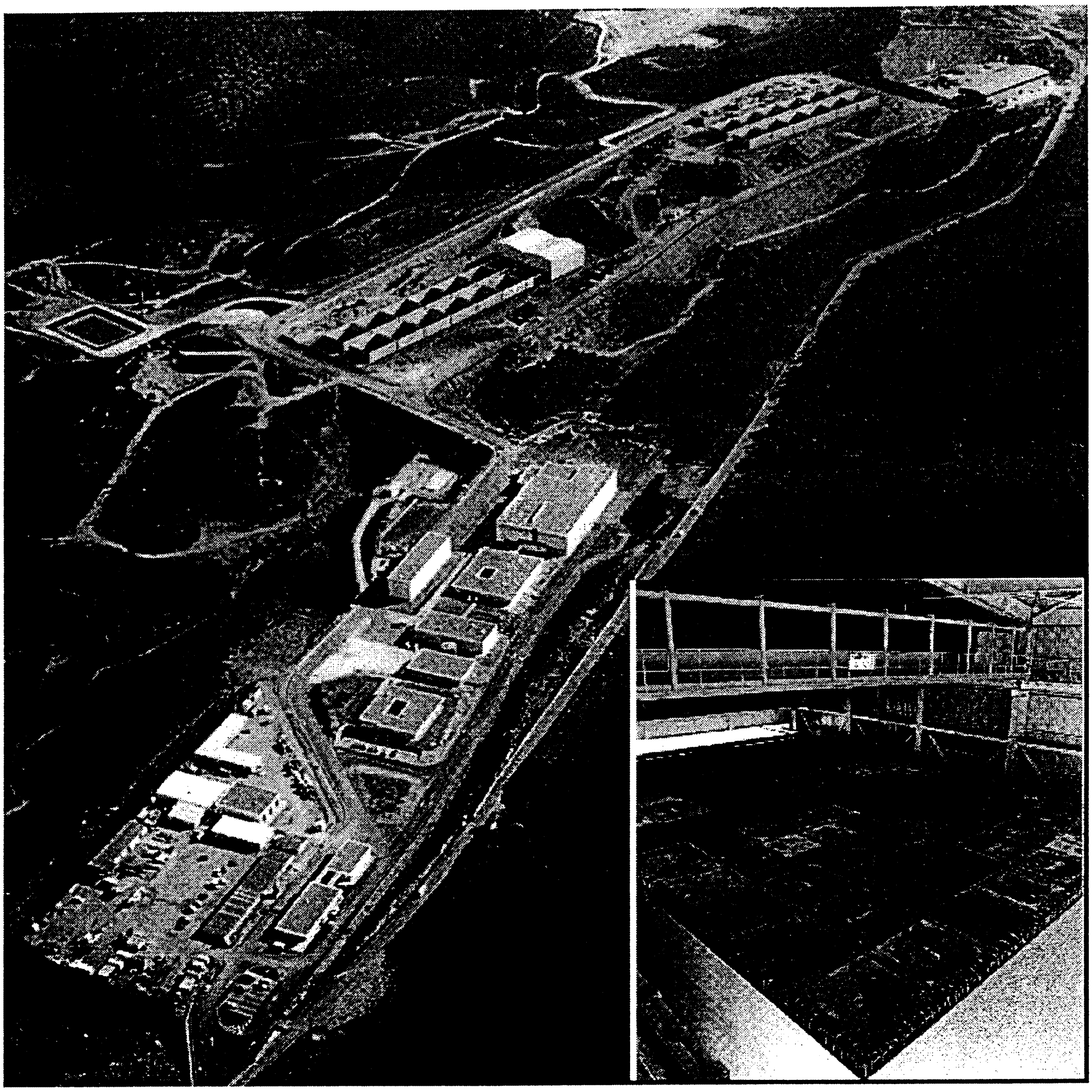

Figure 2. An aerial view of ENRESA's low-level radioactive waste disposal facility at El Cabril in Cordoba, Spain (ENRESA 1994). Two arrays of concrete disposal cells are visible in the top part of the main picture. The disposal cells are covered by a temporary roof (white) to limit the entry of rainwater while they are filled with waste. The inset shows waste in concrete boxes within a concrete disposal cell.

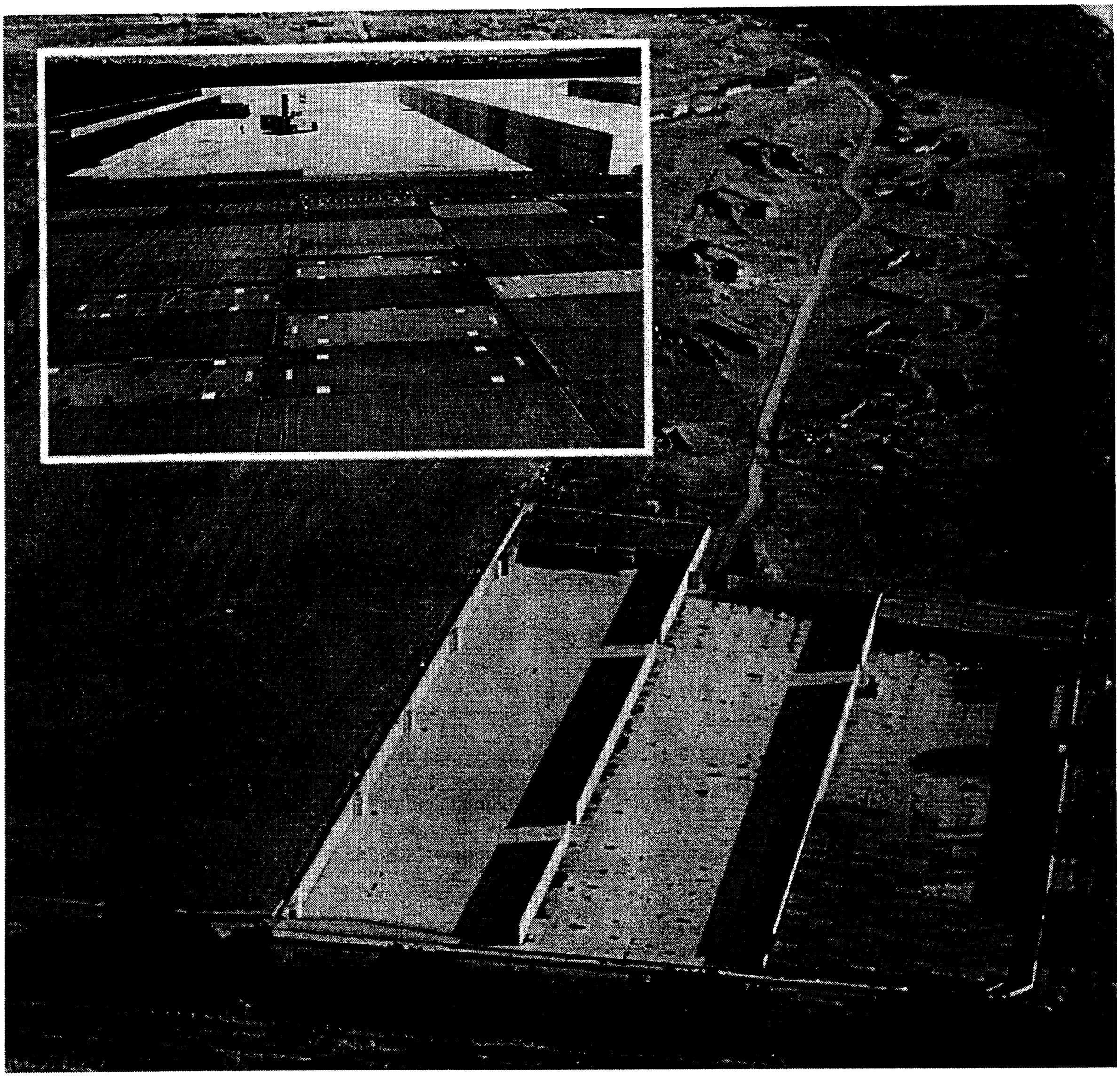

Figure 3. **An aerial view of BNFL's low-level radioactive waste disposal facility at Drigg in north west England (CEC 1994). The bottom right-hand part of the main picture shows the concrete vault (known as Vault 8) which is divided into three sections by concrete walls. Super-compacted waste is loaded into steel ISO containers which are then filled with a fluid cement grout. Waste containers can be seen partially filling each of the vault sections. The inset gives a more detailed view of the tops of emplaced waste containers within the vault, and the emplacement method using a conventional fork-lift.**

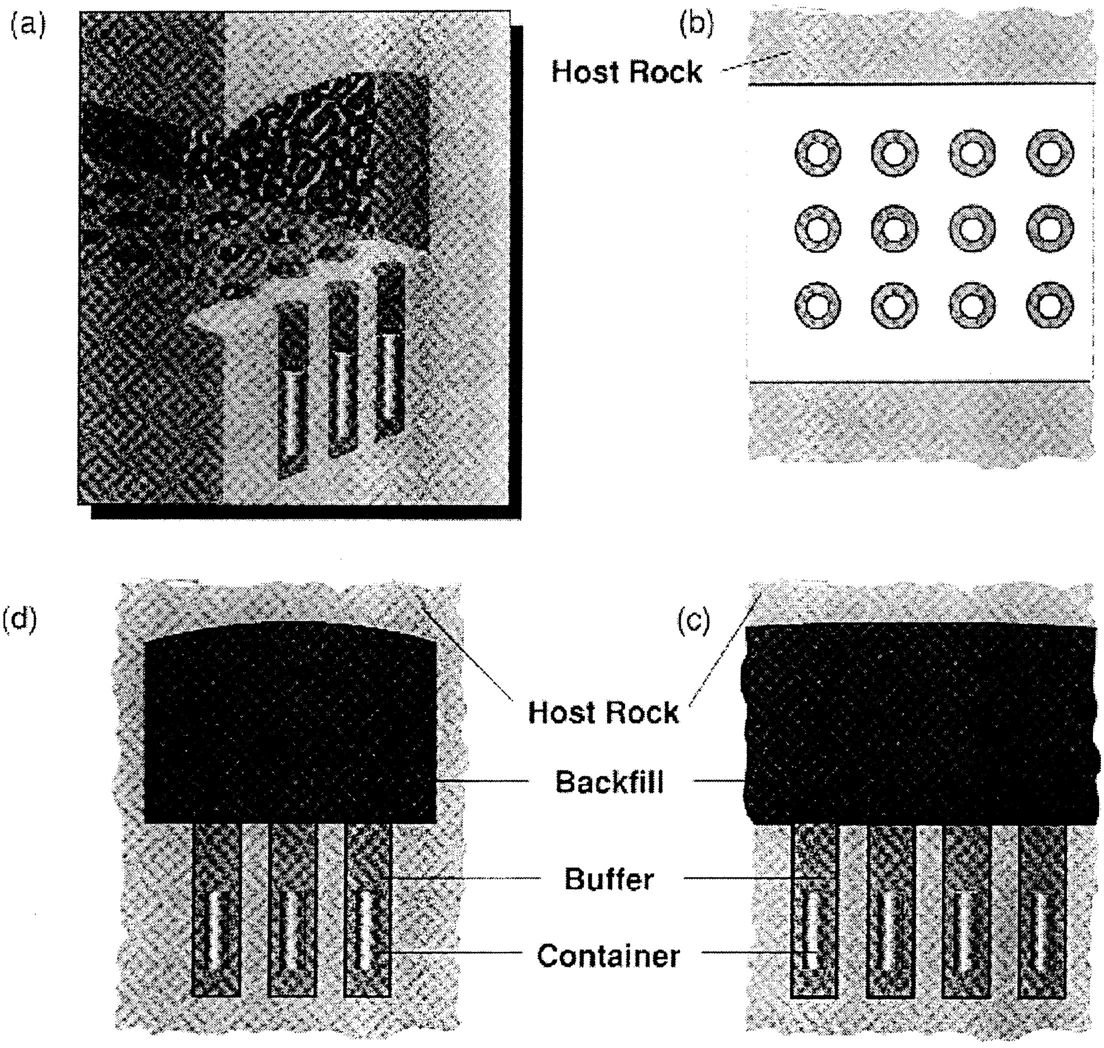

Figure 4. Four views of AECL's disposal room concept from the Canadian reference disposal system (AECL 1994b). View (a) is a three dimensional view of part of a room. View (b) is an overhead view showing the pattern of boreholes drilled in the floor of the room. Views (c) and (d) are cross sections taken down the length and across the width of the room respectively. The waste containers are placed into the boreholes, surrounded by a thin layer of sand (not shown in the figure), which in turn is surrounded by a thicker layer of a low-permeability bentonite clay called the buffer. After closure, the remainder of each room is filled with a mixture of glacial lake clay and crushed rock called the backfill.

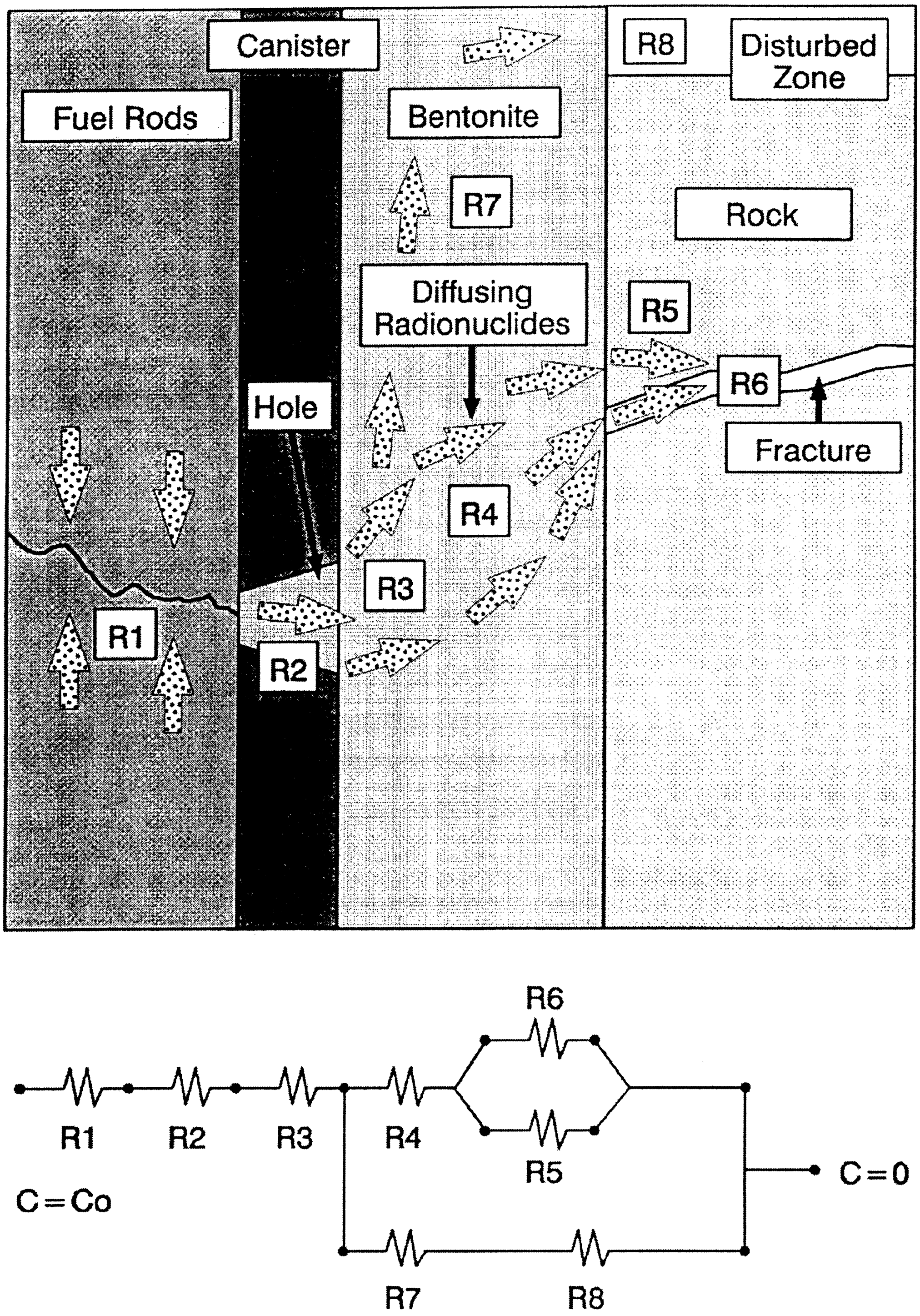

Figure 5. SKB's SR95 performance assessment resistance network model of the transport of radionuclides from spent fuel via a hole in a waste container, through a bentonite backfill, and into the disturbed rock zone surrounding the waste repository (SKB 1995).

THE USE OF DATA FROM NATURAL ANALOGUES OF BACKFILL MATERIALS IN PA

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ABSTRACT

Natural system evidence for the behaviour of backfills in repositories for radioactive wastes has been reviewed. Studies of natural system behaviour generally produce qualitative data for safety assessment studies but can be extremely useful to demonstrate the long-term applicability of concepts and processes. They may be particularly useful in demonstrating concepts employed in numerically-based safety assessments. It may be difficult to achieve regulatory or public acceptance for the long-term performance of a backfill material without supporting natural system evidence. It is concluded that research should be pursued in the following areas to provide natural system information for safety assessment studies: the behaviour of bentonite in hypersaline, hyperalkaline and iron-rich environments; gas migration mechanisms in bentonite; the physical scale of the alkaline disturbed zone surrounding cementitious repositories; and the effects of alkaline alteration on rock matrix diffusion.

1. INTRODUCTION

Most data used in performance assessment (PA) studies are quantitative or 'hard' data derived from laboratory experimental, site characterization, underground research laboratory, or data elicitation studies (e.g., Chapman and Grindrod 1994, Savage 1995). In contrast, data from natural systems are often qualitative or 'soft', due to uncertainties concerning physical and chemical conditions, or time scales (Chapman and Grindrod 1994). Unsurprisingly, there is a reluctance to use such data in safety assessments. However, natural system data or "natural analogues" may provide a perspective which is lacking from more quantitative sources of data, namely the long-term behaviour of repository materials and processes. Data derived from these studies may thus provide confirmatory evidence (or not) for relatively short-term experiments regarding mechanisms or broad time scales of repository-relevant processes. Consequently, natural system data may not be fully quantitative, but may provide assessors with confidence in their choice of models or data. The exclusion of this type of information from repository safety assessments may be due to an over-reliance upon scenario-driven assessments, rather than simulation-based equivalents (Chapman and Grindrod 1994).

Regarding the selection and design of backfills in repository configurations, it is almost inevitable that choices are made by engineers rather than earth scientists. In a parallel situation, earth scientists may have the dominant rôle in the choice of geological site for a radioactive waste repository. These different interests and perspectives may not only produce a compatibility problem regarding the repository backfill and the surrounding geosphere, but also a potential lack of adequate natural system evidence to guarantee long-term performance of certain backfill compositions. Purely engineering solutions to backfilling problems are unlikely to produce systems which have naturally-occurring equivalents. Alternative solutions using naturally-occurring materials may lead to impracticalities of emplacement. For example, the use of compacted bentonite blocks in many HLW repository designs is viewed in some cases as not "robust" enough from an engineering and economic perspective (McKinley 1997). In some instances, backfills have been tailored with specific host rocks in mind (e.g., the use of MgO backfill at the WIPP site - Papenguth *et al.* 1998), whereas others are viewed as 'generic' and suitable for any geological site (e.g., Nirex 1995). Clearly, some compromise between engineering function and evidence for longevity is necessary to achieve a satisfactory solution, both from the perspective of the disposer and regulator, as well as those of the earth science community and general public.

Many natural analogue studies of potential backfill materials have been carried out over the last 20 years (as summarized in Miller *et al.* 1994). It is not intended to reproduce this information here, but attention instead will focus on what PA-relevant information has been provided by natural system studies of backfills, and where uncertainties still remain. This review has concentrated on backfills where appreciable natural system data have been accumulated (bentonite and cement/concrete).

2. ANALOGUE STUDIES OF BACKFILL MATERIALS

2.1 Bentonite

Bentonite is present as a backfill constituent in a number of concepts for the disposal of radioactive wastes, e.g., Finland (NEA 1992), Korea (Cho *et al.* 1995), Sweden (Wiborgh 1995), United States (Butcher 1994) and its primary function is to act as a low permeability barrier. Most research on natural analogues of bentonite behaviour has been aimed at HLW concepts, i.e. with regard to thermal stability (Pusch and Karnland 1988), illitisation (Pusch and Karnland 1988), or interaction with HLW canister metals (Neretnieks 1986). From a perspective of safety assessment, the following issues are apposite:

- hydraulic behaviour;
- chemical buffering properties;
- colloid filtration properties;
- diffusion properties;
- compatibility with other engineered barrier system (EBS) components (canister metals, cement and concrete);
- behaviour in hypersaline systems; and

- mechanisms of gas migration.

The capability for clay to act as a low-permeability medium is documented by studies of the preservation of organic materials in clay, such as the 1.5 million-year-old fossil forest at Dunarobba, Italy (Valentini *et al.* 1997, Miller *et al.* 1994) and a 2100 year-old cadaver in China (Lee 1986, Miller *et al.* 1994). The geological sequence at Dunarobba consists of lenses of montmorillonite-rich clays and silty clays which have acted as closed, chemically reducing systems, helping to preserve the tree wood.

There is good natural systems evidence for the preservation of chemical buffering properties of bentonite/clay for very long time periods. However, natural systems show the dominance of dissolution-precipitation processses in the buffering of pore fluid compositions (Arthur 1996), questioning the use of ion exchange models widely employed in safety assessments (e.g., Wanner *et al.* 1992).

The Cigar Lake natural analogue study indicates that clay acts as an efficient colloid filter (Vilks *et al.* 1991, Smellie and Karlsson 1996, Miller *et al.* 1994), despite the clay consisting predominantly of illite, rather than smectite. Studies of uranium and thorium colloid abundances from the ore zone, sandstone and clay show higher abundances in the ore and the clay, indicating that the latter had filtered them from passing into the surrounding sandstones.

Studies of the mobility of halides around a marine band in a lacustrine clay at Loch Lomond, Scotland indicate a profile consistent with diffusion in the clay without appreciable fluid advection (Falck and Hooker 1990, Miller *et al.* 1994).

There is natural system evidence that clays are chemically compatible with copper canister materials (e.g., Neretnieks 1986), but evidence for compatibility with iron or steel is lacking. There is currently no relevant analogue information available for the reaction of bentonite with hyperalkaline fluids. A lack of identifiable smectite clays at the Maqarin site in Jordan precluded the evaluation of clay stability under hyperalkaline conditions (Smellie 1998). The mechanisms of interaction, products and effects are thus uncertain from a natural system perspective.

There have been no radioactive waste-specific studies conducted to evaluate the stability of bentonite in hypersaline environments.

Stenhouse and White (1997) have reviewed natural system evidence for gas migration through a variety of rock types (including clays) and concluded that considerable controversy exists concerning gas migration mechanisms. Migration via diffusion, water transport, and as microbubbles are all plausible explanations of gas seepage phenomena. Studies focussed on relevant clays with radioactive waste objectives paramount are warranted.

2.2 Cement and concrete

Cement and concrete will be present in most repositories for the disposal of radioactive wastes, either as structural supports/plugs or as a backfill to condition chemically the pore fluids in the waste vault or silo. From a PA perspective, the following issues are relevant to assess the behaviour of the repository near-field environment:

- the longevity of pH-conditioning solids;
- element solubility and sorption, thermodynamic database testing;
- the behaviour of organics in a hyperalkaline environment;
- microbial activity in a hyperalkaline environment;
- metal corrosion in a hyperalkaline environment;
- colloid generation and stability; and
- clay stability in a hyperalkaline environment.

A number of natural systems, such as those at Scawt Hill, Northern Ireland (Milodowski *et al.* 1991), the Semail Ophiolite in Oman (McKinley *et al.* 1988), and the Maqarin site, Northern Jordan (Khoury *et al.* 1992), together with studies of old concretes (Lagerblad and Trägård 1994, Miller and Chapman 1995), have been used to provide evidence of the above processes.

Hyperalkaline groundwaters at Maqarin, Jordan result from the dissolution of portlandite and ettringite-thaumasite minerals generated by the hydration of naturally-produced cement clinker mineralogy in bituminous limestones (Khoury *et al.* 1992). Groundwaters have a pH of 12.5, are Ca-K-Na-OH in type, and are analogous to cement pore fluids dominated by portlandite and CSH solid phases. There are no groundwaters at Maqarin which are analogous to so-called "early" Na, K-type cement pore fluids with pH in the range 13-13.5. Seepages in railway and adit excavations have enabled sampling of groundwaters and examination of reactions between hyperalkaline fluids and a variety of rocks (limestone, marl, chert and basalt). Age dating studies at the Maqarin site suggest that dissolution of naturally-occurring cement minerals has been taking place for at least 10,000 years (Smellie 1998). Calcium (aluminium) silicate hydrate gels typical of cements have been preserved over this time period at Maqarin.

So-called "blind" modelling exercises to predict the concentrations of naturally-occurring elements of interest to repository safety assessment in cement-like pore waters were carried out at the Oman (McKinley *et al.* 1988) and Maqarin natural analogue sites (Alexander *et al.* 1992, Linklater *et al.* 1996). These studies have shown that data for simple oxide and hydroxide phases incorporated in thermodynamic databases used in PA overestimate some trace element concentrations by one or more orders of magnitude, and thus provide conservative (pessimistic) estimates. More realistic modelling of trace element concentrations requires the development of solid-solution models.

Semi-quantitative evidence exists for the mobility of kerogenous organic matter and the stability of a variety of carboxylic acids in hyperalkaline groundwaters at Maqarin (Smellie 1998).

However, organic matter does not appear to play a major rôle in the chemical behaviour of the trace elements studied. No data were identified which suggested the breakdown products of cellulose (e.g., isosaccharinic acid).

Microbial abundances in groundwaters at Maqarin have demonstrated that populations are capable of withstanding hyperalkaline conditions (West *et al.* 1995), but their activity levels and the lack of biofilms suggest that these populations are not especially active at high pH (Smellie 1998).

To the author's knowledge, there has been no natural system or archaeological study of metal corrosion in a hyperalkaline environment to provide long-term data concerning metal corrosion rates. Studies of reinforcement rods in concrete in the foundations of historic buildings could merit study to provide such data.

Colloid abundances in groundwaters at Maqarin are similar to those in near neutral pH groundwaters (Smellie 1998). The colloids are cementitious with no evidence for association with uranium or other trace elements.

Some disposal concepts envisage the use of large amounts of cement and concrete, perhaps upwards of 10^5 tonnes (e.g., the Swedish SFL 3 and SFL 5 repositories for I/LLW, Wiborgh 1995). The use of such large amounts of cementitious material raises the possibility of considerable potential for chemical reaction not only between cement and groundwater saturating the repository, but also between migrating hyperalkaline pore fluids and the host rock, driven into the geosphere by regional hydraulic gradients. The type and magnitude of these interactions are of considerable debate (Savage 1997). Conceivably, a large part of the far field could be perturbed by alkali-rock reaction prior to release of radionuclides from the engineered barrier system (EBS). However, since both deleterious and beneficial effects may be gained from such interactions, their overall effects must be considered on a repository- and site-specific basis. Although disposal agencies have been aware of such issues for 10 years or more (e.g., Jefferies *et al.* 1988), no formal safety assessment study has yet incorporated these effects.

Natural systems could, in theory, provide information concerning the following:

- processes at pH fronts, such as element solubility and colloid generation; and
- behaviour of the alkaline plume with regard to spatial extent, and impact upon sorption, permeability, and matrix diffusion properties.

Analogue studies to address these issues have been principally directed at the Maqarin natural analogue site in Jordan.

pH fronts have not been observed directly at Maqarin, so there is no relevant information concerning element solubility or colloid formation (Smellie 1998). However, the occurrence of mineral reaction sequences in rocks containing fractures which acted as conduits for hyperalkaline water document "fossil" reaction between hyperalkaline fluids and rock. Here, qualitative evidence exists for the coprecipitation of elements such as uranium, selenium and nickel with a variety of hydroxide, sulphate and aluminosilicate minerals.

The extent of the altered zone at Maqarin is not directly transferrable to estimating the likely extent of an alkaline disturbed zone around a radioactive waste repository due to differences in rock physical and chemical properties (mineralogy, porosity, permeability) and associated boundary conditions (hydraulic gradients, tectonic environment). However, the Maqarin system does provide confirmatory evidence for migration mechanisms of an alkaline plume in terms of observed mineral paragenetic sequences and those produced by computer simulation of water-rock reaction (Smellie 1998).

Fractures at Maqarin are self-sealing due to the relative volumes of products and reactants of water-rock reaction. The precipitation of portlandite, ettringite-thaumasite, calcium silicate hydrate gels, calcite and zeolites all serve to reduce porosity in rock matrices and fracture networks. Evidence concerning the availability of rock matrices to diffusion is ambiguous, but some natural series radiolement data (^{226}Ra) suggest that rock matrices remained accessible to fluids contained in fractures (Smellie 1998).

2.3 Magnesium oxide

Magnesium oxide is planned as a backfill material at the Waste Isolation Pilot Plant (WIPP) in New Mexico, USA. Magnesium oxide occurs naturally as the mineral periclase which is found in high temperature, low pressure metamorphosed dolomitic limestones (Deer *et al.* 1992). Typically, grains of periclase are surrounded by hydrated rims of brucite, $Mg(OH)_2$ in these rocks. Analogue studies of MgO are reported elsewhere in this volume (Papenguth *et al.* 1998).

2.4 Salt

Salt is planned as a backfill in repositories in bedded salt formations. Salt may be used alone or in conjunction with other materials such as MgO or bentonite. As far as the author is aware, no natural system studies have been specifically carried out to investigate its use as a backfill.

3. REMAINING UNCERTAINTIES

It is relevant to summarise where analogue information has been useful to PA and where uncertainties still exist. Table 1 summarizes accepted and uncertain information concerning the behaviour of natural analogues of bentonite and cement as backfill materials. It may be seen from Table 1 that data are either lacking or inconclusive for:

- the behaviour of bentonite in hypersaline, hyperalkaline, and iron-rich environments;
- confirmation of gas migration mechanisms in bentonite;
- the physical scale of the alkaline disturbed zone; and
- the effects of alkaline alteration on rock matrix diffusion.

4. CONCLUSIONS

Studies of natural system behaviour generally produce qualitative data for safety assessment studies and can be extremely useful to demonstrate the long-term applicability of concepts and processes. They may be particularly useful in demonstrating the applicability of concepts employed in numerically-based safety assessments. It may be difficult to achieve regulatory or public acceptance for the long-term performance of a backfill material without supporting natural system evidence. It is recommended that research is pursued in the following areas to provide natural system information for safety assessment studies:

- the behaviour of bentonite in hypersaline, hyperalkaline and iron-rich environments;
- gas migration mechanisms in bentonite;
- the physical scale of the alkaline disturbed zone surrounding cementitious repositories; and
- the effects of alkaline alteration on matrix diffusion in, and the physical structure of, the repository host rock.

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Table 1. Natural system evidence for key processes and phenomena for bentonite and cement.

Process or Phenomenon	**Natural System Evidence**
Bentonite	
Hydraulic behaviour	low hydraulic conductivity maintained for periods > 1 million years
Colloid filtration	clay acts as a colloid filter
Diffusion properties	diffusion is dominant mass transport mechanism
Behaviour in hyperalkaline environment	no published evidence
Behaviour in hypersaline environment	no published evidence
Behaviour in iron-rich environment	no published evidence
Cement	
Longevity of pH conditioning	portlandite, C(A)SH gel and ettringite-thaumasite may preserve pH at 12.5 for > 10,000 years
Element solubility and sorption	databases for PA are conservative
Microbial activity in hyperalkaline environment	microbes stable, but have low activity
Colloid generation and stability	similar to neutral pH groundwaters
Processes at pH fronts	no published evidence
Alkaline disturbed zone	confirmation of alkali-rock reaction mechanisms and decreased porosity accompanying $Ca(OH)_2$-type fluids; no direct evidence for Na, K-type fluids

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