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Extrapolation of short term observations to time periods relevant to the isolation of long lived radioactive waste

Results of a co-ordinated research project
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EXTRAPOLATION OF SHORT TERM OBSERVATIONS TO TIME PERIODS RELEVANT TO THE ISOLATION OF LONG LIVED RADIOACTIVE WASTE
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FOREWORD

Safe disposal of radioactive wastes relies on several independent barriers (multi-barrier system) in order to prevent potential harm to humans by radionuclide release. The barriers include the waste form and the packaging of the wastes as engineered barriers, the buffer and backfill materials or sealing systems as geo-engineered barriers, and the host formation itself and the overlaying strata as the geological or natural barrier. The adaptation of such a multi-barrier system to the requirements defined by the type of wastes and the geological conditions is a typical multidisciplinary scientific and technical issue. Development, operation and closure of repositories, the characteristics of the waste forms and the corresponding safety analyses have been described in many publications of the IAEA. One of the key tasks is the safety assessment of a disposal facility for very long periods of time, which may reach orders of tens to hundreds of thousands years. Many safety problems have been identified and technical solutions have been proposed. However, the periods of extrapolation exceed the human experience, and both the natural environment and the engineered barriers will undergo significant changes. For this reason a strong need was identified to pay special attention to methods which can be used for the long term extrapolation of features, processes and data which result from short term observations in the laboratory and field.

As a consequence, the IAEA initiated in 1995 a Co-ordinated Research Project on Extrapolation of Short Term Observations to Time Periods Relevant to the Isolation of Long Lived Radioactive Waste that would demonstrate the approaches of some laboratories to the extrapolation problem. Using practical examples, some principles are shown that may be involved in repository planning, construction and closure stages, in particular for performance assessment of individual disposal systems.

The present publication is based on results obtained at ten different laboratories worldwide. The draft document was prepared and discussed during the last research co-ordination meeting held in South Africa, 13–17 September 1999.

The IAEA gratefully acknowledges the contributions of the participants from various Member States, the consultants and all other persons who participated in the drafting, reviewing and approval processes. It is trusted that this report will be of value to authorities and specialists who are responsible for or involved in the safety assessment of deep geological disposal facilities. The IAEA staff members responsible for this publication were J. Heinonen and M. Raynal of the Division of Fuel Cycle and Waste Technology.

CONTENTS

ANNEX: CONTRIBUTIONS BY PARTICIPANTS IN THE CO-ORDINATED RESEARCH PROJECT ON EXTRAPOLATION OF SHORT TERM OBSERVATIONS TO TIME PERIODS RELEVANT TO THE ISOLATION OF LONG LIVED RADIOACTIVE WASTE

Studies on near field barriers

Studies on far field barriers

Studies on complete whole disposal systems

1. INTRODUCTION

1.1. BACKGROUND

The development, operation and closure of repositories [1–5], the characteristics of the waste forms [6] and the corresponding safety analyses [7] have been described in many publications of the IAEA. Recent scientific and technical developments have demonstrated the feasibility of disposal of radioactive wastes in deep geological formations [8]. For regulatory purposes and also for convincing the general public that the disposal system will behave as expected, it is required to prove that long term predictions are based on validated and verified experimental and mathematical procedures. Reliability and acceptability of this evidence is considered as one of the key issues of a repository development. Furthermore, long term predictions are important for the whole life-cycle of a repository, including its planning, research and development, construction, commissioning, operation, closure and post-closure periods.

The studies of extrapolation of present observations to the far future are based on different approaches, e.g., natural and anthropogenic analogues, studies of natural features, laboratory and field experiments, investigations carried out in underground laboratories, etc. All of these studies consist of two phases: (a) collection of data, and (b) subsequent interpretation of results for the periods where the waste remains hazardous (hence referred to as 'repository lifetime'). The first step is well elaborated. However, questions may be raised with respect to measured parameters, experimental approaches and their links to the overall problem and uncertainties which may considerably affect the final results.

1.2. OBJECTIVE

The present report aims at advising Member States on methods and approaches that may be applied for long term predictions in the development of a disposal system. General factors which may affect the extrapolation of short term observations to long term periods of the repository lifetime are discussed. References are provided by investigations performed and examples obtained in some laboratories.

1.3. SCOPE

The report addresses safety analyses of the whole repository life-cycle that may require long term performance assessment of its components and evaluation of potential impacts of the facility on the environment. Generic consideration of procedures for the development of predictive tools are completed by detailed characterization of selected principles and methods that were applied and presented within the co-ordinated research project (CRP). The project focused on different approaches to extrapolation, considering radionuclide migration/sorption, physical, geochemical and geotechnical characteristics of engineered barriers, irradiated rock and backfill performance, and on corrosion of metallic and vitreous materials.

The topics dealt within the frame of this CRP do not exhaustively cover all problems that may appear in the extrapolation of short term observation to the long term performance of a disposal system; rather, they represent several typical experiments of chemical, geotechnical and contaminant transport nature. Topics related to the biosphere were not considered within this project.

1.4. STRUCTURE OF THE PUBLICATION

The TECDOC is divided into two main parts: a comprehensive discussion of the overall problem, including a general description of potential extrapolation methods, and an annex summarizing the practical results of the individual projects performed within the CRP.

The main report first provides an overview of the principles of long term extrapolation, enumerates applied methodologies and discusses reliability of extrapolation and uncertainties involved. It then reviews predictive methods to assess long term performance of engineered barriers and the surrounding host rock. Finally, migration and sorption processes are considered, and various modelling issues described. Synthesized results obtained from laboratory experiments and field observations illustrate how a long term extrapolation approach can be applied to different components of a geological disposal system as they were studied within the CRP.

The individual contributions by the participants in the CRP presented in the Annex all follow the same structure: theoretical basis of the method used, description of the technical background for its application, explanation of the extrapolation principle, discussion of the results obtained, conclusions, as well as proposals for future work. The papers are presented thematically following the structure of the main report. The contributions from the Republic of Korea, Argentina, Ukraine, the Czech Republic and South Africa are near field related, the contributions from Hungary and Malaysia cover far field aspects, whereas the Belgian, German and Indian papers discuss the whole disposal systems and cover more or less the complete field of extrapolations needed for performance assessment.

2. PRINCIPLES OF LONG TERM EXTRAPOLATION

2.1. GENERAL PRINCIPLES OF EXTRAPOLATION

The development and design of a repository system faces several problems, of which the selection of solutions providing long term performance is of utmost importance. As required among others including the licensing bodies, performance assessment shows how the characteristics of the system as a whole and its particular components will change during the lifetime of the repository. The following aspects of the long term extrapolation have to be considered: (a) identification of key parameters with the highest significance to the characterization of the studied system; (b) investigation of the evolution of the system; (c) development of modelling and mathematical tools to be applied in predictive studies; and (d) provision of evidence that these tools will reliably describe the long term performance of the considered system.

The basic principle of an extrapolation procedure is the transfer of investigations carried out within a short time frame to periods that are well beyond the horizon of the existence of the investigator. Typically, laboratory and field experiments may last up to several years; but the results are applied to assess the status of the system after hundreds to millions of years.

For long term extrapolations the approaches have to cover predictive and retrospective aspects. In order to create confidence in an extrapolation, the approach have to be tested by its capability to describe observed behaviour of a system based on its evolution in the past.

In the development of an extrapolation method, several steps have to be followed:

- Definition of a system with respect to the extrapolation task,
- Understanding of processes and boundary conditions characterising the system,
- Experimental investigations,
- Model development,
- Interpretation of the observation and modelling results to long term performance of the studied system.

This is not a straightforward process, but iterations of some of the steps may be required.

The Belgian contribution on Boom clay studies demonstrates the practical implementation of these steps.

Modelling, in principle, is based on simplifications of processes and related mathematical expressions. An agreement of computed and observed behaviour depends directly on the level of simplification. Nevertheless, even sophisticated mathematical tools may be inadequate to describe complex processes. Such processes control the behaviour of the system in the nature. Therefore, building confidence in models is the most essential part of the extrapolation approach [9, 10].

As ab initio models are not available, model results used in the extrapolation studies depend on parameters as well as on initial and boundary conditions for the calculations. The parameters are normally derived from laboratory experiments, the initial and boundary conditions are site specific and have also to be determined experimentally.

2.2. EXTRAPOLATION METHODOLOGIES

Many approaches are used for generating inputs to extrapolation procedures. These include experimental investigations, modelling and studies of natural analogues. Methodology depends on the availability of credible procedures, level of knowledge of a studied system, know-how and experience of the laboratory staff, and the technical and financial backgrounds of the project.

2.2.1. Generation of data

Some data can be obtained either from existing databases and literature, other important data through experiments. Relevance of data may play an important role as many data in published data bases could have been generated for different purposes. For this reason, experimental data has to be given priority in most cases.

The scale of an experiment may also influence data reliability. Some tests may be performed concurrently under different conditions; nevertheless, most projects involve a combination of studies. They may typically include:

- Laboratory experiments:
  - accelerated tests (high velocity or frequency of a process),
  - testing under cumulative effects,
  - tests under extreme conditions (temperature, pressure, irradiation, chemical composition);
- In situ tests:
  - geophysical, geomechanical, geochemical and hydraulic tests in boreholes and in underground laboratories,
- Natural analogue studies and field observations.

In the initial phase of most projects a literature survey is conducted prior to the start of the experimental work. Predictive calculation may be performed using published data of other laboratories. This helps to understand studied features and to optimise the experiments.

2.2.2. Development of extrapolation tools

A model is a core part of the extrapolation to long periods of time. The models to be applied for extrapolation of short term results to real systems and to long terms should in principle be independent on specific scenarios. Such models focus on different aspects depending on the specific extrapolation task. A few basic approaches are given below. Actually the trend in the scientific community is directed to integrate different basic approaches.

Thermodynamic models: Predictive geochemical modeling of thermodynamic properties of radionuclides in complex natural systems requires a fundamental thermodynamic database as well as an appropriate thermodynamic model for the aqueous and solid phases, valid for a wide range of temperature, (pressure), chemical composition and ionic strength. Different approaches for calculating activity coefficients in electrolyte solutions have been proposed. Accurate model parameters specific for interactions of radionuclide species in trace concentrations are available only to a certain extent. Experimental data allow the development of comprehensive sets of thermodynamic data (chemical potentials and thermodynamic constants) and model parameters which can be used for computing dissolved radionuclides concentrations and corresponding solid phases independent on time. This extrapolation tool is demonstrated in the German contribution.

Kinetic models: The risk to humans of a radioactive waste disposal does not depend only on the thermodynamics of radionuclides but also on the rate of radionuclide release. The models used in this context extrapolate the dissolution or corrosion behaviour of waste forms and the attributed radionuclide release. Simple approaches rely only on measured leaching rates, more complicated models combine a general law of thermodynamics and transition state theory according to Aargaard and Helgeson [11]. This type of models allows the consideration of saturation effects, influence of the groundwater chemistry, etc.

Migration models: These models have to consider basic mechanisms such as the counterbalance of mobilising and immobilising processes of the radionuclides and other substances involved. The mobility of radionuclides depends strongly on the chemical nature and stability of species in groundwater and the geochemical characteristics of various surfaces of minerals, rocks and engineered barrier materials. Typical mobile species are complex ions or colloids. Key factors for the mobility of radionuclides are charge differences between surfaces and solution species and specific chemical interaction affinities. In contact with groundwater most mineral surfaces are negatively charged. Radionuclide mobility is highest, if the solution species has the same charge (negative) as the surface. Approaches applied in this CRP quote mostly on linear sorption isotherms.

Other models: Many models and computer codes are available which provide a great potential to extrapolate experimental findings in the fields of heat dissipation, mechanics and hydraulics. In this CRP mainly analytical models for temperature development and the resulting thermomechanic effects as well as for fractured zones transport are applied.

Mathematical models are formed by a set of equations reflecting each hypothesis of the relevant model. These equations may also express empirical observations. The mathematical models have to be translated into numerical or analytical codes. Even sophisticated models include simplifications of the real situation. Therefore, verification of computer codes is essential. Applications of the developed models e.g. on natural analogues, increase confidence in the model results. The steps in the long term extrapolation involve iterative processes which are summarised in Fig. 1.

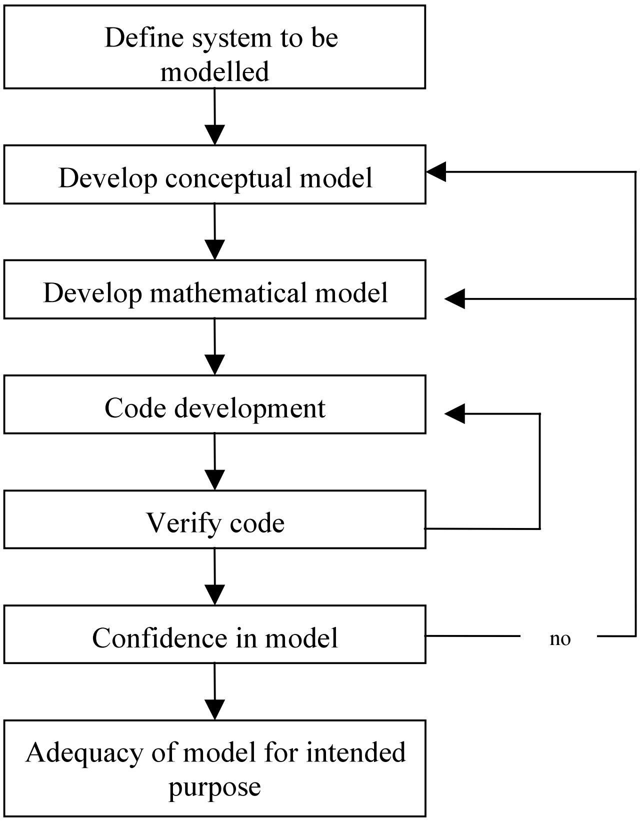

Fig. 1. Modelling tool development for extrapolation purposes.

2.3. EXTRAPOLATION IN PERFORMANCE ASSESSMENT

Performance assessment provides the main framework for extrapolations. The extrapolations can be subdivided into several sequential steps [12, 13], namely in:

- Scenario development[1],
  - identification of features, events and processes (FEPs),
  - definition of critical combinations of FEPs,
  - estimation of probability of scenario occurrence,
- Consequence assessment,
  - development of tools for mathematical description of a disposal system,
  - calculation of consequences of scenarios,
- Uncertainty and sensitivity analyses,
- Comparison of the results with standards and/or criteria.

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[1] The definition of a scenario given by NEA [14] is as follows: "A scenario specifies one possible set of events and processes and provides a broad brush description of their characteristics and sequencing".

Models have to be developed according to the scenarios. The procedure is similar to those demonstrated above: Conceptual models consist of a set of hypotheses defining the behaviour of the investigated system. Their development is based on systematic studies of the system, on understanding phenomena occurring in it, and on implication of general knowledge in the system. They require systematic collection of data quantifying parameters typical for the system which, in case of lack of such data, may be replaced by an expert judgement.

Within the context of scenario development, extrapolations have to be performed. These extrapolations, however, cover different fields of science and are not the topic of this CRP. In the following sections examples of the extrapolation methods used in consequence analysis are presented by the participants of the CRP.

2.4. RELIABILITY OF EXTRAPOLATION AND UNCERTAINTIES INVOLVED

The credibility of long term predictions is an important issue in licensing procedures and vital for public acceptance. An adequate credibility can be achieved provided the following issues are addressed:

— Reliability of modelling inputs
Data used for calculation should be obtained by appropriate procedures, under clearly defined and recorded conditions. It is desirable that their reproducibility is exemplified. These requirements can often be achieved by application of quality assurance principles [15] which can be interpreted as establishing, documenting and recording experimental conditions and all features that may affect determination of a parameter value.

— Consideration of uncertainty [16]
Sources of uncertainties include simplifications in the conceptual models, unknown boundary conditions, representative for the whole range from samples to complete systems and the limitations of the models.

Uncertainties can be reduced by different methods. These include the selection of appropriate methods for data collection and for model development [17].

Short term in situ experiments may provide a rough information about validity of models/codes by comparing their outputs with observations and observed evolution of systems with time [18].

— Verification
It is vital for long term extrapolation that models describing natural and human induced processes and mathematical codes used, work as intended. This is assured by the verification process.

Natural analogue studies [19] can be applied for proving adequacy of data for long term observations. Such studies cover investigations on systems displaying some relevant features. In contrast to laboratory and field experiments measured results characterise the present state of the analogue system.

Method for verification of computed results has been widely applied and published [20–22]. Confidence building which is an important issue and often discussed in this context was not considered within this CRP.

3. STUDIES ON NEAR FIELD BARRIERS

Safety assessments of a repository should take into account all barriers, natural or engineered, built or selected to protect the environment from possible impacts of the disposed waste or spent fuel. In general, the barriers are evaluated as mutually dependent systems. The role of the natural barriers should not be underestimated because of their long term geological stability. Engineered barriers in contrast allow to influence more actively the expected longevity of the repository.

The principle role of engineered barriers in a repository system is to prevent or delay the migration of radionuclides or other contaminants originating from buried wastes, and thus, to improve performance of the whole disposal system [23].

Some typical engineered barrier studies are illustrated in the following sections together with references to the results of CRP participants.

3.1. WASTE FORMS

A primary barrier preventing release of radioactive contaminants is the waste form, which is either spent fuel or solidified waste (waste glass, cement and other solid waste). A major task of studies is the description of degradation processes and quantification of contaminant releases to determine the source term for safety analyses. Dissolution, decomposition, and corrosion are the leading mechanisms that should be taken into account for long term considerations. For evaluation of the effectiveness of the barriers, both physical and chemical forms of radionuclides released from the waste form is a significant input. The chemical nature of releases and their changes or evolution with time, as well as the chemical interactions of different barrier materials are thoroughly studied.

Long term performance of the waste forms was investigated within this CRP by some participants.

The Indian studies focused on the degradation of borosilicate high level waste glasses in granitic environments. Leaching of glass was found to be high where rust is in conjunction with granite. For long term prediction, it is therefore essential that the source term be computed based on stabilized leach rates and geochemical environments.

Experiments performed in the Republic of Korea included leaching behaviour of borosilicate glasses in contact with compacted Ca-bentonite in flowing synthetic granitic groundwater at 80°C. An extrapolation method for the prediction of radionuclide release through the bentonite buffer has been introduced and showed that predicted concentration of caesium agreed with the experimental results. However, to verify the results due to changes in solubility and retardation coefficients which may be significant, longer term experiments are to be pursued.

The corrosion behaviour of HLW glasses, spent fuel and cemented waste forms has been investigated in Germany. The corrosion/dissolution of waste forms is not necessarily associated with a proportional release of radionuclides. The formation of new secondary phases, such as silicates, molybdates, uranates, carbonates, etc. gives rise to a new barrier for the re-immobilization of dissolved radionuclides from the waste form.

3.2. CONTAINERS

The container/canister[2] and/or overpack which contains the conditioned wastes constitute the main barrier in some disposal concepts. While canister is only a migration barrier, the overpack can be made of such massive material that it also provides shielding. The overpacks are made preferably of metals. Thermodynamic stable materials for the selected disposal system is considered in some designs.

The process of corrosion of overpack materials is widely investigated, including interactions between the waste form and the overpack, the surrounding backfills and/or undergroundwater is considered as well.

Constituent materials of these barriers were studied in the following CRP projects.

Argentina investigated corrosion resistance of carbon steel and lead in different repository-like conditions. It was found that in a closed containment to reduce the oxygen flux the steel samples are corroded uniformly. Lead and tin alloys have better corrosion resistance than commercial leads.

India included container behaviour studies aiming at determination of corrosion rates and mechanisms of both stainless and carbon steels in the presence of bentonite. It appears that bentonite generates some organic compounds which are absorbed on the carbon steel surface and leads to decrease the corrosion rate with time.

Pitting corrosion mechanisms of sensitized stainless steels were investigated in Cl^- solutions and in synthetic granitic groundwater in experiments carried out in the Republic of Korea. Corrosion tests for extended time periods of sensitized stainless steel (SS316L) were carried out under the conditions of Ca-bentonite and synthetic granitic groundwater at 80°C. Crevice corrosion could be initiated after three months exposure of sensitized SS316L. Long term experiments are pursued to verify that this corrosion might result from the fabrication techniques of specimens.

In the initial phase of the CRP a short overview of corrosion mechanisms was presented by the US participant who considered different container materials. This overview, however, did not cover new aspects of corrosion models as tools for time extrapolation.

3.3. BUFFER, BACKFILL AND SEALING SYSTEMS

The buffer, backfill and sealing system of a repository should perform three functions that may be provided by one or more materials [24].

- *Buffer:* a buffer material is often in direct contact with the waste package or overpack. The buffer must be selected to provide an optimal physical and/or chemical environment for packages.
- *Backfill:* the main function of a backfill is to fill voids in all underground openings such as drifts, galleries, shafts, etc. In some cases backfill can also act as a buffer.
- *Seal:* the role of a seal is to limit water and gas flow in the repository structures.

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[2] Canister refers to containers for spent fuel or vitrified wastes.

The properties studied in connection with engineered barriers include radiation and thermally induced changes, migration/retardation processes, influence on the groundwater chemistry and its evolution due to the contact with barrier materials. The mechanical properties and combined heat/pressure effects on geomechanical behaviour of the repository system are investigated as well.

In the Belgian contribution the influence of concrete on the near field chemistry and the effect on radionuclide solubility is evaluated. The influence of heat and radiation on geochemical and hydromechanical properties are also reported. In the long term performance assessment of these effects are addressed by stochastic calculations.

The Czech project aimed at development of a method for evaluation of the role of discontinuities in the buffer, backfill and sealing system. Extrapolation relied on analytical tools which consisted of cyclical application of experimental conditions (temperature and moisture) on bentonite blocks. Formation of discontinuity faults in the blocks induces irreversible changes of the geotechnical properties of the bentonite.

The thermal stability of smectites with respect to its sealing (swelling properties) and cation exchange capacity was investigated by the South African participant. Since high temperatures in a high level radioactive waste repository cannot be avoided, it is recommended from the experimental findings to provide the clay content in the backfill barrier as high as technically possible. Further on it is recommended to keep the potassium content sufficiently low. This means it makes no sense for long term considerations to mix bentonite with K-bearing minerals as they are present in granite.

The Ukraine project focused on the investigation of the radiation and thermal effects in granite minerals. Special attention was given to the study of radiation defects formation in the mineral structure and an analytical approach for the long term extrapolation was tested using the variation of radiation defects concentration. The methodology was not applied satisfactorily. It has been shown that simultaneous contributions from chemical, physical and biological studies are required.

3.4. OTHER ELEMENTS OF A REPOSITORY STRUCTURE

The construction of a repository may introduce foreign materials which had not been considered in the initial performance assessment. The effects resulting from the interaction of these materials with the barriers of the repository system must be thoroughly evaluated in the long term, as they may initiate processes affecting the disposal system adversely. This was not considered in the frame of the present CRP.

4. STUDIES ON FAR FIELD BARRIERS

4.1. ROLE OF NATURAL BARRIERS

For a geological disposal system the natural barrier is equivalent to the repository host rock with all its properties, discontinuities, heterogeneity, groundwater, gases, etc. Rock formations were formed at least many million years ago. Thus, it can be hardly expected that their nature could significantly change during a lifetime of a repository without any significant impulse.

Conditions may be different for radioactive waste disposal in soil or in permafrost strata which may undergo very fast changes.

The repository itself is an intrusion into a previously stable formation, and changes are expected mainly in the intensity and direction of groundwater flow and in the stress distribution pattern. These features must be characterised and long term evolution of the formation must be assessed.

The role of natural barriers is twofold:

- To protect the repository system from effects caused by the natural evolution (erosion, climate, seismicity),
- To complete the isolation function of engineered barriers and to retard migration of contaminants that may be released from the waste forms and from near field.

To accomplish both functions, the long term prediction of a system evolution must be carried out with respect to initiating events.

In the CRP, the Indian project addressed in situ experiments developing the physical and thermomechanical processes which affect the behaviour of the candidate host rock over time. Thermomechanical modelling of the rock mass was established using experimental data with respect to rock stability, structural changes, groundwater flow and radionuclides migration. Long term extrapolation based on short term thermomechanical behaviour of the host rock can be generally well established.

4.2. MIGRATION OF RADIONUCLIDES

In general, migration of contaminants can be characterised as a far field issue, nevertheless, its near field part should not be neglected. As migration is directly related to the presence of groundwater both saturated and unsaturated conditions in rock/soil have to be considered.

Migration involves sorption and desorption processes. Sorption processes are complicated phenomena depending on the characteristics of the fluid, the contaminant, and on the materials through which they penetrate. Therefore, experimental investigations focus on definition of the physico-chemical form of a contaminant, on groundwater flow, the chemical characteristics of fluids and on the geological formation.

In migration studies of radionuclides deterministic [25] and stochastic approaches [26] are also used.

Different experimental methods were applied within this CRP by the participants.

In Germany, thermodynamic data especially for actinides and long lived fission products as inputs for geochemical and transport models were determined. Empirical and deterministic tests were interpreted by use of coupled models considering both chemical and physical parallel processes. In situ K_a values were determined in equilibrated groundwaters and in waters extracted from sediments in order to relate laboratory experiments to natural conditions.

Within the Hungarian project, migration and sorption of radionuclides in Boda mudstone were studied. This formation is considered as a prospective host rock. Experiments under ambient and simulated in situ conditions were extrapolated using diffusion based mathematical approaches. The result shows that under steady conditions the migration distance for the most mobile radionuclide, is only of a few hundred metres during the first 10^4 years of the life of the repository.

India included in its project the development of a deterministic model for prediction of migration of radionuclides applying source terms determined from HLW glass leaching experiments in the presence of granitic material.

Malaysia provided results which are related to a planned repository for U/Th mining tailings in soil. The methodology aimed at determination of sorption/desorption characteristics of Th and U in soil having different competing cation concentrations. Experimental results were extrapolated to determine Kd values and were processed using stochastic modelling tools. The results were applied in order to compute safety analyses of the site.

In the frame of a Belgian analogue study the distribution of Th/U and their daughter nuclides in the Boom clay were measured. From the geochemical changes observed in the sequence (30 million years) an ongoing mechanistic approach is applied to support the time extrapolation of radionuclide migration.

5. MODELS IN PERFORMANCE ASSESSMENT

The performance of a disposal system can only be demonstrated by models [27]. The models allow computation of the relevant physical and chemical processes observed experimentally. Models are developed for different subsystem, the set of which composes the whole system. The main subsystems may be identified as follows:

- ***Source term*** for which models describe the release of radionuclides from the waste forms to a transport medium (water, air); in general they consist of two parts:
  - waste degradation model,
  - containment failure model.
- ***Near field transport*** for which models cover all processes and features which affect the migration of radionuclides/contaminates from the waste forms through the engineered barriers to the host formation; two possible pathways are to be considered:
  - aqueous transport,
  - gas facilitated transport,
- ***Far field transport*** for which models provide the description of processes within the geological environment up to the biosphere.
- ***Biosphere*** models are not considered in this CRP.

Development, verification and validation of models include a number of problems which are beyond the scope of this publication. For further information the reader is referred to the specialized literature, e.g. Ref. [28].

A large variety of models describe only one phenomenon (e.g., transport of radionuclides by water), which does not fully correspond with real situation on-site: under natural conditions the transport is affected by geochemical changes, microbial activities, mechanical mass transfer (erosion), etc. Recently, studies are directed to more complex description of processes by coupling different models (typically geochemical and transport models).

For performance assessment the models have to consider the behaviour of the system as a whole, starting from the source term (waste degradation and radionuclide mobilization) through the transport of radionuclides in near field (engineered barriers) and far field (natural barriers) to the environment [29]. Models covering the whole system have been demonstrated to a certain degree in the following CRP projects.

Belgium presented a complex evaluation including both, near and far field aspects. Near field problems encompassed various issues such as HLW glass corrosion, links between solubility and geochemical conditions, buffer properties of concrete, heat and radiation influence on host clay, while far field aspects dealt with changes of clay properties and studies of the aquifer system. In the whole system the underlying phenomena and mechanisms were identified based on short term experimental observations and the obtained results were processed using both deterministic and stochastic modelling tools.

Germany followed a similar schematic approach for a repository located in a salt formation. The study incorporated mechanisms of mobilization of actinides from different waste forms, their penetration into an aquifer system and the transport to the environment. To model the processes, a coupled geochemical/kinetical model was applied. The parameters of the model were determined via laboratory experiments.

The Indian approach also considered both near and far field aspects. The approach included description of degradation of HLW glass, corrosion of container materials, changes of geochemical environment, thermomechanical behaviour of granitic host rock, and migration.

The results of the CRP showed that real systems are often very complex and the short term observation may not always provide sufficient information to allow a mechanistic/ deterministic approach. In such cases a stochastic approach can be applied as most research teams successfully achieved. In applying sensitivity and uncertainty analysis, it can be shown which part of the repository system is the most important for the long term safety.

6. CONCLUSIONS

General consensus exists among specialists, regulators, politicians and the public at large that realization of a repository for radioactive wastes requires convincing evidence about its safe performance. This can be achieved by different approaches, which are, however, in all cases indirect. Therefore, extrapolation of short term observations to periods comparable with the half-lives of the radionuclides is the most crucial issue in evaluating long term performance of the disposal system.

Predictions of the behaviour of a barrier system are based on a thorough understanding of processes involved. In order to perform predictions one has to define systems and scenarios and to develop conceptual models. Those models are then translated into mathematical models and codes. Complete input information to the models calls for intensive experimental work: experiments form a basis for successful modelling as they provide not only data but also information about uncertainties associated with their values. The model parameters have to be representative enough to characterise the processes; their importance and relevancy belong to vital tasks of evaluation of the repository performance.

As measurements are carried out over very short periods (comparing with the repository lifetime), uncertainties or inaccuracies in data may lead to significant distortion of results during extrapolation. It should be considered carefully in interpreting the obtained results that second order processes and coupled effects may become significant.

Many models have been developed and tested to describe particular elements of a repository system. However, models incorporating concurrent, competing and second or third order processes are not yet available for long time extrapolations.

Methodologies presented in this publication indicate ways how short term observations can be extrapolated to very long periods of time. Procedures described here, do not cover a complete list of available methods. The results of the investigations carried out by the different laboratories represent attempts of the extrapolation methods corresponding to different levels of complexity. Nevertheless, this publication is one of the first to present extrapolation as a separate problem within development of disposal systems of the Member States involved in the CRP. To investigate the concurrent, competing and second order processes much more research is required. In this CRP, further steps needed for the systematic treatment are recognized. The participants of the CRP conclude that adequate long term extrapolation procedures require additional research, especially in the fields of:

- Thermodynamics of radionuclides at elevated temperatures
- Kinetically controlled processes
- Redox processes
- Meta stable systems
- Open versus closed systems
- Longevity of engineered barriers.

More efforts should also be devoted to develop approaches to increase the confidence of regulators and public in the long term assessment [30].

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Annex

CONTRIBUTIONS BY PARTICIPANTS IN THE CO-ORDINATED RESEARCH PROJECT ON EXTRAPOLATION OF SHORT TERM OBSERVATIONS TO TIME PERIODS RELEVANT TO THE ISOLATION OF LONG LIVED RADIOACTIVE WASTE

CORROSION BEHAVIOUR OF STAINLESS STEELS AND VITRIFIED WASTE PRODUCTS UNDER GEOLOGICAL REPOSITORY CONDITIONS
(REPUBLIC OF KOREA)

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Abstract

The long-term corrosion behaviour of SS316L and simulated borosilicate waste glasses has been investigated. The specimens were exposed to the domestic Ca-bentonite in a synthetic granitic groundwater at 80°C. The well-defined crevice site could be initiated within 3 months after the exposure of sensitized SS316L even to 100 g/m^3 Cl^- solution with Ca-bentonite. The boron can be used as an indicator on the dissolution of a borosilicate glass. For the prediction of radionuclide release from a waste through a bentonite buffer, a method has been introduced.

INTRODUCTION

A generic disposal concept for high-level radioactive waste (HLW) is being developed under assumptions that an underground repository would be located in a type of crystalline rock in Korea and an appropriate multi-barrier system (such as engineered and natural barriers) would be provided for the isolation of the HLW from the biosphere. For assessing the long-term performance of waste isolation, the effects of various reactions and interactions occurring in the engineered barrier system, such as corrosion of waste form, canister and overpack, alteration of buffer materials, and chemical interactions of the constituents released from waste products with them [1], should be fully understood. The related program for member countries was formulated by IAEA, and so KAERI has participated in this program to understand the long-term corrosion behaviour of stainless steel, which is one of the candidate container materials for radioactive waste, and the long-term release behaviour of radionuclides from vitrified waste products under repository condition.

This paper describes briefly the results on the corrosion behaviour of SS316L and simulated borosilicate waste glasses with domestic Ca-bentonite buffer for exposure of about 2 years in synthetic granitic groundwater at 80°C. And an extrapolation method for release of radionuclides from a borosilicate waste glass through a buffer zone has been introduced.

CORROSION BEHAVIOUR OF VITRIFIED WASTE PRODUCTS

Experimentals

Three kinds of simulated borosilicate waste glasses were fabricated with oxides, carbonate and fly ash at around 1200 d, and then annealed at 500, for 1 hour [1]. The dimensions of disc-type specimens for the observation of the surface alteration phenomena were 18 mm (diameter) and 2.5 mm (thickness), and the crushed samples were used to evaluate their leach behaviour under the compacted Ca-bentonite, with the density of 1.4 Mg/m^3, flowing synthetic granitic groundwater at 80. Each leachant was analyzed by ICP-AES, IC, AA and TIC, and the surface of each disc type specimen and the bentonite before and after its leaching were observed by EPMA, XRD, XPS and an optical microscope.

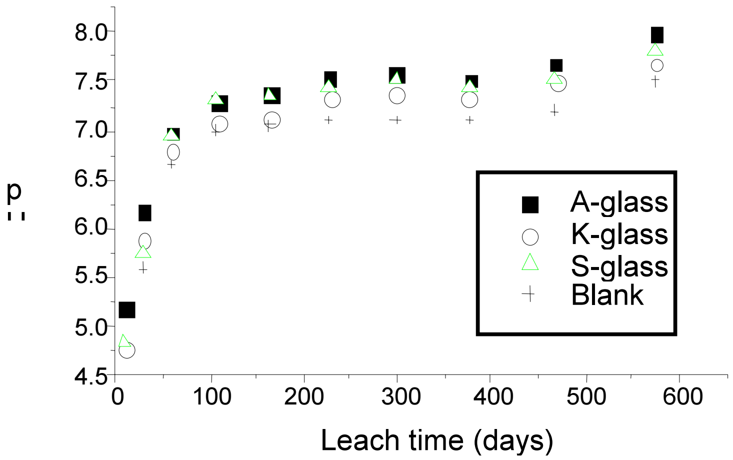


Fig. 1. Variation of pH of leachates as a function of leach time.

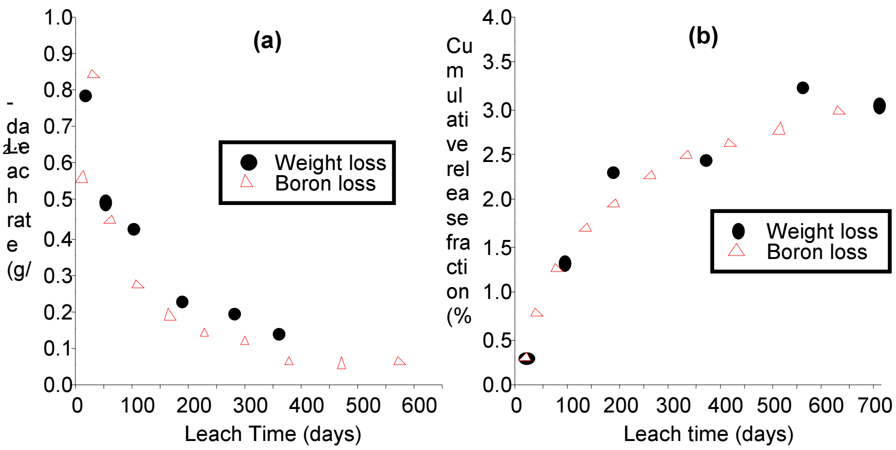


Fig. 2. Comparison of weight loss of and boron released from K-glass disc; (a)leach rates and (b)cumulative release fractions.

RESULTS AND DISCUSSION

Analysis of leachates

As shown in Figure 1, the pH of leachates was gradually increased from 4.8 to about 8.0 for the leaching up to 632 days. The initial pH was mainly due to the dissolution of sulphate from bentonite. The weight loss of and the boron released from disc specimens of K-glass were measured, and their leach rates and the cumulative release fraction are illustrated in Figure 2. As shown in this figure, the mass loss is almost the same as the boron released. This means that the boron is an indicator on the dissolution of a borosilicate waste glass [2].

The concentration of silicon in the leachates with the crushed glass samples was in the range of 30ppm to 60ppm, which was comparable with that from the bentonite without the glass sample and independent upon their leaching time. However, the cumulative release fraction of boron from the crushed glass samples was decreased with the increase of leaching time (Figure 3). The release fraction of boron from A-glass is higher than those from K- and S-glasses. This may be due to the difference of their components and the high flow rate of about 1.82 ml/day, compared with the K- and S-glasses of around 1.38 and 1.02 ml/day, respectively. The leach rates of boron from K- and S-glass at around 630 days after beginning to flow the synthetic groundwater through their specimens were approximately 3.4×10^{-2} and 2.9×10^{-2} g/m^2-day, respectively, and the leach rates of molybdenum from these specimens were almost the same values of their boron leach rates. However, the release rates of caesium through the bentonite block from these specimens were about 1/10 of the release rate of boron. This may be due to its adsorption on the bentonite.

By the analysis using ICP-mass, the concentrations of U, Nd, La and Zr in the leachates were below 1 mg/m^3, and the leach rate of uranium from A-glass specimen is too low, below 4×10^{-7} g/m^2-day. Though a large amount of uranium was found on the surface of bentonite in contact with A-glass, these low concentrations in the leachates suggest that uranium and actinides hardly move in compacted bentonite. On the other hand, the leach rates of Cs from K- and S-glass were almost same around 2.5×10^{-3} g/m^2-day.

Analysis of disc-type specimens

XPS spectra of specimens before and after their leaching up to about 2 years are shown in Figure 4. As shown in this figure, the leach resistant elements such as U, Ti, Fe and Zr on the surface of the specimens are enriched, while the soluble element such as Na and Si are depleted due to the dissolution of these elements from the specimens into the groundwater.

And SEM pictures of the samples before and after their leaching up to about 2 years are shown in Figure 5. By these pictures, all three kinds of glasses before leaching have the same appearance. After leaching, the caves of a honeycomb shape were formed in the surfaces of the specimens and the break-out of the scales on the surface layers of A- and S-glass was discovered. However, the break-out phenomenon on the surface of K-glass has not appeared until 23 months leaching period. This suggests that the leaching mechanism of K-glass could be different from the other glasses.

By the EPMA analysis, the contents of Na and Ca on the S-glass specimen surfaces were sharply decreased, while the contents of Mo, Fe, Zr and U increased. In K-glass specimens the contents of Na and K were sharply decreased after leaching, while the contents of Mo, Fe, Zr, U and Ti were increased. In A-glass specimens the contents of Na sharply decreased after leaching, while the contents of Mo, Fe, U and Ti increased.

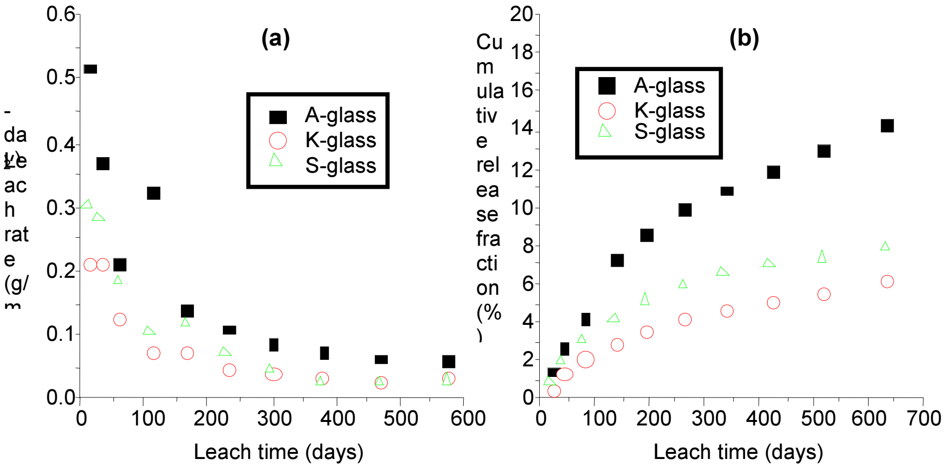


Fig. 3. Comparison of the amount of boron released from crushed A-, K- and S-glass; (a)leach rates and (b)cumulative release fractions.

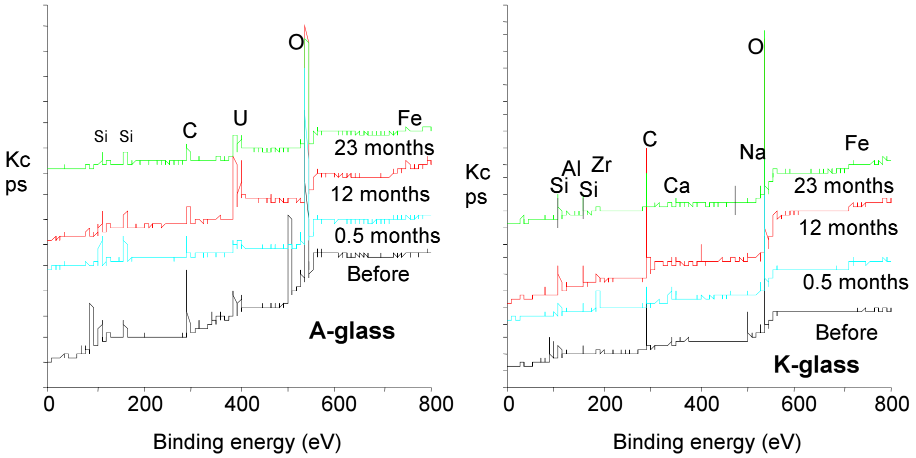
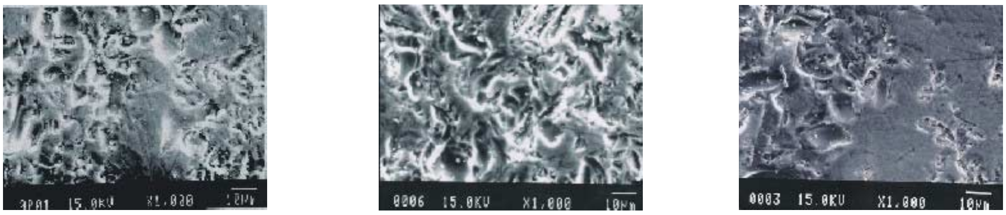
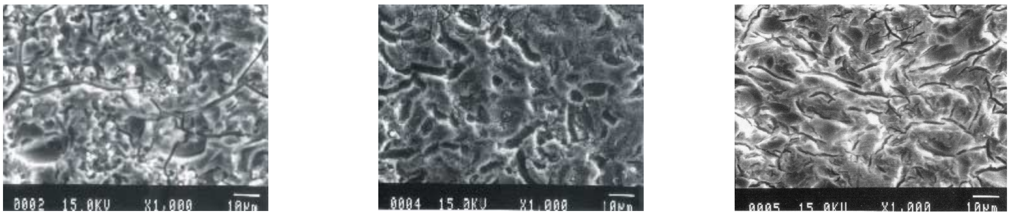


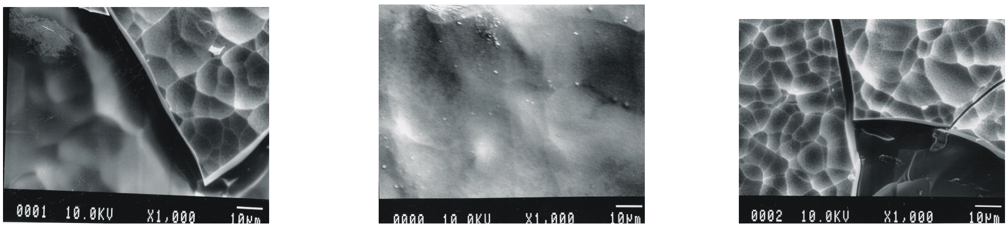
Fig. 4. XPS spectra of specimens before and after leaching.



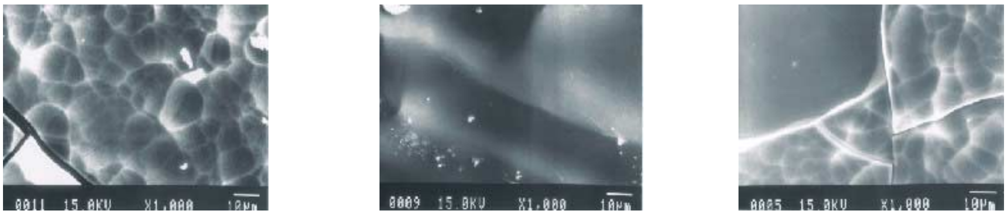
(a) Before (a’) Before (a”) Before



(b) 0.5 months (b’) 0.5 months (b”) 0.5 months



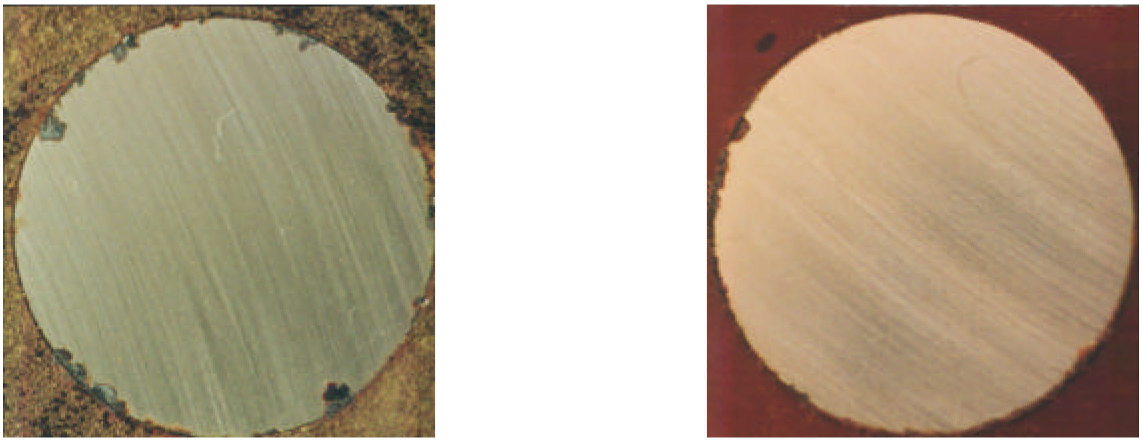
(c) 12 months (c’) 12 months (c”) 12 months



(d) 23 months (d’) 23 months (d”) 23 months

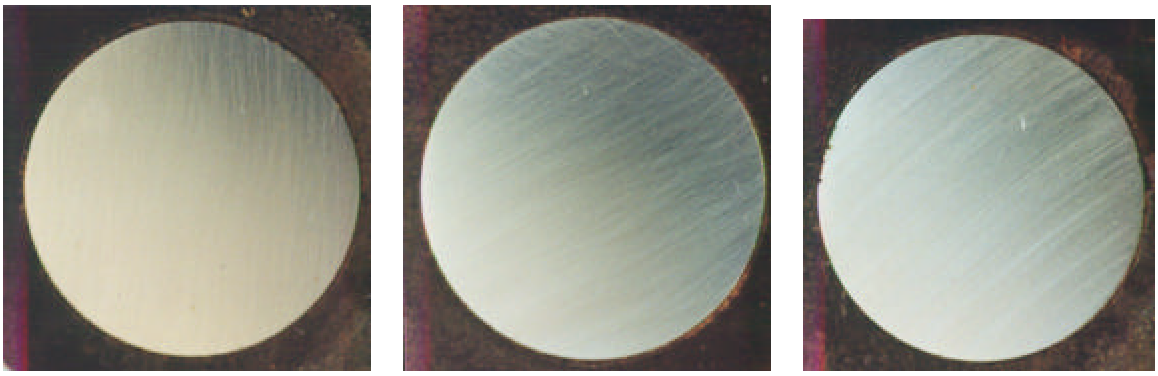
A-glass **K-glass** **S-glass**

Fig. 5. SEM images of specimens before and after leaching.



(a) 100 ppm cl^{-}, 18 months

(b) 1000 ppm cl^{-}, 12 months



(c) Non-sensitized
25 months

(d) Sensitized for 24 hrs
25 months

(e) Sensitized for 96 hrs
25 months

Fig. 6. Photographs of SS316L specimens after their exposure to chloride solution with Ca-bentonite.

Analysis of bentonite

EPMA results indicated that there were no differences, except the depletion of sulphur, between the bentonite samples before and after flowing synthetic groundwater through the bentonite layers with glass specimens up to about 2 years. However, a yellowish uranium compound was deposited on the surface of bentonite in contact with A-glass specimen.

EXTRAPOLATION METHOD

Generally the solubility of caesium is much higher than that of the glass matrix so that caesium is expected to be released by the congruent release mechanism. However, the solubility of uranium much lower than that of the glass matrix. Therefore, the release of uranium is expected to be dissolved into the groundwater by the solubility limited mode. The major features of the program, which has been developed by KAERI to predict the release of radionuclides from a waste product in a geologic repository, are combined with (1) the congruently released mode with chain decay [3] and (2) the solubility limited release mode.

Under the conditions that the distribution coefficient of caesium is 500 m^3/Mg and the solubility limit of silica is 40 g/m^3, the predicted concentration of caesium is agreed well with the experimental values. However, since the effect of changes in diffusion coefficient, solubility and retardation coefficient is expected to be significant, to verify the results, longer-term experiments are to be pursued.

CORROSION BEHAVIOUR OF STAINLESS STEEL 316L

Pitting characteristics of SS316L

Pitting corrosion of sensitized stainless steel (SS) 316L has been investigated as a function of the degree of sensitization in aqueous NaCl solution with various Cl^- ion concentrations at room temperature. The squared rod specimens of SS316L were thermally annealed at 700er for various duration (0 h: non-sensitized specimen A; 8 h: moderately sensitized specimen B; 96 h: severely sensitized specimen C). The pitting corrosion resistance of the three kinds of specimens was evaluated by the potentiodynamic anodic polarization method, abrading electrode technique and ac-impedance spectroscopy [4].

Over the whole applied anodic potential range, it was found that the parameter values fell in the order of specimen A, B and C. And also, the pit growth rate increased with increasing Cl^- ion concentration in synthetic granitic groundwater and degree of sensitization. At the range which the applied anodic potential is higher than the pitting potential, the resistance was sharply decreased due to the local breakdown of oxide film. On the other hand, the oxide film resistance of sensitized specimens in value were evaluated to be lower than those of the non-sensitized specimen.

Based upon the combined results of the abrading experiment and ac-impedance measurement, it is indicated that the instantaneous formation of the passivating oxide film is more retarded by the impoverished chromium (Cr) concentration over the wider Cr-depleted zone adjacent to the grain boundaries in sequence of specimens A, B and C. This means that the thin oxide film formed on the sensitized specimens B and C is less protective than that formed on the non-sensitized specimen A.

Corrosion behaviour of SS316L in compacted Ca-bentonite

To understand the long-term corrosion behaviour of SS316L under a repository condition, the chloride concentration in the groundwater was adjusted to 100 g/m^3 and 1000 g/m^3 with NaCl to investigate the effect of chloride ion on the corrosion of the specimens, which are moulded with epoxy resin, except one side which is to be exposed into the mixture of Ca-bentonite and synthetic granitic groundwater as the ratio of 1 to 1. And to evaluate the influence of their sensitization degrees on their corrosion, the non-sensitized and sensitized specimens were prepared.

After about 2 years of exposure at 80Af, the appearances of the specimens were examined. There was no evidence of general and pitting corrosions in all the specimens, while crevice corrosion at the boundary between specimens sensitized for 24 hours and the molded epoxy resins were remarkably observed as shown in (a) and (b) of Figure 6. However, as shown at the bottom of this figure, crevice corrosion at the boundary of only the highly sensitized specimens exposed to 1000 ppm Cl^- solution with Ca-bentonite was perceived. On the other hand, several metal contents in the bentonite were measured and the iron content in the bentonite sample directly contacted with the specimen was relatively higher than that in the top one due to the dissolution of iron by the crevice corrosion. These results suggest that crevice corrosion might be dependent on the fabrication technique of specimens.

Sridar et al. [5] reported that a crevice corrosion in SS316 not be initiated within 40 days after its exposure in 1000 g/m^3 Cl^- solution, while our results pointed out that the well-defined crevice site could be initiated within 3 months after the exposure of sensitized SS316L even in 100 g/m^3 Cl^- solution at 80°C.

CONCLUSION

The boron can be used as an indicator on the dissolution of a borosilicate glass. The leach rate of boron was related to the ratio of the surface area to the volume of leachate passed through the specimens.

The uranium and actinides can be retarded by a compacted bentonite, though there was no difference in the component, except the depletion of sulphur, and property of bentonite before and after leaching up to about 2 years.

The well-defined crevice site could be initiated within 3 months after the exposure of sensitized SS316L even to 100 g/m^3 Cl^- solution at 80°C with Ca-bentonite.

The longer-term experiments are to be pursued in order to verify the predictive model and the species of yellowish uranium should be identified to understand clearly the release mechanism of uranium from vitrified waste with high content of uranium.

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LEAD CORROSION EVALUATION IN HIGH ACTIVITY NUCLEAR WASTE CONTAINER
(ARGENTINA)

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Abstract

This report describes a study of high activity nuclear waste canister corrosion in a deep geological disposal. In this canister design, the vitrified nuclear waste stainless steel container is shielded by a 100 mm thick lead wall. For mechanical resistance, the canister will also have a thin carbon steel external liner.

Experimental and mathematical modeling studies are aimed to asses the corrosion kinetics of the carbon steel liner in first instance and then, once this liner has been corroded away, the corrosion kinetics of the main lead barrier.

Being the oxygen reduction the main cathodic reaction that supports the anodic oxidation of iron, a model is described predicting the rate of oxygen consumption in a sealed deep nuclear waste disposal vault as a result of the canister corrosion. Oxidation processes other than container corrosion, and that can account also for oxygen depletion, are not taken into consideration.

Corrosion experimental studies on lead and its alloys in groundwater are also reported. These experiments are aimed to improve the corrosion resistance of commercial lead in groundwater.

INTRODUCTION

In a repository study, based on the concept of multiple barriers to assure a long term isolation from the biosphere, lead could be chosen as one of the metal components for the high activity nuclear waste canisters.

This metal has a good radiological protection quality and good corrosion resistance in natural waters. A canister based on lead as a main metal barrier, must have a thick lead wall. In this canister design, the vitrified nuclear waste stainless steel canister is shielded by a 100 mm thick lead wall. For mechanical resistance, the canister will also have a 10 mm thick external carbon steel liner.

For the disposal, the canisters will be placed 500 meters deep in a granitic rock vault. Bentonite/sand mixture will be used as a buffer once the container has been placed in the repository borehole. Temperature of the rock, once the repository has been completed, will be 60° C, while the canister external wall surface temperature is expected to reach 75°C.

Taken into account that the main degradation phenomenon of the metallic barrier is corrosion in groundwater, a model based on oxygen diffusion and depletion on the buffer is being developed. The model proposed takes into account the oxygen retained in the bentonite pores of the buffer in the borehole where the canister is placed and in the gallery, as the main source. For this particular canister design, other oxygen sources such as water radiolysis and groundwater are not taken into consideration. This model can predict the long term corrosion kinetics of the canister metallic barrier that must be compatible with the isolation period of the nuclear waste disposal (1000 years). Long term experiments are being performed to validate the model.

Experimental studies are also under way to improve the corrosion resistance of commercial lead in groundwater.

Lead corrosion behaviour in groundwater and in other corrosive environments has already been studied [1, 2]. High purity lead showed good corrosion behaviour in natural carbonated groundwater, the corrosion rate being of the order of micrometers per year (0.001 mm/year at 75ºC) [2]. This good corrosion performance is due to the presence of a basic lead carbonate passivating film on the lead surface [3].

Lead corrosion is affected mainly by some types of salts present in the environment. Nitrates and acetates induce high lead corrosion rates [4]. Chloride effect depends on its concentration. Very low chloride concentration produces lead corrosion rates almost as high as those found in distilled water (0.56 mm/year) [1]. This corrosion rate decreases with the increase of chloride concentration [5, 6].

In a galvanic corrosion evaluation it has been found that commercial lead has higher corrosion rates than high purity lead [7].

In order to improve the corrosion resistance of commercial lead, several lead binary alloys with Tin, Antimony and Bismuth have been tested in synthetic groundwater and seawater. In the present paper, results of these tests will be given. A model for the canister long term corrosion processes will also be proposed along with the proposal for experiments to validate this model.

EXPERIMENTAL

In order to validate the proposed model long term experiments are under way. A disk sample of SAE 1010 carbon steel are placed at the bottom of a PTFE tube which then is filled with a bentonite/sand 50:50 mixture and compacted to a 1.45 g/cm^{-3} density. That mixture is previously humected with groundwater (synthetic seawater). In the top of the buffer a frit glass is placed and fixed with an open cap. Then the tubes are immersed in synthetic seawater contained in a vessel that is kept in an oven at 75^{o}C. The carbon steel samples are removed after long periods of time and weight loss and corrosion rates are measured. Oxygen transport process is controlled by varying the density of compacted buffer material.

At regular periods of time, PTFE tubes are removed from the oven and, after begin allowed to cool and opened, carbon steel sample and buffer columns are analyzed for weight loss, localized corrosion and corrosion products at the metal-buffer interface. The model will be validated if it is found that carbon steel corrosion rate decreases with time and no severe localized corrosion is detected.

Corrosion resistance of lead alloys are tested trough electrochemical and weight loss experiments. The electrochemical experiments were performed trough potentiostatic polarization experiments in synthetic seawater at 75^{o}C. Extension and current densities of the passive range of alloys and commercial lead are comparatively evaluated. These tests are complemented with long term weight loss experiments in the same conditions of temperature and environment.

EXTRAPOLATION METHOD

Taking into account that the canister is placed in a rock bore hole filled with a buffer material (bentonite and silica sand mixture), the corrosion process to take place in the repository will be controlled by the diffusion of reactants and corrosion products through a porous medium.

Therefore, diffusion processes must be considered in the corrosion kinetics, in order to predict the long term canister corrosion behaviour.

Oxygen in saline water plays a relevant role in canister corrosion processes in deep repository vaults. The main cathodic reaction that supports the anodic reaction of metal corrosion, is that of oxygen reduction.

In a first stage, the model is aimed to predict the corrosion behaviour of the 10 mm thick SAE 1010 carbon steel external canister wall in groundwater. The corrosion of the lead canister main barrier will be modeled in a second stage. Because localized corrosion is the most dangerous phenomenon for the integrity of the canister, corrosion in saline water, such as seawater, will be studied. Generally, groundwaters in deep granitic repositories are saline waters, with high contents of aggressive anions, such as chlorides and sulfates.

Usually, localized corrosion processes are much faster than uniform corrosion and therefore they will account for a large fraction of the overall corrosion allowance of the canister metallic barrier. This type of corrosion refers to isolate penetrations, like pits and crevices.

Rock temperature, once the repository has been filled, will be 60°C, while the external surface canister temperature has been estimated to be 75°C.

Electrochemical behaviour of low alloy steel in chloride containing saline waters is similar to that of high purity iron. There is a corrosion potential with very low current densities (low uniform corrosion rate) in these anaerobic corrosion conditions. We observed three zones in the anodic curve: an active zone, a narrow passivity zone and, at higher overpotentials, a big increase in the current associated to a pitting phenomenon. Cathodic curve is related to a hydrogen reaction evolution [8].

When oxygen is present in saline water, the corrosion potential of iron equals its pitting potential (oxygen reduction curve intersects the anodic curve at pitting potential). Therefore, iron will suffer fast localized corrosion. When oxygen concentration is very low, when it has been depleted due to corrosion processes, the potential decreases to the corrosion potential value in anaerobic conditions, and a general corrosion will take place. As the oxygen reduction current is controlled by a diffusion process, its value will be proportional to the oxygen flow to the iron surface. Consequently, according to its corrosion potential value, carbon steel may corrode by localized corrosion or by general corrosion.

In deep disposal vaults, the amount of oxygen in water-saturated geological formations is expected to be limited. Most of the available oxygen is trapped in the air-filled pores of the compacted buffer and backfill materials that will surround the canister. In this particular canister design, where no water radiolysis is expected to occur, the other oxygen source is the groundwater itself. Over time, this oxygen will be gradually depleted due to the corrosion process of the canister external wall (cathodic reaction), and also by other oxydizable materials present in minerals containing Fe(II), and organic compounds. Provided that there is no other oxygen source, usually deep groundwaters have very low oxygen concentrations (few ppb), and when the oxygen was consumed by those reactions, the canister corrosion process will be governed by the cathodic hydrogen reduction reaction.

According to the literature, two distinct corrosion periods for canisters placed in a deep vault can be defined [9]:

— A hot, oxidizing period, where a localized corrosion process is expected.
— A cool, non-oxidizing period, where stifling and repassivation of localized corrosion sites should occur, followed by a general corrosion process.

The fastest corrosion process should occur at the initial oxidizing period of the vault, when oxygen saturated groundwater in the buffer pores reaches the metal canister surface. There will be a time delay for groundwater to wet the entire thickness of the buffer material before reaching the metal surface. This time delay will depend on the buffer compaction and the hydraulic pressure, among other factors. A swelling pressure will develop during the wetting process, therefore the total pressure on the canister surface will be the sum of this buffer swelling process and the hydraulic components [10].

On the other hand, the effective oxygen diffusion coefficient in the buffer material will depend on its water saturation degree [11].

According to the literature, groundwater in a deep granite repository has very low oxygen concentration (about 3.1×10^{-7} mol/dm^3) [12]. As groundwater flows through the buffer material towards the canister surface, it will be gradually saturated with the oxygen present in the buffer material pores. To estimate the initial oxygen concentration other different approach have been taken, according to the models adopted. In the Canadian model oxygen concentration in the buffer is supposed to be equal to the oxygen solubility in water at room temperature and at 25^{o}C (2.54×10^{-7} mol·cm^{-3}) [12]. In the UKAEA (UK) model it is considered that all the oxygen trapped in the back-fill material is completely solubilized in the groundwater at 25^{o}C at normal pressure. This assumption gives higher oxygen concentration than in the former model (8.16×10^{-6} mol·cm^{-3}) [13]. In the model proposed here, the initial oxygen concentration in the buffer pores groundwater, is the oxygen solubility that corresponds to the pressure and temperature in a deep disposal site.

Once oxygen solubility in groundwater attains the saturation concentration for this conditions, the excess of oxygen will be displaced from the buffer pores, which became filled with oxygen saturated groundwater.

Taking into account that the hydraulic conductivity in the buffer material is very low, less than 10^{-10} m·seg^{-1} [12], we shall focus on a system in which mass transport dominates, so the advective flow term can be ignored. Therefore, the oxygen cathodic reduction reaction will be controlled by the oxygen diffusion through the water retained in the buffer pores. Buffer material thickness between the canister and the rock wall is 20 cm.

In order to solve analytically the mass transport process by diffusion, Fick's differential equation law has been applied. In a first approximation, it was considered a one-dimensional diffusive mass transport with a planar plate geometry, with a perpendicular unidirectional diffusion through the buffer material. This arrangement will represent the buffer/canister lateral wall interface and where the oxygen is supposed to be quickly consumed by the cathodic reaction. At the opposite planar surface, the rock/buffer material interface, it is supposed that oxygen diffusion is restricted. According to these assumptions, the initial conditions for this model are:

$$for \quad t = 0 \qquad c = C_o \qquad \forall x$$

where:

t: time after buffer material has been saturated with groundwater

c: oxygen concentration ($mol \cdot cm^{-3}$)

C_0: initial oxygen concentration ($mol \cdot cm^{-3}$)

x: co-ordinate perpendicular to the plate

Boundary conditions are:

$$for \quad t > 0 \quad ; \quad x = \frac{L}{2} \qquad c = 0 \qquad \text{(buffer/steel interface)}$$

$$for \quad t > 0 \quad ; \quad x = 0 \qquad \frac{\partial c}{\partial x} = 0 \qquad \text{(buffer/rock interface)}$$

where L/2 is the buffer material thickness (20 cm).

The boundary conditions being fixed, the problem is equivalent to that of the oxygen discharge on both sides of a plate with thickness L and x = 0 in its center. In this case, the second boundary condition is accomplished due to symmetry conditions. Other authors have studied the concentration profile in function of time [14]. Once the differential equation (second Fick's law) has been solved:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad 0 < x < L$$

and c = c(x,t) is obtained, then $J = -D \left[\frac{\partial c}{\partial x} \right]_{x = \frac{L}{2}}$ is calculated.

Thus the following oxygen flux equation for the buffer/steel interface is obtained for the oxygen diffusion to the lateral and bottom walls of the canister:

$$J = \frac{D_{ef} C_0}{L_1 \sqrt{\pi T_1}} \sum_{n=0}^{\infty} \left[(-1)^n \left(e^{-n^2 / 4T_1} - e^{-(n+1)^2 / 4T_1} \right) \right]$$

For the top of the canister the following equation is valid:

$$J = \frac{D_{ef} C_o}{L_2 \sqrt{\pi T_2}} \left(1 + 2 \sum_{n=1}^{\infty} e^{-n^2 / T_2} \right)$$

being:

J: oxygen flux on the steel surface ($mol \cdot cm^{-2} \cdot seg^{-1}$)

$D = D_{eff}$: effective diffusion coefficient for wet bentonite (1.7×10^{-7} $cm^2 \cdot seg^{-1}$) [13]

C_0: initial oxygen concentration in the occluded water in buffer pores at 25°C (2.54×10^{-4} mol·dm^3) [14]

L_1: buffer thickness between canister and rock

L_2: diffusion path between the gallery floor and the top of the canister

$T_1 = D_{ef} t / L_1^2$ Adimensional time (t in seconds)

$T_2 = D_{ef} t / L_2^2$

It can be seen that for short exposure times ($T_1 << 1$, $T_2 << 1$), the equations between brackets tends to be 1 in both cases. The resulting expression is that of diffusion in a semi-infinite medium, independent of L_1 or L_2:

$$J = Co \sqrt{\frac{D_{ef}}{\pi t}}$$

therefore, J vs t log-log plot has a slope of –1/2.

It can be seen that up to 10 years both fluxes are identical. For longer times, $T_1 << 1$ is not longer valid and the oxygen flux at the lateral and bottom walls of the canister decays very fast due to the oxygen depletion in the buffer, considering that there is no oxygen flux from the rock. By other hand, the oxygen flux from the gallery to the top of the canister does not change (diffusion in a semiinfinite medium, with a flux inversely proportional to the square rot of time). The condition of $T_2 << 1$ will be valid to time up to 2000 years. For longer times, the oxygen flux at the top of the canister will approach to the value of steady state.

The oxygen flux J at the metal/buffer interface being known, it is possible to calculate the limiting current for the oxygen reduction reaction:

$I_L = J\,(mols.cm^{-2}.s^{-1}).\ F\,(coulombs.mol^{-1}).\ e$

Being F the electrochemical equivalent (9.65×10^4 coulombs·mol^{-1}) and e the electrons involved in the reduction reaction:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$

Localized iron corrosion in saline waters is closely related to the pitting potential. Through current-time measurements at constant potential for iron in 0.5M NaCl solutions, a pitting phenomenon at electrode potentials higher than $-0.32\ V_H$ has been found [8]. The current increase observed at this potential is due to pit nucleation and growth. In saline waters, this pitting potential is closely related to the oxygen concentration. For high oxygen concentrations (6–8 ppm) in the bulk electrolite, the cathodic oxygen reduction and the anodic iron dissolution curves intersect at the pitting potential, and therefore, iron and low alloy steel will undergo localized corrosion (pitting).

As mentioned above, this cathodic oxygen reduction reaction is governed by diffusion. When the oxygen flux is not enough to sustain the anodic iron dissolution current, the corrosion potential will decrease below the pitting potential, and uniform corrosion and low corrosion rates are expected to occur.

Limiting currents values for different reaction times have been calculated and it was found that these currents decay very fast in a short period of time. By comparing these current values with those minimum current values necessary to sustain the pit grow in the current-time experiments for iron we can assume that pitting corrosion on the steel canister wall will be unlikely, according to this model.

Therefore, the model predicts that the oxygen flux on the steel/buffer interface is inadequate to sustain the corrosion potential at the pitting potential value and we can expect that the corrosion potential will correspond to a uniform corrosion in an active dissolution potential region.

For longer times, when the oxygen limiting current falls to very low values (10^{-9} A·cm^{-2}), the iron corrosion potential will be fixed by the hydrogen reduction reaction, and very low corrosion rates are expected to occur (anaerobic conditions).

$H^{+} + e \rightarrow H^{0}$

This corrosion behaviour prediction is based on experimental data at 25°C.

Average rock temperature near the canister can be estimated to be 75°C. In order to make an approach to these conditions, the work will be focused on the study of the electrochemical behaviour of SAE 1010 carbon steel at 75°C in saline water. These results will be compared with the oxygen fluxes in the buffer material at the same temperature, using the present model. Preliminary calculations show that there is limited influence of temperature on oxygen limiting current.

This effect will accelerate the initiation and propagation of localized corrosion at the carbon steel canister external wall in the initial oxidizing period of the vault.

In this study, we are beginning to perform simple exposure tests designed to simulate disposal result conditions. Under these conditions, electrochemical techniques to study the individual reactions are very difficult to perform.

RESULTS AND DISCUSSION

Experiments being carried out are:

Validation the canister corrosion model

These are long term experiments where carbon steel samples are exposed to compacted buffer material (50:50 bentonite/sand mixture) humected with synthetic seawater at 75°C in a closed PTFE containment in order to reduce the oxygen flux. At the moment qualitative results were obtained. In these conditions it was found uniform corrosion in the steel samples.

Improvement of commercial lead corrosion resistance in groundwater

Binary lead alloys with tin, antimony and bismuth have been tested in synthetic groundwater and seawater at 60 and 75°C by electrochemical and long term weight loss tests. It was found that lead-tin alloys with tin content of 3.5% or higher have a better corrosion resistance than commercial lead and that Pb–Sb and Pb–Bi alloys.

Lead corrosion products characterization

Corrosion products developed on commercial lead in groundwater with and without chloride at 75°C were characterized by X-ray diffraction technique. In both environments, lead carbonate and basic lead carbonates were detected.

Taking into account the oxygen reduction reaction current, it is possible to estimate the life prediction of the 10 mm thick carbon steel liner of the canister. If for conservative reasons the maximum current density is taken into account, which corresponds to few days elapsed time and with a high oxygen flux to the canister wall, a 0.926 mm y^{-1} uniform corrosion rate can be estimated. According to this result, the carbon steel liner will have an estimate life of 92.6 years. This value should be higher because the oxygen flux decays with time and therefore the corrosion rate should decay also. The extrapolation of short term tests, such as those in progress, to very long times, should be complemented with corrosion rates of archaeological artifacts. Nevertheless, there are limited ancient metallic artifacts (copper, lead, iron) whose corrosion rates could be evaluated and be useful for deep nuclear waste disposal studies.

On the other hand, short term corrosion techniques for life prediction must be re-evaluated for their usefulness. In general, for systems other than nuclear waste disposal, the goal of being able to compare life prediction versus actual performance is yet to be achieved.

CONCLUSIONS

These preliminary studies show that the oxygen flux towards the steel/buffer interface is not enough to sustain a pitting phenomenon on the canister steel external wall. Therefore it can be expected than this steel liner will last for decades after the repository has been sealed. Lead–tin alloys have a better corrosion resistance than commercial lead.

This work should be continued with the modeling the corrosion of the lead main barrier in order to predict its long term integrity . In this model, iron oxides from the former carbon steel liner as well as lead corrosion products, should be taken into account in lead corrosion mechanism.

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STUDIES OF THERMAL AND RADIATION EFFECTS ON WATER–ROCK SYSTEMS RELATED TO ENVISAGED ISOLATION OF HIGH LEVEL RADIOACTIVE WASTES IN CRYSTALLINE FORMATIONS OF THE UKRAINIAN SHIELD (UKRAINE)

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Abstract

In this work there are presented the general data on the study of thermal and radiation effects in minerals separated from rocks of the Ukrainian shield. These minerals (quartz, feldspar, amphiboles, apatite, biotite, kaolinite, etc.), exposed by doses 10^4, 10^6, 10^8 *G*y by Co^{60} source, were studied by the complex of physical methods. The special attention was given to the study of radiation defects formation (electron-hole paramagnetic centres, OH– groups destruction, changes in a charge state of ions) in a mineral structure. The mentioned radiation defects were used in the extrapolation method.

The connection between structural peculiarities of minerals, containing uranium and thorium, and processes of their metamyctization is considered. It is demonstrated that the minerals, which have large channels or interlayer spaces in their structure, as a rule, is not metamyct. Using the spectroscopic methods of the extrapolation it is shown, that the crystalline massifs, which have not detectable amounts of hydroxylcontaining minerals (biotite, amphibole, etc.) and ions Fe^{2-}, are perspective for long-lived radioactive wastes (RAW) dumping. As it follows from obtained results, the rocks, containing minerals with OH- groups and gas–liquid inclusions, should be considered as the "mineral-water" system.

INTRODUCTION

The problem of the long-lived radioactive wastes dumping in geological formations lays down a number of requests to rocks, where storage is planned to be built. One from these requests is the thermoradiactive stability of minerals and rocks made up the bulk of the storage as the engineering construction. First of all it concerns the stability of physical and chemical properties of minerals and rocks during a time of their contact with radioactive wastes.

It should be noted that in the literature there is a great quantity of data on the study of influence of various sources of irradiation to physical and chemical properties of minerals and rocks. The nature of the formation of various types of radiation defects in minerals has been investigated in detail. The methods used in dating and dosimetry [1] have been developed around obtained results. As to the methods of the prognosis (the extrapolation) by which one can predict the behaviour of physical and chemical properties of minerals and rocks during long times of their contact to RAW, they are practically not present.

In the work the study of thermal and radiation effects in minerals separated from rocks of the Ukrainian shield has been performed. The minerals (quartz, feldspar, amphiboles, apatite, biotite, kaolinite, etc.), exposed by doses 10^4, 10^6, 10^8 Gy by Co^{60} source, were studied by the complex of physical methods. The special attention was given to the study of the radiation defects formation (electron-hole centres, structural OH-groups destruction, and changes in a charge state of ions) in mineral structure.

The connection between structural features of minerals, containing uranium and thorium, and processes of their metamyctization is considered.

The main aid of this work was the use of results of the investigation of radiation defects in minerals for the extrapolation methodology. Such methodology can be used for the solution of the following problems:

(1) The choice of crystalline massifs which are suitable for RAW dumping.

(2) The predict of the thermoradiactive stability of materials which can find use in sealing of spent nuclear fuel and also that for backfill.

EXPERIMENTAL

The investigated samples are represented by minerals separated from rocks of the Ukrainian shield (quart, feldspar, amphiboles, apatite, biotite, kaolinite etc.). The minerals were subjected to the chemical and X-ray structure analyses.

The specimens were exposed by γ-irradiation doses 10^4, 10^6, 10^8 Gy from Co^{60} source with 13.8 Gy/sec intensity. After that they were investigated by the methods of electronic paramagnetic resonance (ESR), nuclear magnetic resonance (NMR), IR-spectroscopy, nuclear gamma-resonance. The main attention was given only to those radiation defects, which concentration could exceed critical under treatment. Such concentrations, above which the fundamental changes of physic-chemical properties of a mineral could be observed, were selected as critical.

From this viewpoint the following radiation defects in minerals are of principal importance: electron-hole centres, structural OH-groups destruction, changes in a charge state of ions.

Quartz – SiO_2. Under g-irradiation in the quartz structure there appears a number of radiation defects varying both concentrations and thermostabilities [3]. E-centres (O_2^{3-}) are of particular interest. The availability of a vacancy in the quartz structure results in the capture of a hole by two ions of oxygen with formation of O_2^{3-}-centre. The concentration of these centres in a specimen upon g-irradiation was determined from the intensity of the characteristic band (g = 2000) in ESR spectrum of this sample. Figure 1 shows the E-centres concentration as a function of exposing dose. The dependence of the E-centres band's intensity in ESR spectrum on an annealing temperature of a sample is presented in Fig. 2. The specimen was heated during 20 min at each temperature.

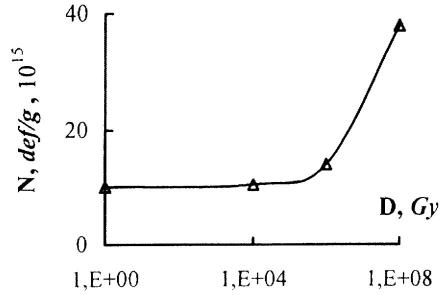

Fig.1. The influence of g-irradiation upon the E-defects formation in quartz.

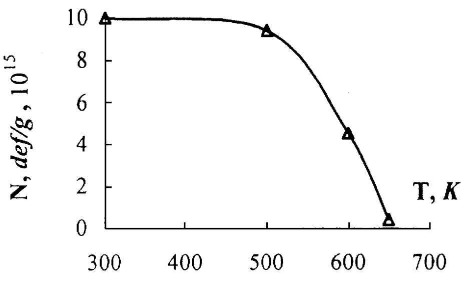

Fig.2. The dependence of E-defect quantity in quartz on the annealing temperature.

Feldspar – $KAlSi_3O_8$. In feldspar there was studied the E_1-centre that was the radical SiO_3^{3-}, in which the electron is captured by an oxygen's vacancy [4]. Figure 3 illustrated the concentration of E_1-centres versus an exposing dose by ESR data. The dependence of an amount of E_1-centres on an annealing temperature of a sample is displayed in Fig. 4. The specimen was heated during 20 min at each temperature.

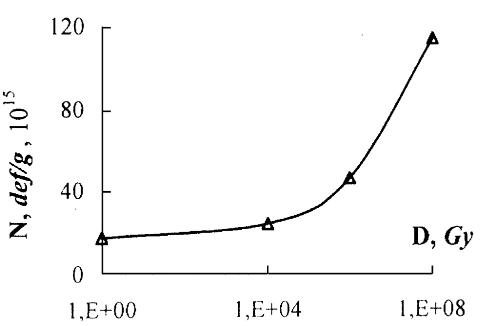

Fig.3. The influence of γ-irradiation on the E_1-defect formation in feldspar.

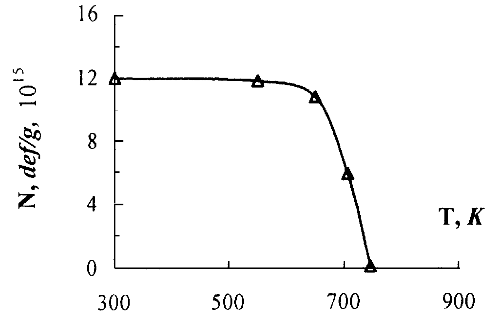

Fig.4. The dependence of E_1-defect quantity in feldspar on annealing temperature.

Amphibole – $Ca_2(Mg, Fe)_5[Si_8O_{22}](OH)_2$. The influence of g-irradiation to the oxidation processes of ions Fe (Fe^{2+}, Fe^{3+}) in hornblende was investigated. In such structure the iron ions are located in M1, M2, M3 positions. Located in these positions Fe ions respond variously to g-irradiation [5]. In the present work the Fe ions state in the M1 position was controlled. Under g-irradiation the Fe^{2+} amount reduction with the Fe^{3+} one increase is observed (Fig. 5). The ion concentration was determined by the method of nuclear gamma-resonance.

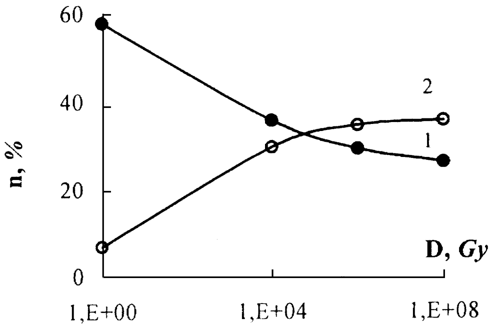

Fig.5. The relative amount of Fe ions (**n**) in amphibole *vs.* dose **D** (1 - Fe^{2+}, 2 - Fe^{3+}).

Biotite – $K_2(Mg,Fe)_6[Al_2Si_6O_{20}](OH)_4$. Under g-irradiation in the biotite structure the Fe^{2+} ion oxidation with OH-groups destruction is noted [5]. Since 10^6Gy dose the detectable iron oxidation is found. By nuclear gamma-resonance data the velocity of iron oxidation in 1 g biotite is equal to $3\cdot10^{13}$ ion/sec.

Kaolinite – $Al_4[Si_4O_{10}](OH)_8$. In kaolinite under g-irradiation influence the structural OH-groups destruction proceeds [2]. The velocity of OH-groups disruption was determined by the dependence of an amount of destroyed OH-groups on the value of an exposing dose. The control over the destroyed OH-groups amount was carried out both the weight losses upon igniting and the methods of NMR and IR-spectroscopy.

Apatite – $Ca_{10}(PO_4)_6(F, OH)_2$. Under g-irradiation there arises a number of radiation defects (PO_3^{2-}, F^--O^--F^-, O^--OH^-, etc.) in apatite. In present work the most intensive paramagnetic centre F^--O^--F^- in ESR spectrum of apatite was chosen to the extrapolation.

THE EXTRAPOLATION METHOD

In the present work there is used the extrapolation method based on the analysis of radiation defects, which appear in mineral structures under g-irradiation. The following radiation defects were analysed:

(1) Electron-hole paramagnetic centres;
(2) Structural OH-groups destruction;
(3) Changes in a charge state of ions in mineral structures (for example, transition Fe^{2+}, Fe^{3+}).

It is need to mention briefly the description of the extrapolation method for each from these cases.

1. The use of results of the study of electron-hole centres in the extrapolation. It is known that, depending on the radiation source type and the dose magnitudes, in substance there arise radiation defects of a various kind, which models and nature are described in the literature in detail enough. The defects in a paramagnetic state are convenient to investigate by the method

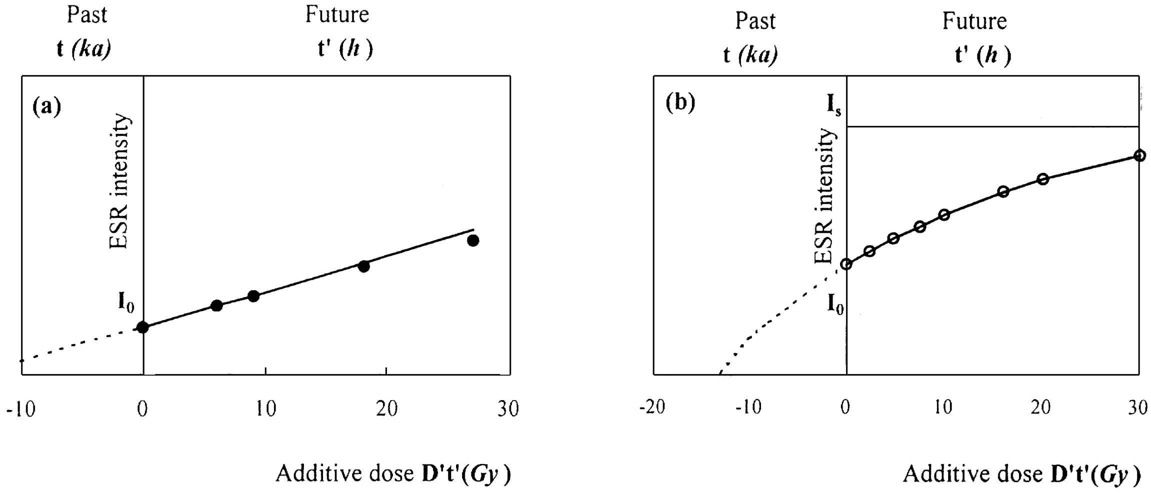

Fig.6. An additive dose method. The enhancement of ESR signal intensities by an additive artificial irradiation with the doze **Q** [*Gy*] (**Q=D't'**). The **ED** is obtained by the extrapolation to the zero ordinate. The additive irradiation is a kind of *"time machine"* to proceed an event to the future. (a) A linear growth of the signal intensity and least-square fitting to a line. (b) Saturation growth fitting to a saturation curve of Eq.(2).

of electronic paramagnetic resonance (ESR). This method is rather sensitive: so, for example, in a number of cases, by ESR the defects concentrations from the magnitudes $\geq 10^{10}$ g^{-1} can be determined (usually in minerals their amount can achieve 10^{20} and more defects in 1 g of substance).

The methodology, which is used, for example, in archaeology for the determination of a subject age or in retrodosimetry [1], has been laid the foundation for the extrapolation. Its essence lays in the construction of the dependencies of radiation defects formation in a substance on g-irradiation dose. As an example such curves borrowed from [1] are indicated in Fig. 6. The dependence (Fig. 6, a) is described by the equation

$$\mathbf{I = I_0\,(1 + D't' / ED)} \tag{1}$$

and the another (Fig. 6, b) – by the equation

$$\mathbf{I = I_s\,[1 - \exp\,(- Dt + ED) / SD)} \tag{2}$$

where

I – the relative intensity of the characteristic band in ESR spectrum of a sample;
I_0 – the relative intensity of the same band in ESR spectrum of an initial sample;
D – the intensity of g-ray source;
t ' – the time, during which the source influences on a sample;
D't' – the dose absorbed by a sample;
ED – the dose absorbed by a sample before an artificial exposure;
SD – the absorbed dose, upon which the saturation of defect formation proceeds.

It is easy to see that the presented equations described the experimental curves have the parameters, using which not only the age and the dose collected by a sample in nature but also the time, during which to a sample will not change essentially its physico-chemical properties at the certain dose, can be determined.

2. The use of data of the structural OH-groups destruction in a mineral under γ-irradiation. It is known that minerals containing OH-group under temperature can lose them owing to the dehydroxylation effect [2]. The OH-groups destruction follows by the formation of water or hydrogen molecules, which will diffuse outside the sample. The same effect is observed under g-irradiation effect. These data were used in the extrapolation methodology. Its essence lays in the determination of the OH-groups destruction velocity in 1 g of mineral subjected to a given exposing dose. For this purpose the experimental dependence of the destroyed OH-groups amount on an exposing dose must be obtained. The OH-groups amount was determined by the methods of weight losses, proton magnetic resonance (PMR) and IR-spectroscopy.

3. The use of data of the changes in a charge state of ions made up the bulk of a mineral structure, for example, Fe^{2+}. On exposure to temperature or γ-irradiation the fundamental changes of the iron ions valency result from its oxidation in a mineral. By the experimental dependence the iron oxidation velocity in 1 g of mineral under the g-irradiation source can be determined. With a knowledge of this velocity, one can determined the time, during which upon g-irradiation in a considered mineral there will not happen the fundamental changes influencing to its physico-chemical properties. The control over the charge state of iron ions was carried out the nuclear gamma-resonance method.

RESULTS AND DISCUSSION

In Table 1 there are listed the results of the extrapolation short-term experimental observations to time (**T**), after which the mineral physico-chemical properties can vary over 10% on exposure to γ-irradiation. In order to **T** calculation it was supposed, that the parameters of g-irradiation source with 1000 R/hour intensity would not change. The velocity (**V**) of the defect formation in a mineral structure was determined from experimental data.

It is evident from Table 1 that iron and hydroxylcontaining minerals are less stable upon g-irradiation. The smaller sets of electron-hole centres have been found to form in layered minerals. Uranium and thorium containing minerals were analysed in order to elucidate of the structural peculiarities influence the radiation defects formation. The availability of g-emitters in a structure of these minerals stimulates the metamyctization processes. However not all uranium and thorium containing minerals are subject to such processes. The performed analysis has demonstrated that, as a rule, the minerals, which structure has large channels and interlayer space, are not metamyctical. Most likely, the various type molecules located in indicated hollows are responsible for this. These molecules accelerate the radiation defects recombination. This fact is verificated of the montmorillonite structure, in which, by ESR data, the g- irradiation does not generate the detectable concentrations of paramagnetic centres [7].

However, it should be noted that the used extrapolation methodology is not yet perfect. First of all, the variations of radiation defects concentration must be checking immediately on exposure to g-irradiation and heat. It should also be taken into account all radiation defects, including that which are detected by the luminescence methods. Besides the processes of the exchange in the OH-chain were not taken into consideration when a parameter **T** was determined. Earlier [8] it was demonstrated that in a system „clay mineral - heavy water“ there was the exchange between heavy isotopes of hydrogen and protons of structural OH-groups in normal conditions and under g-irradiation.

Table 1. Extrapolation data

Mineral	**Quartz**	**Fieldspar**	**Apatite**	**Amphibole**	**Biotite**	**Kaolinite**
Defect type	O_2^{3-}	SiO_3^{3-}	$F^- - O^- - F^-$	$Fe^{2+} - Fe^{3+}$	$Fe^{2+} - Fe^{3+}$	OH^-
$\mathbf{N}^{\mathbf{max}}$, def/g	$1 \cdot 10^{22}$	$1.2 \cdot 10^{22}$	$0.6.10^{21}$	$0.3 \cdot 10^{21}$	$1.9 \cdot 10^{21}$	$9 \cdot 10^{21}$
V, def/g.sec	$0.3 \cdot 10^{10}$	$1.4 \cdot 10^{10}$	$0.2 \cdot 10^{10}$	$0.2 \cdot 10^{14}$	$0.3 \cdot 10^{14}$	$0.6 \cdot 10^{13}$
T, years	$5 \cdot 10^{7}$	$1.35 \cdot 10^{7}$	$7 \cdot 10^{7}$	$1.5 \cdot 10^{3}$	$1 \cdot 10^{3}$	$5 \cdot 10^{3}$

CONCLUSIONS

(1) It has been shown that the complex of spectroscopic methods can be successfully used in study of the processes of the radiation defects formation in minerals (rocks) for the development of the methodology of the extrapolation short-term observations to a period of long-lived RAW dumping.

(2) That rocks which minerals do not contain appreciable quantities of ions Fe^{2+} and OH-groups have been demonstrated to be perspective for long-lived RAW dumping.

It was found that extrapolation to long periods is a complex problem, and contributions from geological, chemical, physical and biological sciences are required.

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THE INFLUENCE OF DISCONTINUITY INTERFACES ON PHYSICAL, CHEMICAL AND MECHANICAL PROPERTIES AND THE BEHAVIOUR OF REPOSITORY BACKFILL MATERIALS (CZECH REPUBLIC)

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Abstract

Safe disposal (isolation) of high radioactive waste requires solving many non-standard engineering problems which are complicated due to the demand of reliability of underground repository construction with respect to long term safety. Required durability of most engineered structures is about 10–100 years. Proposed underground repository construction must guarantee the demand for safe disposal of highly radioactive waste for 100 thousand to 1 million years.
Extrapolation methodologies are developed and applied on findings of experimental research. One of the techniques used in geotechnical sciences to determine data needed for the extrapolation the cyclical impact of different processes. Repeated impact of the same action or diversifying the different actions can accelerate some processes which are slow at normal conditions. Long term cyclical impact of moisture on a section of the barrier system (loaded by temperature) may cause changes of the quality of properties, such as permeability, sorption capacity, thermal conductivity and swelling capacity.

INTRODUCTION

In the Czech Republic high-level radioactive waste will be, most probably, stored in a deep underground repository situated in granite medium. Bentonite will be used as a basic material of engineered (geotechnical) barrier. The type of the physical consistence of bentonite (powder mixture, pellets, prefabricates with high volume density) is subject of research in the Czech Republic and abroad.

The Czech Republic belongs to the countries with extensive deposits of bentonite. Due to the genesis of bentonites, all deposits are similar to each other. There are magnesium–calcium bentonites or calcium–magnesium bentonites. Sodium bentonites are not found at all. In the Czech Republic there are about 50 sites where bentonite can be extracted. Due to the fact that the construction of a deep underground repository presumes the consumption of approximately 100,000 m^3 of natural bentonite, these amounts may be supplied by practically any site. Therefore, selection of the best bentonite extraction site bases on tests determining which raw material will provide the most suitable properties.

The only plant in the Czech Republic which is presently dealing with the extraction and processing of bentonites is the Obrnice plant (North Bohemia). 90% of its products are aimed for foundry purposes. The rest are construction or geological bentonites of G series. Industrial bentonites are produced raw, granulated or grinded.

The research of engineering barrier based on bentonite was started in the Centre of Experimental Geotechnics – Czech Technical University in co-operation with Radioactive Waste Authority and Nuclear Research Institute at Řež in 1997. Three parts of research were defined:

- basic research on bentonite based materials (natural and industrial bentonite)
- research of discontinuity fault impact to barrier´s behaviour
- research of barrier behaviour (cyclically loaded by temperature and moisture).

EXPERIMENTAL

Basic research of bentonites

The basic research of material (which will be used for multibarrier system construction) represents the considerable part of the whole research. The natural analogues research and the results of research applied on "candidate" material had proved that materials based on bentonite are the most suitable basic materials for engineering barrier construction of underground repository. It was shown that the durability of compact bentonite is approximately hundred thousands years. On the other hand it is estimated that the durability of bentonite injection mixtures amounts only to several thousands years. Durability of cement or concrete materials is considerably shorter.

The basic functioning of the barrier will be the prevention of radionuclide propagation. From the geotechnical point of view this functioning is affected especially by following properties:

- low permeability ($k = 10^{-9} - 10^{-14}$ m/sec)
- high sorption capacity (preventing radionuclide propagation)
- good thermal conductivity (diversion of heat from the source)
- swelling capacity ("self-healing" capacity)
- plasticity (moisture range between w_L and w_P).

A special unusual demand for all properties is:

- extreme rheological stability of the material.

Rheology (rheological properties, behaviour) is defined as the time impact on the change of geotechnical parameters. It is mostly interpreted as the change of parameters in time with one parameter remaining constant. An example is the changes of deformation in time under a constant load. The demand for extreme rheological stability of barrier materials represents the invariability of material properties and behaviour for the long time (the time of dangerous activity of disposed waste). For this period the barrier material must provide such properties (impermeability, swelling capacity, thermal conductivity etc.) which ensure safe function of the system. Material degradation caused by insufficient rheological properties could be:

temporal (fatigue), appear for material e.g. by increase of permeability, reduction of swelling capacity, reduction of thermal conductivity as function of time, impact of cyclical loading, etc.;

thermal, shown by the creation of irreversible changes of the material when crossing the certain thermal limit. Geotechnical parameters are commonly changed continuously with increasing temperature. If certain thermal limits are exceeded mineralogical changes occur. Then, geotechnical parameters also change according to these mineralogical changes. Irreversible changes of particular geotechnical parameters could occur at different thermal limits.

The problems defined above caused the demand of broad research of the materials based on bentonite. The goal of this research is to find a compromise in the composition of the selected material from two points of view: the potential of the raw material, and its required properties including the rheological stability. Resulting prescription will be affected by the required functioning of the material in the multibarrier system. That means, if the material (depending on the place of usage in the repository) has to provide absorbing, filling, sealing or construction properties.

Experimental research has been started with 4 natural bentonites and with one industrial bentonite of G type.

With regard to the fact that the research on bentonites has been orientated to foundry purposes in the Czech Republic by now, Centre of Experimental Geotechnics defined the basic set of geotechnical tests for bentonite and for mixtures of bentonite with filling materials (sand, graphite, grinded limestone).

In the course of 2 years the model of the behaviour of Czech bentonites for usage as engineered barrier was described. More than 500 laboratory tests and measurements of basic geotechnical parameters of raw materials were carried out.

Research on discontinuity faults impact

The usage of compacted prefabricates especially as buffer part of a multibarrier system (at the contact with containers) seems to be very probable. Powder or granulated bentonite based materials will be used for sealing and filling purposes.

CEG was concerned with two problems: the optimal composition of prefabricates´ material and technology of their manufacture and with the problem of discontinuity faults impact on the whole system behaviour. It is possible to find several different types of discontinuity faults:

Discontinuity faults originated from manufacturing of multibarrier system parts

Cracks in bentonite prefabricates which occur during insufficient technology or non adequate storage belong to this group.

Discontinuity faults originated from multibarrier system construction

These faults can rise as joints between prefabricates during the barrier construction. Regarding the experience from underground structures, it is very difficult to avoid discontinuities at the boundary of two different materials (lining – rock mass). In multibarrier system there will be contact areas between containers and barriers, between barrier layers (buffer, filling, sealing), between barriers and lining (construction layer) or between lining and the natural (geological) barrier. Discontinuity faults also may occur atn contact areas of the same material due to application of different technologies (e.g. layers which differ in compaction).

Discontinuity faults occurring during long term operation of underground repository

Such faults are cracks caused by exhausting the strength parameters of barrier, unvarying (local) loading, temperature loading, volume changes (swelling, shrinkage, thermal tensibility), cyclical impact of different effects, rheological instability of the system, etc.

Every type of discontinuity faults has different characteristics and may cause special safety relevant problems. The problem of discontinuity fault impact on barrier behaviour has not been systematically solved yet.

One of the hypothetical possibilities of discontinuity fault forming (as an irreversible effect) is a cyclical impact of moisture and temperature on prefabricated barrier. The subject of this kind of research was a result of the following consideration: If the joint between bentonite prefabricates comes into contact with water, the prefabricates' surface swells, the joint is sealed resulting in a practically local homogenization of the prefabricated barrier. The intensity of the swelling reaction by water will diminish with growing distance from the joint. Due to low permeability of the material, the rate of this action's progress will come practically to a stop after some time. If the water flow stops at this point and afterwards the joint is affected only by the heat spreading from HLW, the joint will dry up, if no additional moisture is supplied: the homogenised joint will be disturbed by cracks due to the shrinkage (drying up). Thermal load may re-open the cracks. After some time, this process will come to rest again. The existing cracks, however, may gradually develop into a system of channels through which water may penetrate over larger distances. These passages can be clogged again by the repeated impact of moisture. Thus, theoretically, a situation may occur that so long as joints are subjected to cyclic „loading“ by moisture impact and heat, water may penetrate directly to the containers. By these migration paths radionuclides may overcome the engineering barrier, enter the natural barriers and may migrate further on to the biosphere.

Experimental simulation the discontinuity fault model

The described problem is simulated by a physical model constructed first in steel boxes using compacted bentonite and a vertical joint (discontinuity fault) backfilled with fine-grained sand. The joint is moistened by water and the development of swelling pressure is continuously measured. After the maximum measured pressure values is reached and stabilised, water flow is interrupted and the joint is subjected to drying processes due to influence of heat. After shrinkage is finished, the process of moistening the joint is restarted. By the created cracks the contact surface increased causing a significant increase of the maximum swelling pressure already in the second cycle .

Experiment using a physical model of a prefabricated barrier

A further step in the investigation of these problems is the implementation of an experiment using a smaller physical model — a bentonite prefabricated barrier stand. The stand is backfilled with building blocks with dimensions of 100 × 100 × 35 mm, made of industrial bentonite or of the mixture of industrial bentonite of G type (60%) and quartz sand (40%). The blocks are made by pressing in special moulds to reach a volume density of 2000 kg/m^3. The bottom part of the stand was equipped with heating elements reaching a maximum temperature of 300^{o}C, while a system of watering devices for the discontinuity faults is mounted on the upper side of the stand. Two walls of the stand have been designed flexible providing allowing 2D measurements of the swelling pressure (in two directions – vertically and horizontally). By means of flexible walls the pressures are transmitted onto hydraulic pressure cells. The front wall consists of special glass resistant to high temperature and pressure. Temperature sensors are sited inside the barrier. All measured data (temperature, swelling pressure, deformations) are continuously recorded by a PC central measuring unit with automated data reading in adjustable ranges of 5 sec–99 hours. The experiment No. 1 was launched in December 1997 and was finished in June 1998. Experiment No. 2 started in February 1999 and it is supposed to be finished after 12 months (January 2000).

EXTRAPOLATION METHOD

Due to the required durability of the underground repository the extrapolation of experimentally obtained results from short term tests to long term validity is necessary. The verification of the extreme rheological stability (behaviour of engineering barrier) belongs to the most complicated parts of the research on safe disposal of highly radioactive wastes.

In the scope of research performed in this CRP the cyclical application of chosen impacts (temperature, moisture) was used to accelerate the degradation of bentonites. In geotechnics the cyclical loading belongs to the most widespread methods of determining the rhelological stability of parameters. With regard to the required validity of research results (invariability of parameters and system´s behaviour for hundred thousands years) which is extremely different from common engineering problems, it is necessary to use this tool (cyclical repeating phenomenon) very careful.

RESULTS AND DISCUSSION

Within the scope of bentonite behaviour research it is necessary to investigate also the basic geotechnical properties. Bentonite has been used mostly for foundry purposes by now. In civil engineering it was used only to a minor extend, therefore also research is not completed. It is necessary to carry out basic laboratory tests and experiments. Results of these tests will credibly define the input parameters of the barrier's material. Parameters determined within this CRP are sufficiently reliable to be used for modelling the problem of multibarrier system. Without knowledge of material's behaviour it would be impossible to start physical modelling of the problem. More than 500 laboratory tests (most of which are very expensive) of natural and industrially modified bentonites has been carried out in the Centre of Experimental Geotechnics by 1996.

The results of research determined in the small physical model (steel boxes with compacted bentonite) considerably demonstrated the danger of gradual spreading of discontinuity faults. Radionuclides could migrate through these faults by the simultaneous (gradual) increase of swelling pressure.

Investigation of the behaviour of a prefabricated bentonite wall under cyclically loaded heat resulted as follows:

- Joints between prefabricates locally became wider due to the impact of repeated thermal load.
- Volumetric changes by thermal load of the prefabricates caused stress development, which resulted in forces especially in the narrow gap between prefabricates. At a certain thermal degradation of material a development of secondary discontinuity faults was observed.

Both findings promote the hypothesis that new paths for moisture transport may be created.

Results of volumetric thermal expansion measurement showed that the course of temperature does not correspond to volumetric changes of the material. These changes which continue even after stabilization of temperature have to be studied and verified in the future.

Coefficient of thermal conductivity of natural bentonite is in the range between 0.2 and 0.4 $Wm^{-1}K^{-1}$, values for prefabricates are found to be 1.2 to 1.4 $Wm^{-1}K^{-1}$. The value of the heat conductivity coefficient depends on the initial water content and on the temperature for which the material is tested. The value of the thermal conductivity coefficient extremely drops with increasing temperature (down to 60% of the initial value) and drops also with decreasing water content. Decrease of thermal conductivity is also caused by originating more discontinuity faults. These findings can be interpreted by the possibility of the development of a different thermal conductivity. Close to the containers the thermal conductivity will decrease even in the initial state and heat removal from the container will be impeded.

Investigations were directed to a barrier load only by temperature so the hypothesis on possible water penetration to the container was not demonstrated. Formation of new discontinuity faults does not disprove the hypothesis.

CONCLUSION

Performance of research presented above needs a lot of time and money. The research is not yet finished, it is urgently necessary to continue. Findings do not indicate reasons to change the initially defined programme.

- Thermal cycling of the barrier materials
- Cyclic wetting of the barrier materials
- Combined effect of thermal load and wetting on joints between blocks
- Determination of impacts of the cyclic load in terms of creation of pathways for water.

There is a need to concentrate work on determining the conditions for which irreversible changes of geotechnical parameters of the barrier may occur, that means to emphasise the research on rheological stability of the materials.

Common errors of performed research is attributed to monodisciplinarity. There is a lack of work by teams of experts from different fields of science. This gap has to be closed in connection with chemical, geological, geotechnical, etc. aspects.

CONTACT-METAMORPHIC ILLITIZATION AND RELATED CONSEQUENCES FOR THE FUNCTIONING OF BACKFILL BARRIERS IN HIGH LEVEL RADIOACTIVE WASTE REPOSITORIES (SOUTH AFRICA)

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Abstract

A clay barrier, consisting of smectite, is common to most disposal designs for HLW repositories. Concerns are that elevated temperatures and long time periods may alter the two properties, the barrier is employed: a high swelling as well as cation exchange capacity (CEC). A "natural analogue" approach has therefore been attempted to predict smectite characteristics and stability in relation to time/temperature. Following investigations were performed in order to determine changes in swelling capacity and CEC:

(1) Conversion of smectite to other clay minerals.
(2) Changes in the layer charge characteristics of the clay minerals.
(3) Swelling potential measurements of the smectitic interlayer.

Smectite was thermally unstable and transformed into illite via illite/smectite interstratifications (I/S) and chlorite at temperature exceeding about 100°C. The swelling potential was directly related to the proportion of smectite. As a conclusion it can be stated that elevated temperatures (>70°C) result in the transformation of smectite into illite. For backfill purposes it is recommended that the clay content in the backfill barrier should be as high as technically possible and that mixing the bentonite with K-bearing minerals (granite) should be avoided.

INTRODUCTION

A multi-barrier design is most likely to become the standard reference concept for the disposal of high level radioactive waste all over the world. A clay engineered barrier forms an integral part of all proposed designs and the safety of a disposal site is strongly dependent on the functioning of this clay containment barrier, generally referred to as backfill barrier.

Bentonite (smectite) is considered the most likely component for the backfill barrier due to its dual properties: a marked swelling and a high cation exchange capacity (CEC). Swelling will limit access of water to the metal container and accordingly reduce corrosion, while a high CEC helps to retain radioactive nuclide, once they escaped the metal container. Any change in either of the two smectite properties will greatly retard the barrier's functioning.

According to a thermal model of a potential waste repository, the maximum temperature in a barrier material would initially be 200°C, later drop to 150°C and remain so for about 500 years. Smectite would therefore be exposed to these elevated temperatures over a time period of many hundreds of years.

Evidence from various low-temperature environments indicates that smectite is unstable at temperatures above about 70°C and transforms into illite through intermediate illite/smectite interstratifications (I/S; Velde, 1985). Random (R=O) I/S structures with about 30% illite form at a palaeotemperature of about 70°C, transform to R=I arrangements at temperatures of about 100–120°C and to R=3 I/S at 170–190°C. Discrete illite occurs at temperatures exceeding 200–220°C. This mineralogical change from smectite to illite is generally considered to be the most important diagenetic reaction in progressively buried shales. As illites possess neither significant swelling nor cation exchange properties, the overall result of the illitization would be that both the sealing and the radionuclide sorption capacity of the barrier would be greatly reduced. Any aspect, associated with thermal illitization, is therefore of fundamental importance to the long-time performance of backfill barriers in HLRW disposal.

Of particular concern in this respect is that rises in temperature may not only result in the transformation of part of the smectite into illite, but also in changes of the layer charge characteristics of the smectite, possibly long before any illitization takes place (Howard and Roy, 1985). This aspect is crucial for HLRW research, as the magnitude of the layer charge is a governing parameter of the swelling capacity and only low-charge smectites exhibit the type of osmotic swelling required in sealing materials (Slade et al., 1991). The mode of transformation may strongly affect layer charge characteristics of the smectite. The long-term stability of smectites in HLRW repositories can be construed by examining geological analogues, which are of particular relevance with respect to the role of time, which cannot be simulated in laboratory experiments.

It was the objective of the present study to:

(a) Establish the smectite-to-illite conversion using samples from the contact-metamorphic sections in the vicinity of minor dolerite sills where smectitic sediments had been subjected to elevated temperatures of short duration.
(b) Determine potential changes in layer charge characteristics of the smectric interlayers in I/S in relation to stacking.
(c) Determine the swelling potential of the smectite interlayer in relation to stacking order, layer charge and organic matter content.

Geologically, the sedimentary rocks of the Great Karoo Supergroup of the Republic of South Africa constitute the ideal material for studying time–temperature dependent smectite illitization, as in this strata smectite-dominated sediments were subjected to elevated temperature of vastly different degrees and durations due to the basin's complex thermal history. Three different thermal regimes can be discerned, which have singly or collectively contributed to the present thermal maturity levels (Bühmann, 1992; for summary):

(a) Burial diagenesis in connection with geosynclinal subsidence. Burial-related temperatures increase from about 70°C in the north of the Karoo Basin to more than 270°C in the south-west.
(b) Contact metamorphism in the vicinity of igneous intrusives. the emplacement of dolerite dykes and sills resulted in local thermal events of relatively short duration, geologically speaking. Sills vary in thickness from a few cm to several hundred metres and the contact metamorphic sections extend to about 1–1.5 time the sill thickness (Bühmann, 1991).
(c) A high heat flow associated with an extensive tectonic lineament areas towards the east of the basin.

Post-burial modifications are controlled by uplift and erosion. Erosion has removed up to 5000 m of sediment in the southwesternmost part of the basin and only a few 100 m in the northernmost part.

The various litho-stratigraphic Karoo subunits are the upper Carboniferous glaciogenic Dwyka Formation, Ecca Group, Beaufort Group and the Jurassic Drakensberg Group, formerly called Stormberg Group.

EXPERIMENTAL

Numerous borehole cores have been drilled through Karoo strata in connection with the exploration for coal, petroleum and precious metals. Some cores have been retained as representative and are available to researchers from the Council for Geosciences. These cores may represent the ideal geological analogue for construing the functioning of the backfill barrier in HLW, provided a set of criteria is fulfilled.

(a) mineralogy: dominated by smectite
(b) temperature: 70°C–200°C range; this restricts core locality to the northern part of Great Karoo Basin
(c) lithology: mudstone
(d) time: "short", geologically speaking, i.e. contact metamorphic section of sedimentary sequences
(e) weathering: below the African Cycle 1 weathering influence (>ca. 50 m depth).

These predictions reduced the number of cores, suitable for the present study, considerably. Two cores have finally been selected.

Samples were gently ground and analysed for whole-rock and clay mineral composition and for b-order spacings by means of X-ray diffractometry (XRD). Random mounts were prepared by pressing the whole-rock powder against a rough filter paper. Samples were analysed by means of X-ray diffractometry. Analyses were carried out on a Philips XRD unit operated at 40 kV and 40 mA at a scanning rate of $1^o 2\ \theta$ per minute, using graphite monochromated Co Kα radiation. Oriented clay specimen were recorded from 2 to $53^o 2\ \theta$, whole rock random powder pattern from 3 to $75^o 2\ \theta$.

For the clay analyses different tests were performed:

Clay minerals were identified and quantified by means of X-ray diffractometry. Layer charge characteristics of smectitic interlayers were determined after solvation with ethylene glycol, glycerol, intercalation with dodecylamine, saturation with K and by applying the Greene-Kelly test. The swelling capacity was determined by recording final volumes of 100 mg clay in 20 ml of a dilute NaCl solution.

The whole-rock mineralogy differed in their non-clay versus clay content. All samples contained quartz, chlorite, mica and I/S, most samples plagioclase. Compared to the lighter coloured ash bands, the dark-grey to black mudstones had a significantly lower clay content, reflected in a (quartz + feldspar)/clay ratio which ranged above 1.7 compared to 1.1–0.1 for the light-coloured ash layers. Superlattice reflections were visible in the random pattern in ash, but not in mudstone layers.

Thermal illitization is observed for di-octahedral smectites only and most of the commercially available bentonites, which will be used as backfill material, are di-octahedral. The distinguishing factor between di- and trioctahedral minerals is the value of the b-parameter, which is determined from the 060 reflection. Di-octahedral mineral have a 060 reflection of 1.47–1.50 Å, tri-octahedral species of 1.50–1.54 Å. All clay minerals, present in the samples investigated, give 060 readings of ≥1.50 Å, confirming their position within the di-octahedral subgroup.

The <0.2 µm fractions also contained chlorite, mica and I/S. Chlorite and mica proportions were considerably lower than in the whole rock fraction, while I/S contents were higher. This finding is in line with results worldwide which document the concentration of I/S in the fine-clay fraction (Strodum, 1980). Small amounts of quartz were identified in all mudstone samples while it was absent from ash layers.

Potassium fixation was determined via the collapse of smectite layers to 10 Å upon saturation.

EXTRAPOLATION METHOD

The "natural analogue" approach has been attempted to predict smectite characteristics and stability in relation to time/temperature. Samples were derived from two borehole cores where a smectite dominated mudstone sequence had been intruded by minor dolerite sills which creating a geothermal gradient in their vicinity. Elevated temperatures were maintained over a time period which is of an order of magnitude similar to that required for reliable functioning of backfill material in HLW repositories. One of the cores also contained ash layers, which differed from the adjacent mudstones by a lower mica (K) and organic matter content and significantly higher clay proportions.

The objective of the extrapolation method from natural observation was to threefold:

(1) to establish the potential conversion of smectite to other clay minerals which lack a high swelling and CEC capacity,
(2) to determine potential changes in layer charge characteristics, a governing parameter in the degree of swelling, in relation to smectite proportions, stacking order and related palaeotemperature, and
(3) to determine the swelling potential of the smectitic interlayer in relation to stacking order, layer charge and organic matter content.

Such data provide the tool to develop models which allow the long-term extrapolation of the functioning of engineered bentonite barriers due to its swelling and cation exchange capacity depending on the thermal evolution of the repository and on the presence of potassium ions.

RESULTS AND DISCUSSION

Smectite was thermally unstable and transformed into illite via illite/smectite interstratificaitons (I/S) and chlorite at temperature exceeding about 100°C. The geothermal gradient in the vicinity of the sills is reflected a linear decrease in smectite proportions (40-5%) with increasing proximity to the sill contact, highlighting the importance of temperature as the dominant factor governing the degree of illitization. Other parameters of importance were clay content and related porosity/permeability and potassium availability. In ash layers the smectite proportions were markedly higher than in adjacent mudstone layers.

The smectite species, studied, consisted of an association of low-and high-charged varieties in all samples. The proportion of high-charge varieties was indirectly related to the smectite proportions in the I/S and, accordingly, palaeotemperature.

The swelling potential was directly related to the proportion of smectite, as expected. The relationship between organic matter and osmotic swelling was inconclusive.

CONCLUSIONS

As a conclusion it can be stated that elevated temperatures (>70°C) result in the transformation of smectite into illite. The extent of illitization, however, is strongly and indirectly related to the clay content of the sediment and directly to the proportion of K-bearing minerals.

From the experimental findings it is obvious that the long-term functioning of a engineered barrier depends on temperature, clay content in the materials applied and on the absence of potassium ions. As high temperatures in a HLW repository cannot be avoided, it is recommended to provide the clay content in the backfill barrier as high as technically possible. Further on it is recommended to keep the potassium content sufficiently low. This means it makes no sense for long-term considerations to mix bentonite with K-bearing minerals as they are present in granite.

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STUDY OF MIGRATION OF RADIONUCLIDES IN CLAYSTONE CONSIDERED AS PROSPECTIVE MEDIA FOR NUCLEAR WASTE DISPOSAL (HUNGARY)

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Abstract

Sorption properties and the migration of ^{125}I, ^{60}Co, ^{85}Sr and ^{137}Cs have been studied in Boda Claystone. The experiments were performed at ambient conditions using equilibrated groundwater and at in situ conditions with pore water under100 bar. I was the most mobile element ($D = 10^{-9}$ to 10^{-11} m^2 s^{-1}). Cations migrate slower by one order of magnitude for Sr, and even more for Co and Cs. In order to extrapolate the data the retardation of isotopes relatively to the groundwater was estimated from sorption (K_d) data. Under diffusively controlled transport conditions the elements considered are able to migrate only a few hundred meters within a period of 10^4 years from a repository.

SCIENTIFIC BACKGROUND AND SCOPE OF PROJECT

The aim of this contributing research was set to characterise a particular claystone from the aspect of the sorption and migration properties shown for certain characteristic radioisotopes. This characterization may contribute to a later evaluation in concern for disposal of high level nuclear waste into this geological formation in a far future. The study of the claystone may serve as a case study as well, and it is supposed that certain results of this particular study may provide more general conclusions which can be transferred for evaluating other geological media as well.

In claystone strong sorption of cations is expected since this media contains several cationic exchange sites. In contrast — as it is foreseen — sorption of anions could be less expressed, due to the lack of bonding sites.

In a simple approximation, spreading of radionuclides in a geological medium can be described so that the isotopes are transported primarily by the hydraulic flow of groundwater, and the isotope transport is retarded by sorption-desorption processes in comparison to the flow of groundwater.

$$v_{rad}/v_{gw} = 1 / \{ 1 + K_d \rho [(1-\varepsilon) / \varepsilon]\} \tag{1}$$

where v_{rad} and v_{gw} are the transport rates of isotopes and groundwater, respectively ρ is the density, and ε is the porosity of the rock.

As it is seen, here the extent of retention is primarily determined by the K_d values. It should be mentioned that the specific hydraulic circumstances of the final repository are not known yet (location is not selected). Thus, only the relative retention (w_{rad}/w_{gw}) values can be determined by means of K_d values at the present stage.

In the case of absence of the filtration (in equilibrium conditions, $v_{gw} \approx 0$) the previous approximation cannot be used. However, the effective diffusion coefficient values can be applied for the estimation of migration distances in this second instance.

In correspondence with these considerations, the scope of project covers sorption studies in one hand, and determination of diffusion coefficients in the other hand.

Sorption studies were performed on each isotopes studied (^{60}Co, ^{85}Sr, ^{137}Cs and ^{125}I). K_d value of iodine was found to be the smallest one by far, thus diffusion measurements were performed primarily by studying the migration of this anion in flow-less cases.

By determining the diffusion constant of iodine a minimal migration distance can be estimated which will probably be exceeded in real instances. Since this value is important, the diffusion constant of iodine was estimated by three different procedures: (i) from breakthrough across 13 mm thick slices of borecores equilibrated with groundwater, (ii) by determining the amount of iodine in solid bore cores (equilibrated with groundwater), and (iii) from distribution of iodine in "dry" borecores kept under conditions, similar to the geological ones (100 bar, 50°C).

EXPERIMENTAL METHOD

Experiments at ambient conditions

Distribution coefficient values (K_d) were determined at 1:10 solid to liquid ratio.

Sorption capacity was also determined by isotope dilution.

Migration studies were performed on borecores (with diameter of 46 mm, and thicknesses of 13 and 70 mm) in two-compartment migration cells. In the case of the 13 mm thick samples the activity concentrations were measured in the equilibrated solutions, and corresponding breakthrough curves were plotted. From the rate of the breakthrough [(c'' – c') / (t'' – t'), c is the concentration of iodine, t is time elapsed] the apparent diffusion coefficient can be determined:

$$D_{app} = (V \cdot d) / (A \cdot c_0) \cdot (c'' - c') / (t'' - t') \qquad (2)$$

(V is the volume of the inactive solution, d is the thickness, A is the cross section of the sample disk, c_0 is the concentration of iodine in the active compartment, and the slope is the rate of the increase of concentration of iodine after the breakthrough.)

In experiments with 70 mm samples the migration depth was determined directly, by measuring the activity in 3–4 mm thin slices cut from the end of the cores equilibrated with the solutions for c.a. one year. Determination of the apparent diffusion constant of iodine is more simple in this case (constant source, semi-infinite diffusion):

$$D_{app} = s \cdot l / (q \cdot t \cdot c) \qquad (3)$$

(s is the amount of iodine migrating, l is the characteristic length, q is the cross section, t is the time elapsed, c is the surface concentration at the end of the core).

Influence of microcracks and macroscopic fractures on the migration of isotopes were also investigated in separate experiments.

Experiments under in situ ("dry") conditions

These experiments were performed under high pressure (100 bar) on samples containing only the pore water present originally in the samples (ca 1 wt%). The respective isotopes were put in small volume (200 ?l) droplets to the end of borecore. After drying of the droplets the samples were placed to the high pressure cells and had been kept for different length (100–300 days) in them. After removal slices were cut and the migration distances were determined by direct activity measurements applying the appropriate (point source, semi-spherical diffusion) equation:

$$c = s\,(4\,\pi\,D_{app}\,t)^{-3/2}\exp(-r^2 / 4\,D_{app}\cdot t) \qquad (4)$$

(c is the actual concentration at distance r, s is the total amount of iodine).

The Boda Claystone and the groundwater related

At the end of the Experimental section a short description of the geological medium studied is appropriate. The investigated Boda Claystone is a typical metamorphosed sedimentary rock. The main mineral constituents are: quartz (ca. 10%), albite (20–40%), illite-muscovite (20–40%), chlorite (ca. 10%), calcite (<10%) and hematite (<10%). Typical values for the chemical constituents are: SiO_2 (≈ 50%), Al_2O_3 (15–20%), Fe_2O_3 (5–8%), CaO, MgO, Na_2O, K_2O (each 1–6%). The weight loss during firing is 1–4%. The pore volume is 0.5–2.3%, with pore diameters 10^{-3}–10^{-5} mm.

The claystone is a compact formation, no considerable filtration of water was detected in it (permeability [K]: 10^{-19}–10^{-15} m^2). The groundwater used in our experiments was obtained from the streams at the boundaries of the formation. A typical groundwater contains mainly Na^+ cation (250–350 mg/l), and HCO_{3-} (500–700 mg/l), SO_4^{2-} (≈ 100 mg/l) anions. The pH is ca. 8.5, the electric conductivity is ≈1 mS/cm.

RESULTS OBTAINED

Experiments under ambient conditions

Distribution coefficient (K_d) values

Fifteen samples were investigated, K_d values were determined after 32 h contact time, the carrier-free isotopes were dissolved in groundwater.

Table 1. Sorption of isotopes on claystone (K_d values)

Isotope	Cs-137	Co-60	Sr-85	I-125
Maximum	4900	5700	142	2.2
Minimum	526	1240	63	0.17
Mean	1554	3273	91	1.2

Sorption capacity measurements

Sorption capacity was determined by isotope dilution in groundwater. This value was determined only for Cs, since SO_4 and CO_3 precipitates are formed with Sr and Co respectively. In an average, 1 g powder of rock is able to sorb 1 mg Cs.

Migration studies: breakthrough in 13 mm thick samples

Breakthrough of iodine was followed in two-compartment cells for 350 days, by determining the increase of the activity concentration in the (originally inactive) solution opposite to the one, containing I-125.

From the slope of increase of the activity concentration $D_{eff} = 5 \cdot 10^{-12}$ m^2 s^{-1} was estimated.

Breakthrough for cations was hardly observed (their count rate was close to the background, thus numerical values were not determined). This proves that the respective diffusion constants for cations are significantly smaller than for iodine.

Migration studies: slices from 70 mm long borecore

70 mm long borecore cylinders were placed to migration cells; their end-planes were equilibrated with solutions containing the respective isotopes. After 60–120 days of storage 2–3 mm thin slices were cut from their ends, and the activities were determined directly in the slices. Radiation from the respective cations was observed only in the first slice, the 35.5 keV radiation of I-125 was detected in 3–4 slices. From the decrease of activity in depth, the apparent diffusion constant can be determined by assuming simple, one-dimension, uni-directional diffusion with constant strength of source. In average, $D_{app} = 10^{-9}$ m^2 s^{-1} was calculated. (This value is apparently larger than that determined from the analysis of breakthrough curves of 13 mm thick samples. The increase can probably be attributed to the filling up of pores during the experiment: these samples were not equilibrated with groundwater prior to the measurements, and partial evaporation of pore water might have taken place during the preliminary storage. Thus, the previous, smaller values seem to be more reliable.)

Influence of fractures and cracks on the migration rate

In certain samples the effect of presence of (macroscopic) fractures and (microscopic) cracks was also studied on the filtration and migration rate of isotopes. In general, no significant increase was observed in the migration rate. (As an interpretation, it can be mentioned that the 1–3% pore volume present originally in the sample provides probably ample space for the migration, the additional contribution from the cracks to this free volume is comparatively small.)

Experiments under in situ ("dry") conditions

200 μl droplets of solutions containing the respective isotopes were put to the ends of the sample borecore cylinders in patches of ca. 5 mm. After drying (and without any further wetting) borecores were put to the high pressure cells. After 118 days storage under 100 bar at 50°C slices were cut from the ends and the activities were determined. In this case, with certain neglections, semi-spherical diffusion was assumed with a constant amount of the diffusing substance starting from a point source. By these assumptions, $D_{app} = 6 \cdot 10^{-12}$ m^2 s^{-1}

was estimated from the measurements. This is almost the same value as was obtained from the breakthrough measurements. (Here empty pores were probably not present, due to the high applied confining pressure, thus the accelerating effect of pore filling on the migration of iodine was not observed.)

CONCLUSIONS

Sorption properties and migration of selected radionuclides (^{125}I, ^{60}Co, ^{85}Sr and ^{137}Cs) have been studied in Boda Claystone (in a prospective geological formation for spent fuel disposal). Sorption properties were characterised by K_d (distribution coefficient) values. For migration studies two types of experiments were performed: (i) at ambient conditions, samples were equilibrated with groundwater, and (ii) at in situ ("dry") conditions: with samples containing only pore water and kept under high pressure (100 bar). Effective diffusion constants were determined; the most mobile isotope is the iodine, with diffusion constants of 10^{-9} m^2 s^{-1}, and 10^{-11} m^2 s^{-1}, found in aqueous and "dry" experiments, respectively. Migration of cations is slower, (with ca. one order of magnitude for Sr, and even more for Co and Cs), and is affected also by the limited solubility of carbonates and sulphates formed with the anions present in the groundwater. With the presumption of filtration of groundwater, the retardation of isotopes can be estimated from sorption (K_d) data. Under steady conditions (without any transport of groundwater) the migration distance can be estimated from the effective diffusion constant values; a few hundred meter migration distance can be estimated for iodine (the fastest migrating isotope) during an expected operation time (10^4 year) of a spent fuel repository.

EXTRAPOLATION STUDIES ON DESORPTION OF THORIUM AND URANIUM AT DIFFERENT SOLUTION COMPOSITIONS ON CONTAMINATED SOIL SEDIMENTS

(MALAYSIA)

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Abstract

By means of batch desorption experiments the thorium and uranium desorption properties of contaminated soil sediments are investigated as a function of the effect of cations present in the groundwater. A phenomenological correlation between the desorption coefficient and the concentration of Ca and Mg in the water is determined.

$Kd_{Thorium} = -0.15849 \pm 0.03237 \log (Ca + Mg) + 5.06715 \pm 0.09106$

$Kd_{Uranium} = -0.11984 \pm 0.03237 \log (Ca + Mg) + 2.99909 \pm 0.09105.$

By these models the sorption/desorption behaviour of soils can be predicted phenomenologically as function of the groundwater composition.

INTRODUCTION

Significant quantities of ^{90} Sr radionuclides from Hanford sites burial sites, Washington, are seeping into groundwater and are entering into the Columbia river [1] The primary sources of groundwater contamination at the burial area are from certain disposal trenches. One of the reason for the observed increase in the concentration of the radionuclides is that the chemical composition of water flowing through the contaminated sediments has changed significantly and is now causing previously adsorbed radionuclides to desorb. Adsorption of the radionuclide is known to be quite sensitive to competing cations such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and H^{+}. Studies conducted shows that ion exchange of Ca and Mg for previously adsorbed Sr is responsible for the increases in Sr in certain monitoring wells [2] Elevated Na concentrations in the groundwater is also likely to cause desorption of Ca and other certain radionuclides from soil exchange sites, resulting in elevated Ca concentrations and certain radionuclides in the groundwater.

Desorption studies are needed to estimate the rate of transport of thorium and uranium in the event of groundwater since there is a potential for contamination of drinking water. Information on adsorption/desorption mechanisms of thorium and uranium helps to understand controls on both radionuclides concentrations in groundwater, and to predict the risk of thorium and uranium release in leachates from mining activity and radioactive wastes.

The purpose of the present study is to gain a better understanding of the desorption properties of thorium and uranium from contaminated soil sediments and how changes in groundwater chemistry can effect this properties. The competitive effect of calcium and magnesium cations on thorium and uranium desorption were conducted in batch type laboratory experiments. The results and K_d values calculated through equations described below make it possible to understand trends in concentrations of thorium and uranium in groundwater at disposal sites. From the results of adsorption studies previously and present desorption studies, a radiological impact assessment on a potential repository can be conducted using the distribution coefficient K_d values which is a very important parameter as input in a computer model tool.

EXPERIMENTAL

A series of batch desorption experiments have been conducted to determine the thorium and uranium desorption properties of a contaminated soil sediments as a function of equilibrating solution composition [3–7]. The soil sediments used were obtained from a potential disposal site. Prior to the desorption experiments, contaminated soil sediments were obtained by conducting adsorption experiments using actual radioactive aqueous wastes containing thorium and uranium on the sampled soil sediments. Equilibrium period was allowed for 14 days, and the contaminated solid sediments were removed by filtering through a 0.45 μm. filter and collected and air dried to be used in the desorption experiments. The contaminated soil sediments contained both adsorbed thorium and uranium radionuclides.

For the desorption experiment, ten (10) stock solutions of 500 ml were prepared with the concentrations of the major cations Ca, Mg and Na varying in the range 0.0 to 3.12×10^{-3} M, 0.0 to 2.5×10^{-3} M, and 0.0 to 3.12×10^{-3} M, respectively. All of the stock solutions its pH was adjusted to 6.70–7.00 with sodium hydroxide or hydrochloric acid. Each batch experiment was conducted in a 40 ml polycarbonate centrifuge tube. One (1) gram of the soil sediments were added into their respective tubes. Twenty (20) ml of spiked solution was then added into each tube. Duplicate experiments were conducted for each soil sample used. All the tubes were equilibrated for 14 days after being shaken at room temperature of 26°C. After the equilibration period, all the tubes were centrifuged at 4000 rpm for 1 hour to separate the solid and the solution. Solution samples were filtered through a 0.2 μm. filter and then 1.0 ml were collected. It was then acidified by adding approximately 100 μl of concentrated hydrochloric acid or nitric acid (6 M or 12 M).

Distribution coefficient K_d (desorption) were determined directly by measuring the concentration both in solution and in the sediment after the 14 day equilibrium period. The solutions were analysed for concentration (ppb) of thorium and uranium by using ICPMS method. Solid sediments were removed from each tube by filtering through a 0.45 μm. filter and then the sediments were allowed to dry. The solid sediments were analysed by the neutron activation method.

The distribution coefficient $K_d^{Th,\,U}$ was calculated as:

$$K_d^{Th,\,U} = \frac{\mu g/g\ (ppm)\ (Th,\ U)\ \text{in solid form}}{\mu g/ml\ (ppm)\ (Th,\ U)\ \text{in liquid form}}$$

Ionic strength which measures the total concentration of charge in a solution was calculated as:

$$I = 0.5\ \Sigma\ [m_i]z_i^2$$

where m_i was the molality or concentration (m) of the ith species of charge z_i [8]. The ionic strength parameter (I) was used to calculate the activity coefficient of each solution. At higher concentrations less than 0.5 M, the Davies equation was used to calculate activity coefficient γ, as this has been shown to better represent experimental data than other equations to be found in the literature [9, 10].

Thus the activity coefficient γ was calculated as:

$$\ln \gamma_i = -1.17\, z_i^2\, [(\sqrt{I})/(1+\sqrt{I}) - 0.2I]$$

and activity was calculated by use of the expression:

Activity (moles) = concentration (moles) × activity coefficient γ.

EXTRAPOLATION METHOD

From the experimental results obtained in the desorption studies, graphs of log K_d (desorption of thorium) and (desorption of uranium) were plotted as a function of the sum of the equilibrium of calcium and magnesium concentration in solutions (moles/L) for the contaminated soil sediments. Detailed statistical regression and variance analyses were performed for each batch experiment to yield values for the extrapolated desorption coefficient K_d for thorium and uranium radionuclides.

Thorium and uranium concentrations and major ion concentrations (Ca and Mg) data can be obtained from a network of wells. The data can be used as input to the extrapolated desorption K_d coefficient equation and extrapolated adsorption K_d coefficient equation [11] (from previous studies) to calculate K_d values for each radionuclides at a specific site.

Resrad computer code will be used to determine radiological impact assessment for the potential repository site using the most important parameters Kd values as input together with other site parameters. Appropriate use scenario and site specific parameters can be used so as to be realistic. The model will derive site specific guidelines for allowable residual concentrations of thorium and uranium in soil. Results from analyses of modelling will be able to calculate doses, risk and guidelines values. Performance and safety assessment of the repository system can be determined from the analyses and also used as an initial assessment to conduct screening assessment in order to determine a proper repository site.

RESULTS AND DISCUSSION

$K_d^{Th,\ U}$ (desorption) values for thorium and uranium were obtained for each of the batch experiments after examining desorption of thorium and uranium from the contaminated soil sediments at different solution composition. Experimental results proved to be reproducible and could be used with confidence to produce the K_d (desorption) equations for the soil sediments. The K_d (desorption) results were plotted in Figures 1 and 2 as a function of the sum of the equilibrium calcium and magnesium concentrations in solution for the soil sediments desorption of thorium and uranium, respectively. From both Figures, shows that thorium and uranium were desorbed from ion exchange sites and that Ca and Mg were effective competitors for these sites.

From the above short term experiments results, an extrapolated equation coefficient K_d for a specific site can be formed from different major ion (Ca and Mg) data, thorium and uranium concentrations. Table 1 lists the desorption coefficient K_d for soil sediments described by the associated best fit equations. Figures 1 and 2 show that good linear correlations can exist where the predicted data were used to calculate the associated best fit equations.

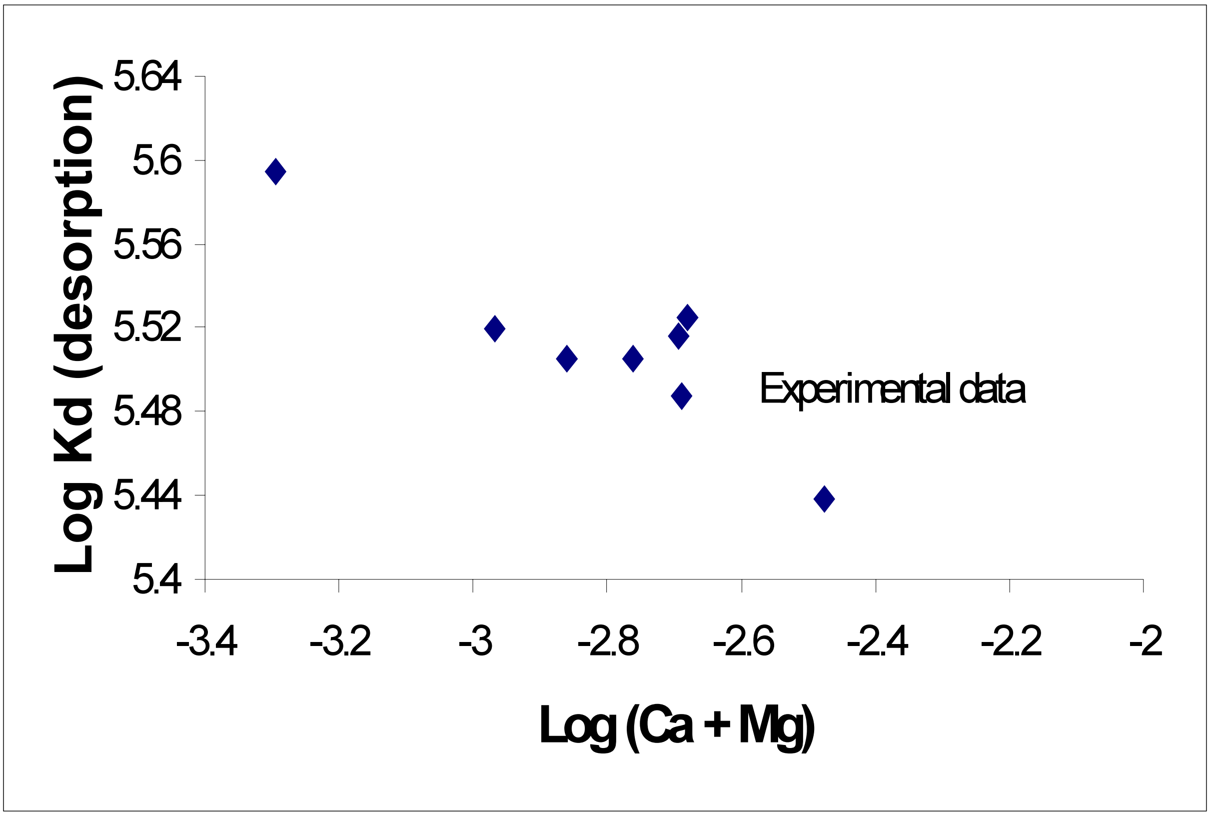

FIG. 1. Thorium Kd values as a function of the sum of the equilibrium Ca and Mg concentrations in solutions (moles/L) for the contaminated soil sediments.

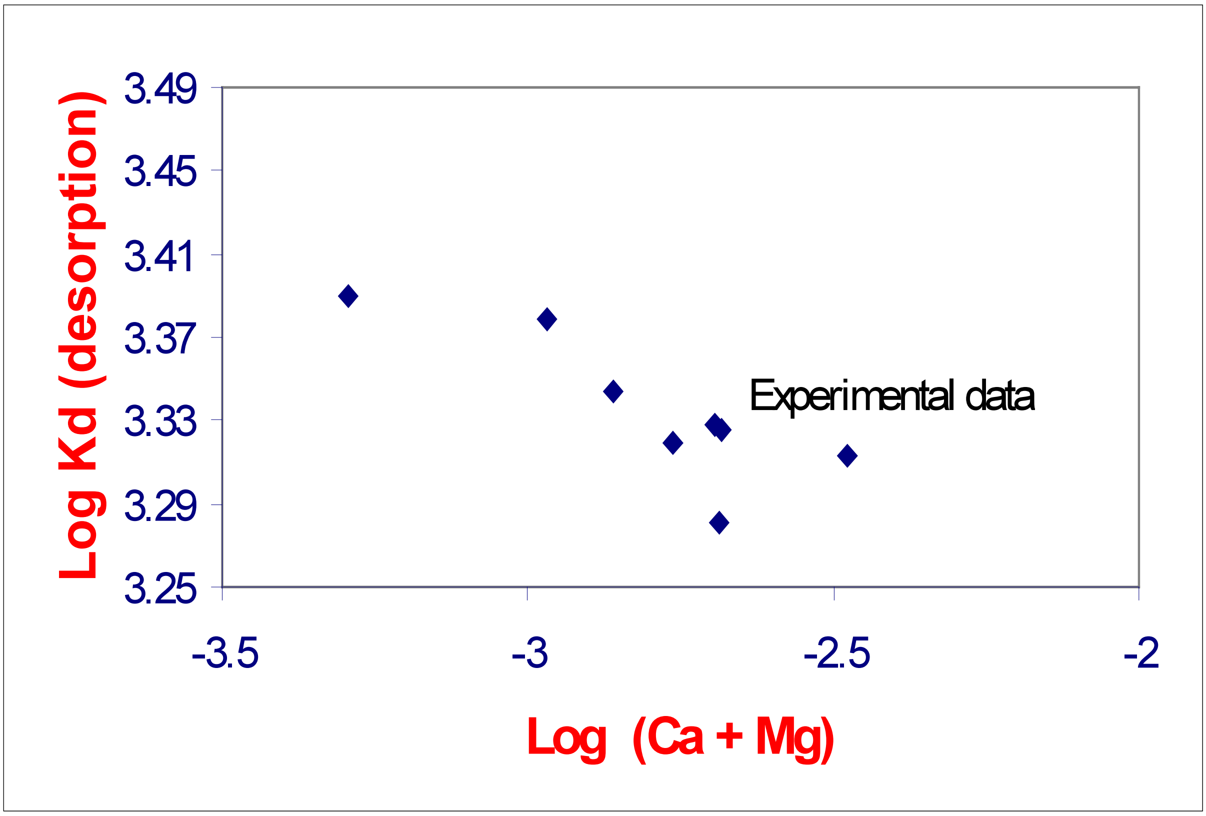

FIG. 2. Uranium Kd values as a function of the sum of the equilibrium Ca and Mg concentrations in solutions (moles/L) for the contaminated soil sediments.

Table 1. Desorption coefficient $K_d^{Th, U}$ equations for soil sediments

Radionuclide	Adsorption coefficient equation, log Kd	R square
Thorium	$-0.15849 \pm 0.03237 \log(\mathrm{Ca} + \mathrm{Mg}) + 5.06715 \pm 0.09106$	0.8
Uranium	$-0.11984 \pm 0.03237 \log(\mathrm{Ca} + \mathrm{Mg}) + 2.99909 \pm 0.09105$	0.7

Changes of the thorium and uranium concentrations with future major ion concentrations can be estimated if the aquifer material resembles the sedimentary material used in the experiments. Significant variation of the K_d values could occur if no resembles of the samples are used. This could result in serious errors in prediction of future thorium and uranium concentration within a contaminated burial sites.

CONCLUSIONS

Changes in groundwater chemistry can affect desorption properties of thorium and uranium from contaminated soil sediments. The competitive effects of calcium and magnesium cations on the desorption of thorium and uranium has been shown. Both thorium and uranium were found to be desorped from ion-exchange sites with calcium and magnesium cations as effective competitors. Ion exchange of Ca and Mg occurred for previously adsorbed thorium and uranium which was responsible for the increased in both radionuclides in the liquid solution. The combined cation concentration of calcium and magnesium in solution correlates linearly with the measured $K_d^{Th, U}$ desorption values. Thorium and uranium concentrations and major ion data can be obtained from a network of wells and can used as input to the extrapolated equation from the present desorption and previous adsorption studies [11] to calculate K_d values for a specific site.

For future works, Resrad computer code will be used to determine radiological impact assessment for the potential repository site using the most important parameters site specific K_d values as input together with other site parameters. By conducting the assessment by modelling, the performance of the repository site can be determined to isolate thorium and uranium radioactives wastes.

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TIME EXTRAPOLATION ASPECTS IN THE PERFORMANCE ASSESSMENT OF HIGH AND MEDIUM LEVEL RADIOACTIVE WASTE DISPOSAL IN THE BOOM CLAY AT MOL (BELGIUM)

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Abstract

SCK•CEN is studying the disposal of high and long-lived medium level waste in the Boom Clay at Mol, Belgium. In the performance assessment for such a repository time extrapolation is an inherent problem due to the extremely long half-life of some important radionuclides. To increase the confidence in these time extrapolations SCK•CEN applies a combination of different experimental and modelling approaches including laboratory and in situ experiments, natural analogue studies, deterministic (or mechanistic) models and stochastical models. In the following an overview is given of these approaches and some examples of applications to the different repository system components are given.

INTRODUCTION

Since 1975 the SCK•CEN at Mol, Belgium is studying the geological disposal of radioactive waste in the Boom Clay layer. The Boom Clay is a plastic clay of Tertiary (Oligocene, Rupelian) age. It was deposited in a shallow sea between 33 to 30 millions years ago. At the Mol site the Boom Clay is situated between 190 and 290 meters depth. The HADES underground research facility was constructed at 225 meters depth in 1983–1984 and further extended in 1987. Currently a further extension of this laboratory, including the construction of a new shaft, is carried out in the framework of the PRACLAY project. The availability of this facility has strongly enhanced the research on the behaviour of radioactive waste and construction materials in the Boom Clay and their influence on the Boom Clay, the research on the geo-chemical and hydro-geomechanical behaviour of the Boom Clay and the study of the migration of radionuclides in the Boom Clay. The HADES facility has allowed us to make observations under in situ conditions over a period of more than a decade. Yet this period is very short compared to the period over which high level radioactive waste or spent fuel remains dangerous.

For the Mol site it is clear that quantitative performance assessments are at the best, only meaningful for a period up to the next expected severe glaciation, i.e. about 60 000 years from now. However the Belgian legislation does not include a cut-off time for these studies. Therefore the assessments are pursued until maximum flux out of the Boom Clay for each radionuclide has been reached. Due to the strong retardation properties of the Boom Clay, the maximum flux for some radionuclides is only reached after several millions or even tens of millions of years. The results of the performance assessment over such time frames should only be regarded as qualitative indications of the confinement capacity of the Boom Clay and not as quantitative predictions of the dose to a critical group far into the future.

In the following, first a short description is given of the methodology used in the long-term performance assessment studies. Then for each component of the repository system, an overview of the available experimental observations is given together with description of the way in which those observations are or can be used to assess the future evolution of the repository system. Finally the main conclusions of the above are given.

EXPERIMENTS

At SCK•CEN three kinds of experimental approaches are taken: laboratory experiments, in situ experiments and the observation of natural systems.

The laboratory experiments are in general performed to measure parameters used in the performance assessment (PA) calculations. To increase the confidence in the PA calculations experiments are also performed to study the underlying mechanisms (e.g. radionuclide complexation studies). The parameters are also measured applying different experimental conditions simulating repository conditions that could occur in different periods of the repository lifetime. Specifically aimed at time extrapolation, experiments can also be performed under accelerating conditions. Typical examples of the latter are corrosion experiments at elevated temperature and leaching experiments using high surface to volume ratios.

In situ experiments are performed to study phenomena under as close as possible repository conditions. In situ experiments are also performed to scale up both in space and time. While in the laboratory we are often limited to perform experiments on centimetre or decimetre scale, in the field experiments can easily be performed on metre, decametre or even larger scale, e.g. hydraulic conductivity measurements. In in situ experiments the boundary conditions are often set by nature and very stable, without active control, while in the laboratory they have to be maintained by carefully controlling them. This makes it for example possible to perform in the HADES underground laboratory migration experiments that last more than a decade. By carefully installing in situ experiments one can also avoid the problem of taking undisturbed samples needed for laboratory investigations.

At SCK•CEN the observation of natural systems in concentrated on performing geological, geochemical and hydrogeochemical studies over the whole area where the Boom Clay occurs. The aim of these studies is to understand the hydrogeological system, to find the hydrochemical signature of the last ice ages and to observe the behaviour of natural radionuclides and trace elements that can be regarded as chemical analogues to some important radionuclides. The paleohydrogeological study is performed to support the time extrapolations for the current hydrogeological system over the next glaciations. The natural analogue study is performed to support the time extrapolations of radionuclide migration through the clay.

TIME EXTRAPOLATION METHODOLOGY AND PERFORMANCE ASSESSMENT

First a description is made of the radioactive waste disposal context for which the performance assessment has to be made. This includes the description of the waste types i.e. in Belgium non-heat generating long lived medium level waste, high level vitrified waste (from reprocessing) and spent nuclear fuel, and the description of the repository system as shown in Fig. 1. Then an extensive list of features, events and processes (FEPs) which can influence the repository system is drawn up. This list is then screened to extract the relevant FEPs.

Reasons for screening out FEPs are for example: low probability of occurrence ($< 10^{-8}$ y^{-1}), not relevant for the considered waste type, host rock or site. Then the scenarios are derived based on the relevant FEPs. Those FEPs which are about certain to occur, are grouped together in the so-called normal evolution scenario and the other FEPs are used to derive the altered evolution scenarios. For the latter scenarios a top-down approach (OECD 1991) is used: first the repository system is split in three components (or barriers), i.e. the near field, the host rock clay and the geosphere (or aquifer system; the biosphere is treated separately); each component is supposed to be either present or by-passed; then the remaining FEPs are listed according to which components they affect. In this way a maximum of eight future repository states is derived. The main altered evolution scenarios for the Mol site are: exploitation drilling (exploitation of the lower aquifer), greenhouse effect, fault activation, severe glaciation, failure of the sealing of the repository, gas effects, exploratory drilling (Marivoet 1997a).

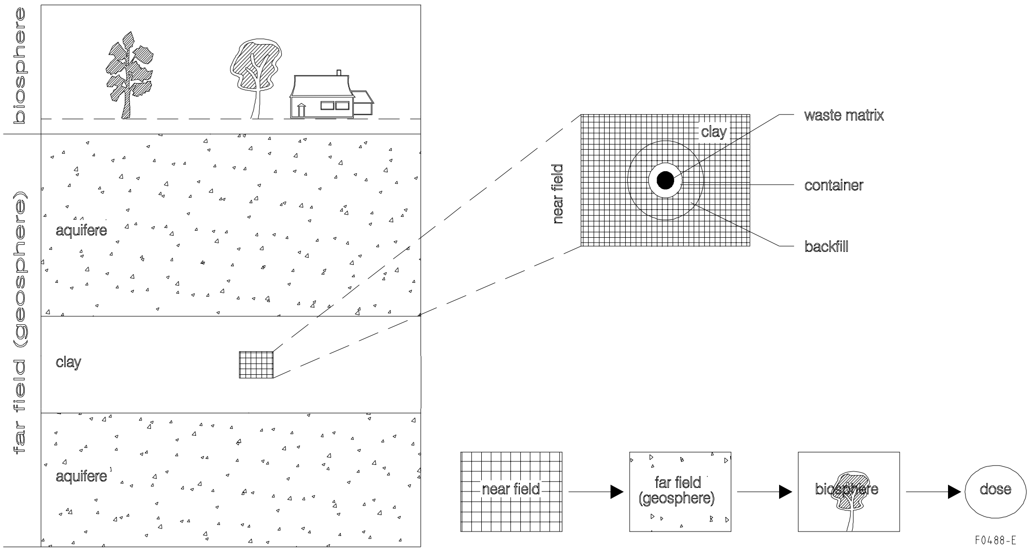

FIG. 1 Scheme of the overall repository system.

Once the scenario descriptions are available, conceptual models covering these descriptions are developed, followed by the translation of the conceptual model into mathematical models and boundary conditions. Then suitable computer codes are selected or developed. The following step, which is often quite difficult, is the determination or selection of the required parameter values. Finally the performance assessment calculations are performed and the results are compared to the risk or dose criteria. Time extrapolation is an inherent part of this process. Therefore, SCK•CEN applies two approaches in parallel, i.e. the deterministic approach and the stochastic approach.

In the deterministic approach, a specific potential future evolution of the repository system is assessed in a single calculation based on physical relations and their parameters describing the considered processes. Those physical relations and their parameters are derived from experimental studies, i.e. short-term observations. In the experimental programme it is often tried to accelerate the studied processes or to simulate possible future chemical or boundary conditions. Often also supporting fundamental research (experimental as well as theoretical) is performed to discover the main underlying process or to discriminate between several possible basic mechanisms. In this approach it is often possible to include detailed research models or time dependent parameters in the performance assessment calculations.

The stochastic approach is used to perform uncertainty and sensitivity analysis. In this approach a large number of computer runs of the performance assessment model for a specific scenario are executed. In this case a distribution (a probability density function) is attributed to each parameter in the PA model. Then a Monte Carlo technique is applied to build the required number of independent parameter sets needed for the computer runs. The results of those runs are then converted into the time evolution of the expectation value (i.e. the mean) with its confidence band and the percentiles (the x percentile is the value of the output for which x % of the output values are smaller than this value). The width of the confidence band and the spread of the percentiles are measures of the uncertainty in the results. An example of such an output for the disposal of spent fuel is given by Marivoet 1996.

RESULTS AND DISCUSSION

NEAR FIELD

Waste packages and engineered barriers

Influence of concrete on the pH in the near field

In the Belgian concept for the disposal of vitrified HLW or spent fuel, concrete is only present in the gallery liner (about 25 cm thick) and its influence will be rather limited. However in the concept for MLW disposal concrete will be present as liner, backfill and waste matrix. In the MLW disposal galleries about 4 ton of cement will be used per meter length of gallery. The use of cement in the near field will result in strongly basic chemical conditions, which will strongly influence the solubility of some radionuclides (e.g. the actinides). The cement will be leached by the groundwater and the pH will drop. Therefore it is important to assess over which time frame the pH will remain high.

Before hydration Portland cement is composed of 60–70% CaO, 17–25% SiO_2, 3–8% Al_2O_3, 0.5–6% Fe_2O_3, 0.1–4% MgO, 1–3% SO_3, 0.5–1.3 Na_2O + K_2O (Jiang 1994). Shortly after hardening hydrated cement will be composed of 40–50 % hydrated calcium-silica gel (CSH-gel), 20–25% portlandite ($Ca(OH)_2$), 10–20 % etteringites, monosulphates and ferritic phases, 10–20% pore water, 0–5% minor components (NaOH, KOH, $Mg(OH)_2$) (Berner 1992). At early times the pH in the concrete will be very high (about pH13.5) due to the NaOH and KOH. Those components are very soluble and reactive and are thus quickly released or neutralised. After this initial phase, the pH will be governed by the Ca^{++} concentration in the pore water and thus by the solubility of portlandite and the CSH-gel. The CSH-gel shows incongruent dissolution depending on the calcium-silica ratio (C/S). On the basis of the analysis of concrete's of different types and with different ageing times, Berner (Berner 1992) has been able to show that the pH in the concrete pore water remains higher than 12 as long as the C/S ratio in the hydrated cement remains higher than 1. If calcium is leached further the pH will quickly drop to about neutral.

In the Boom Clay the calcium leaching will not only be determined by dissolution in water and diffusion through the clay, but also by chemical reactions with the pore water constituents. The Boom Clay pore water contains about 15 mmol of bicarbonate (HCO_3^-) that will react with the Ca^{++} leached from the cement and precipitate as calcite according to the following reaction:

$$OH^- + HCO_3^- + Ca^{++} \Leftrightarrow CaCO_3 + H_2O$$

The precipitation calcite will decrease the Ca^{++} concentration in the pore water and thus enhance the leaching from the cement. Based on the diffusion coefficients for Ca^{++} and HCO_3, derived from diffusion experiments on Boom Clay cores, Walravens (Marivoet 1997a) has been able to show that the phenomenon dominating the leaching is diffusion of calcium from the MLW gallery into the clay where it precipitates as calcite. Based on this model, the estimated period over which the pH in the near field of the MLW will remain higher than 12, was assessed to be about 50 000 years. The concrete can thus strongly influence the release of radionuclides from the MLW galleries over a long time frame.

The above deterministic assessment is a typical example of how short term observations (e.g. diffusion experiments, chemical analyses of concrete) can be used to derive mechanisms and parameters that can then be used in the long-term safety assessment.

Radionuclide release from the nuclear waste

Corrosion of the HLW glass

As for the vitrified HLW glass, the overpack is designed such that it will only fail after about 500 years which corresponds to the thermal transient period. The glass corrosion will thus only occur at the in situ temperature of about 12 to 13°C. Laboratory and in situ experiments with durations up to respectively 5 and 7 years, have shown that the corrosion rate for the vitrified HLW under Boom Clay chemical conditions (pH about 8 to 9) is 0.3 µm/y. On the long-term this corrosion rate will decrease because of saturation of the surrounding medium with glass constituents mainly by silica. In the Boom Clay, the glass constituents accumulate as a result of the strong diffusion limitations. To take this phenomenon into account in the performance assessment model a time variable (decreasing) corrosion rate should have to be used. In the literature mechanistic models taking into account these saturation and diffusion limitations have been developed for various geological waste disposal concepts. Examples of these models are Curtis' model (Curti 1991), Predaver (Jollivet 1995) and Grawnbow's model (Grambow 1988). For the disposal concept in Boom Clay, insufficient data are currently available to incorporate such a model in the performance assessment studies. Therefore we have chosen to apply the stochastic approach for the glass corrosion rate. The corrosion rate distribution has been chosen such that it covers as well the short term as the long-term corrosion rate. Based on the available experimental results and literature data a triangular distribution with 0.4 µm/y as maximum, 0.3 µm/y as mode and 0.002 µm/y as minimum.

Influence of geochemical conditions on solubility limits

Sensitivity studies performed in the performance assessment studies for vitrified HLW and spent fuel have shown that the solubility limits belong to the parameters influencing most the radiation dose to a critical group (Marivoet 1996, Marivoet 1997b). As already indicated above the pH in the near field will be influenced by the presence of a concrete liner and in case of the MLW by the concrete in the waste and the backfill. The CERBERUS test has shown that radiation and temperature has almost no influence on the redox conditions and only lead to a pH decrease with about 1 pH unit. With geochemical codes such as CHESS (Van der Lee 1993) and PHREEQE (Parkhurst 1985) the influence of pH on the solubility of radionuclides can be calculated using thermodynamic constants. However pH is not the only factor determining the solubility: some radionuclides show a complex behaviour in which coprecipitation, organic complexation and the degree of crystalinity of the solubility limiting mineral plays an important role. For some radionuclides the thermodynamic database is not complete or of poor quality. Therefore we have chosen not to incorporate directly the calculation of the pH evolution and the evolution with time of the solubility limits in the performance assessment model. This would also require large computer resources. An alternative is to apply a combination of the mechanistic approach to assess the time over which the pH is controlled by the concrete (i.e. pH >12), combined with the stochastic approach to assess the solubility limits under different pH conditions i.e. two sets of pH distributions have been derived, respectively one for high pH conditions and one for the Boom Clay pH conditions (pH 8 to 10). Table 1 gives the ranges of the solubility limits for some radionuclides.

Table 1. Solubility limits of some important elements under different chemical conditions (mol/l) (Marivoet 1999)

Element	In situ Boom Clay pH			Concrete environment		
	min	BE	max	min	BE	max
Se	1. 10^{-9}	5.5 10^{-8}	3. 10^{-6}	1. 10^{-13}	5. 10^{-7}	3. 10^{-4}
Sn	3. 10^{-8}	5. 10^{-6}	1. 10^{-5}	7. 10^{-10}	3. 10^{-5}	2. 10^{-4}
Tc	3. 10^{-9}	3. 10^{-8}	5. 10^{-8}	1. 10^{-8}	3. 10^{-7}	3. 10^{-3}
Np	1. 10^{-10}	1. 10^{-6}	1. 10^{-5}	3. 10^{-9}	1. 10^{-8}	1. 10^{-7}
Pu	1. 10^{-9}	5. 10^{-7}	5. 10^{-5}	6. 10^{-11}	2. 10^{-10}	1. 10^{-8}
U	1. 10^{-10}	3.2 10^{-8}	1. 10^{-5}	1. 10^{-8}	3.6 10^{-6}	1. 10^{-4}

Influence of heat and radiation on the evolution of the properties of Boom Clay in the near field

The thermal transient period will last in the case of vitrified HLW several hundreds of years and in the case of spent fuel several thousands of years. The longer duration of the thermal transient period in the case of the disposal of spent fuel, will also lead to a larger heat affected zone. Although the containers or overpacks of these waste types is designed such that no radionuclide release might occur during the thermal transient period, irreversible changes can occur in the near field which influence radionuclide release into the biosphere.

Within the framework of the EC CERBERUS project (Noynaert 1999), the effect of heat and radiation on the hydraulic and chemical properties of the Boom Clay are studied. In the CERBERUS in situ experiment the temperature and gamma radiation field of a COGEMA type vitrified waste canister after 50 years cooling time was simulated. The Boom Clay and the experimental set up was heated and irradiated during 5 years.

The analysis of water samples taken before, during and after the CERBERUS test showed that irradiation caused a slight oxidation of the interstitial Boom Clay water mainly indicated by the presence of thiosulphate and oxalate. However the global geochemical conditions remained reducing (Eh <–200 mV) and slightly alcaline (pH about 7.5). The mineralogy of the clay minerals remained nearly unchanged: no illitization could be observed. Pyrite is slightly oxidised leading to high sulphate concentrations accompanied by thiosulphate, an intermediate species in the pyrite oxidation process. Recrystalization of pyrite was observed near the source, a supplementary evidence indicating that the environment remained still reducing. The pyrite and calcite content of the Boom Clay gives it a high buffer capacity, which over a period of 5 years was not exhausted even close to the heat and radiation source.

The results of the diffusion experiments performed with Tc (a redox sensitive element) and Am (a pH sensitive element) close to the CERBERUS radiation source, were very similar to the results on unperturbed clay samples. This observation is consistent with the observed minor changes in hydrochemistry and mineralogy.

Measurements of hydraulic conductivity were also performed before, during and after the heating phase of the CERBERUS experiments. These measurements show an increase in hydraulic conductivity during the heating phase but after cooling no significant difference with hydraulic conductivity measured before heating was observed. The increase in hydraulic conductivity during heating can be largely explained by the decrease of the viscosity of water with increasing temperature. The increase is however slightly larger than what can be explained by the decrease of viscosity, this might be due to a thermo-hydro-mechanical coupling as also observed in the mechanical tests. Similar observations were made around the in situ thermo-mechanical experiments CACTUS and ATLAS (Bernier 1996).

The above mentioned observations of heat and radiation effects on the Boom Clay show no clear trend or mechanism, which could degrade the Boom Clay retardation and diffusion properties. However such effects cannot be completely excluded: the Boom Clay buffer capacity might get exhausted and show mineralogical processes might change the clay mineralogy after several hundreds of years. In this case a mechanistic approach cannot yet be applied, therefore these near field effects can be included in the stochastic approach in two alternative ways: we suppose that the Boom Clay in the near field is not effective in retarding the radionuclides and thus either the range of the effective clay thickness is extended to lower values or the range of diffusion and retardation factors is extended to respectively higher and lower values.

FAR FIELD

The Boom Clay

All performance assessment studies (Marivoet 1988, 1996, 1997b) for the Belgian concept of geological waste disposal in the Boom Clay, have shown that the Boom Clay is the main barrier in the disposal system and consequently its transport parameters belong to the most sensitive parameters. The Boom Clay is such a good barrier because its hydraulic conductivity is so low that all mass transport occurs by diffusion, advection contributes only about 1% to the total radionuclide flux out of the repository. Advective mass transport can only become important if, due to some geological process, the hydraulic conductivity and/or the hydraulic gradient increases. Such processes are not expected over the next few ten thousand years. However over a longer time frame, geological processes such as up-lift and glaciations (with important sea level drop) can lead to an increased erosion and thus unloading of the Boom Clay layer and to dramatic changes in the aquifer system with the possibility of large hydraulic gradients over the Boom Clay.

Since the construction of the underground research facility HADES, a large number (about 100) of measurements of the hydraulic conductivity of the Boom Clay have been performed both in the laboratory on samples and in situ. An overview of these results, related to the geophysical loggings, is given in Wemaere and Marivoet 1997. These results are summarised in Table 2. Reconsolidation experiments (Henrion 1988) and experiments on artificially compacted clay cores (Volckaert 1992) have shown that the hydraulic conductivity of the Boom Clay depends also on the degree of compaction. This hydro-mechanical coupling is well explained in Horseman et al. 1996.

In the framework of an internal SCK•CEN project, with as one of the aims the spatial extrapolation of hydraulic parameters of the hydrogeologic system in north-east Belgium and a project funded by NIRAS/ONDRAF, the Belgian waste agency, three boreholes have been core-drilled over the full thickness of the Boom Clay. At the locations of these core drillings, the Boom Clay is present at different depths (between 0 and 400m). On these cores a large number of measurements of hydraulic conductivity and grain size distribution will be performed. This study is still ongoing. The results for Mol and Zoersel are given in Table 2 (Wemaere 1997). At Zoersel the Boom Clay is situated between 90 m and 190 m depth. The load of the overburden at Zoersel is thus only about half the load at the Mol site. The results in Table 2 show that the hydraulic conductivity of the Boom Clay is a factor of two to three larger at Zoersel compared to Mol.

Table 2. The hydraulic conductivity of the Boom Clay at different locations

Hydraulic conductivity	Mol site (HADES)		Zoersel
10^{-12} m/s	laboratory	in situ	laboratory
Kv (vertical)	1.6	2.2	5.7
Kh (horizontal)	4.6	4.8	11

Another possibility to determine the effect of unloading on the hydraulic conductivity, is to measure the hydraulic conductivity of a fully confined sample and then to unload it step wise and to let it swell while measuring the hydraulic conductivity at each step. The first results of such an experiment (see Table 3) illustrates the influence of unloading on the hydraulic conductivity.

Table 3. Hydraulic conductivity evolution when unloading a clay sample

Sample length (mm)	50.0	52.5	55.0	56
porosity (%)	40	42.8	45.5	46.4
Kv 10^{-12} m/s	4.3	5.2	6.0	7.6

Measurements of diffusion properties of non-retarded species are only performed on samples from the Mol core drilling, or on samples taken from the underground laboratory or are measured in situ (De Cannière 1996). However some measurements have been performed on samples reconsolidated at different stresses (Henrion 1991). On the basis of these measurements De Cannière 1996 has been able to show the validity of the Bruggeman equation, which relates the porosity to the diffusion coefficient in the pore water as follows:

$$D_p = 6.84\ 10^{-10}\ n^{0.5}$$

With: D_p = diffusion coefficient in the pores (m²/s)

n = porosity

For the time extrapolation of the transport properties the following mechanistic approach could be applied in principle: assess from a geoprospective study the expected change in load on the Boom Clay, then derive from the change in load the change in hydraulic conductivity and porosity, and finally derive from the change in porosity the change in diffusion coefficient. However, to be able to apply such an approach, further results of the ongoing studies are required.

The most sensitive transport parameter i.e. the retardation factor, is not covered by the above research. Retardation factors are derived from laboratory or in situ diffusion experiments, which have a maximum duration of 5 to 10 years. Although one can expect that the retardation or sorption properties of undisturbed Boom Clay will not very much change even over long time frames, the problem remains that observations over about a decade, have to be extrapolated over hundreds or even millions of year.

Therefore a natural analogue approach is developed in the framework of a PhD study. In this study the distribution of rare earth elements (REE's), thorium and uranium (and their isotopes) as function of depth is studied as well as the distribution of those elements over the different components of the Boom Clay i.e. pore water, clay minerals, pyrite, carbonates, heavy minerals. The aim of this study is to determine which geochemical changes might have occurred in the Boom Clay over the last 30 million years and to determine from the currently observed distribution of REEs, U and Th and their daughters what their transport parameters (especially the retardation factors) are. Those parameters will then be compared with those obtained with chemical analogue elements in laboratory diffusion experiments and the PA model for migration through the Boom Clay will be applied to explain the observed distributions. In this way a mechanistic approach based on a natural analogue study will be applied to support the time extrapolation of the migration parameters. Figure 2 shows the correlation between lithology, U, Th and their daughter radionuclides for the Mol 1 core drilling (De Crean 1999). One can clearly notice the large disequilibrium between Ra-226 and Th-230 due to the transport to the aquifers.

The aquifer system

The dilution of the radionuclide flux from the Boom Clay into the upper and lower aquifer has direct impact on the radiation dose to the critical group. In the PA studies a local scale hydrogeological model covering a few tens of square kilometres is used. This local model is derived from a regional model covering the whole north-east of Belgium (60 × 80 km). This regional model is based on the piezometric data from more than 100 observation wells located at about 40 locations (Wemaere 1995). The regional hydro-geological model has been calibrated to the hydraulic head in the different aquifers measured over a period of more than 10 years. The current hydrogeological situation is thus rather well characterised. However, based on Milankovitch astronomical model a moderate glaciation can be expected over the next 20 000 years and a more severe glaciation over the next 60 000 years. Three of such glaciations occurred over the last 300 000 years. Although the glaciers and icecap did not reach as far south as Belgium, they came close to only a few tens of kilometres from the Mol site.

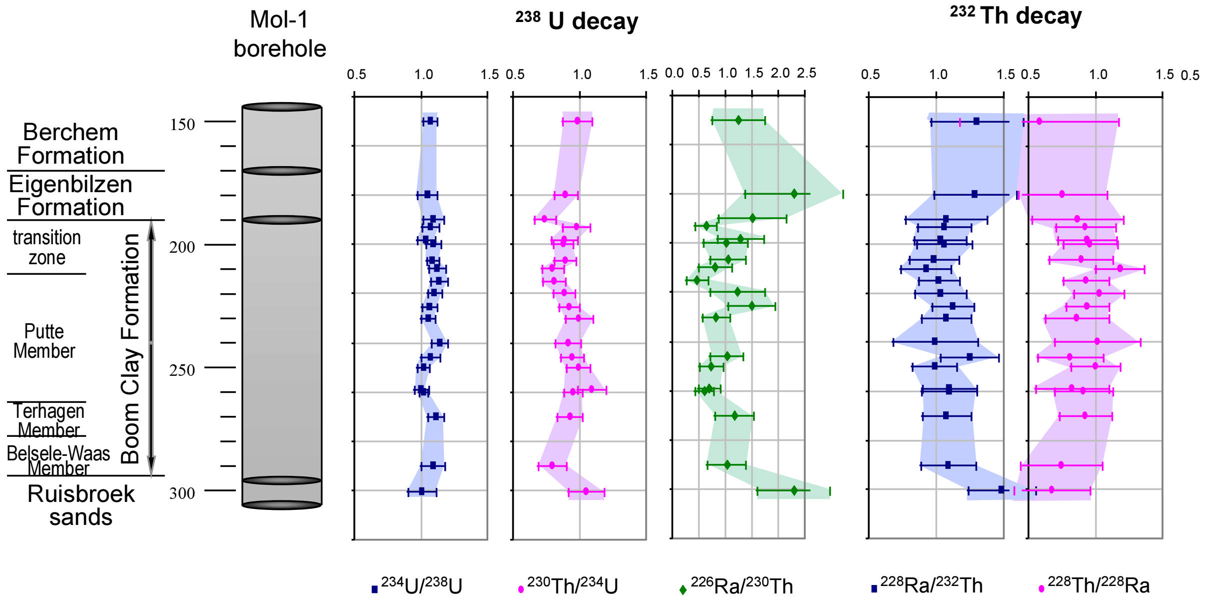

FIG. 2. U and Th natural isotopes in the Boom Clay at Mol (after De Craen 1999).

During such glaciations, permafrost occurred throughout Belgium. It is clear that under such conditions the hydrogeological system undergoes dramatical changes. Therefore SCK has launched, within the EC fourth framework programme, the paleo-hydrogeological project PHYMOL. This project is a co-operation between SCK, as co-ordinator, CEA and Université de Paris Sud in France and the Technical University of Delft in the Netherlands. In this project the aquifer system is geochemically characterised. This geochemical characterization also includes the measurement of stable isotopes such as ^{2}H, ^{16}O, ^{18}O and natural radioactive isotopes such as ^{14}C. The stable isotope composition of a groundwater is an indication for the mean earth temperature when is was precipitated and the radioactive isotope composition can be used to estimate the age of the water.

Although dispersion obscures the picture, the observed ^{16}O/^{18}O ratios still carry the signature of the temperature variations during the last glacial cycle (between –120 000 and –10 000 years) (Marivoet 2000). The C-14 results give a much less clear result due to the combined effect of dispersion and radioactive decay. The modelling results compare rather well with the trend in the observations. However one should remind that the uncertainties in this kind of complex modelling remain large.

In the PHYMOL project a supra-regional hydrogeological model covering the whole North-Sea basin is developed. This model incorporates the hydrogeological effects of a glaciation, e.g. the formation of an icecap, sea level drop and permafrost. This model is coupled to the regional and local model for the Mol site. The next step in the project is to use the hydrogeological model and geological evidence concerning the last glaciations to explain the currently observed hydrogeochemistry and isotopic compositions of the groundwaters. In combination with the predictions of Milankovitch orbital theory, in principle the model can be applied to predict the groundwater flow during the coming glaciation. This is also an example of a mechanistic approach to time extrapolation.

CONCLUSION

Due to the high radiotoxicity and the presence of important quantities of long-lived radionulcides in MLW, vitrified HLW or spent fuel, time extrapolation is an inherent problem encountered during the safety assessment for the geological disposal of these waste types. In countries where the legislation does not include a cut off time for the safety studies and where large/important climatic changes can occur over the next 100 000 years, the time extrapolation problem is even more difficult to treat.

For the time extrapolation of short term observations it is necessary to know the underlying phenomena or mechanisms and to know the potential evolution of the boundary conditions. The evolution of the boundary conditions should be derived from the scenario analysis, including known geological and climatological evolutions. To discover the underlying mechanisms, experiments can be performed under a wide variety of conditions covering the potential future evolutions. In the above several examples of this approach are given. For the assessment of future conditions in the far field, studies of the past geological evolution and their geochemical signature can be very helpful. In a similar way, natural analogue studies can be used to uncover the main mechanisms.

However the real systems are often very complex and the short term observation give not always enough information to allow a mechanistic/deterministic approach. In such cases a stochastic approach can be applied. The parameter distributions should then be chosen such that they cover a wide range of potential future evolutions. The advantage of this approach is that by applying sensitivity and uncertainty analysis, one can show which repository compartments are the most important for the long term safety.

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DEVELOPMENT OF THERMODYNAMIC DATABASES AND GEOCHEMICAL/TRANSPORT MODELS FOR PREDICTION OF LONG-TERM RADIONUCLIDE MIGRATION (GERMANY)

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Abstract

The isolation capacity of a repository system for radionuclides is described by geochemical modeling. The models for interpretation of experimental findings and for long-term extrapolation of experimental results are based on thermodynamic approaches. The geochemical models include dissolution reactions of waste forms, the evolution of the geochemical milieu, interactions of radionuclides with constituents of the groundwater (brines) and the precipitation of new solid phases. Reliable thermodynamic data, understanding of radionuclide complexation in aqueous multi-electrolyte solutions at the relevant ionic strength and knowledge on the formation of pure and mixed solids and on sorption processes are urgently needed for such model calculations.

INTRODUCTION

Depending on the time scales which should be covered by performance assessment, both the natural environment and the engineered structures will change significantly and an unavoidable uncertainty concerning the future state or evolution of the repository system has to be taken into account:

- Rate or frequency of natural processes which act on the system, and
- human activities in the future.

For performance assessment and long-term safety analyses of radioactive waste disposals model calculations are required, which predict the quantity of dissolved radionuclides in the solutions as a function of time. Within the time periods under consideration, both the natural environment and engineered structures have to be taken into account. To evaluate the uncertainties, performance assessment calculations consider different scenarios. Scenarios are based on simplified assumptions and models, but the complete set of scenarios should cover the expected range of possible future conditions and the evolution of the geological repository, the engineered, geo-engineered and natural barriers and the radionuclides. Performance assessment of a repository system including the possible natural evolution, which relies upon the geochemical isolation potential for radionuclides, is the main field of R&D of the INE [1].

The extrapolation of short-term observations to time periods for the isolation of long-lived radioactive waste is based on a multitude of investigations. These investigations cover different fields of science, particularly the investigations with respect to the properties of the radionuclides disposed of, and include the following topics:

- Site selection and description of the geology and hydrogeology,
- Influence of mining technology, temperature and stress development on the rock formation,
- Performance of waste forms, canisters (technical barriers) and reactions of radionuclides,
- Buffers, backfill, sealing systems (geo-engineered barriers) and migration behaviour of radionuclides in the near field,
- Migration of radionuclides in the surrounding aquifer system, and
- Transfer of radionuclides to man, dose factors.

Actual R&D activities of INE are concentrated on investigations on the performance of the multi-barrier system which consists of the engineered, geo-engineered and geological barriers. The activities comprise an experimental investigation of the behaviour of radionuclides in the barriers at relevant temperatures and geochemical conditions, the corresponding geochemical modeling, coupling of geochemical models with transport models, and investigations to evaluate the potential of models and databases developed to describe laboratory-scale results in modeling real and repository-relevant systems. Validation of models and databases is accomplished using natural analogues.

EXPERIMENTAL

Most of the experiments concerning the source term for radionuclide release from waste forms in a repository in a German salt mine were performed in "standard" solutions, namely in 3 solutions defined by the natural system of oceanic salts. Solutions 1 (Q-brine) and 2 are characterized by a high $MgCl_2$ content, whereas solution 3 is a NaCl brine with small amounts of dissolved anhydrite. Most of the experiments were performed in an inert atmosphere without CO_2.

HLW glass

Spent fuel and HLW glass as waste forms contribute significantly to the isolation of radionuclides [2]. Important processes which control the radionuclide release from the waste are:

- Kinetics of corrosion,
- Formation of secondary alteration products (limited solubility)
- Sorption on surfaces in the near field,
- Colloid formation.

These processes are influenced by temperature, pressure, radiolysis and composition and volume of groundwater (brine). The corrosion behaviour of HLW glasses has been investigated for many years [3–6]. The corrosion/dissolution of glass is not necessarily associated with a proportional release of radionuclides. The formation of new secondary phases, such as silicates, molybdates, urinates, carbonates, etc. gives rise to a new barrier for the re-immobilization of dissolved radionuclides from the waste form. On the other hand, glass shows a significant impact on the corroding water (brine): In the presence of brines containing high concentrations of $MgCl_2$ the pH will be decreased to values between 3 and 4. This low pH would strongly affect the solubility of actinide elements.

The presence of iron during glass corrosion effectively reduces the solution concentrations of most measured radioactive elements. Such experiments were performed using a highly active R7T7-type glass in contact with saline solutions. The maximum test temperature was determined by the designed maximum surface temperature of 200°C for vitrified waste in the repository. The findings of these experiments indicate that the concentrations of actinides (Np, Am, Pu) and technetium depend in particular on the presence of reducing components such as iron from container material. In the presence of container materials especially the concentrations of the dose-to-man relevant elements Tc-99 and Np-237 were found to be below the radiologically significant levels, while Pu concentration was found to be increased. This effect might be caused by reduction of Pu(IV) to Pu(III) in the acidic environment.

Spent fuel

Many experiments have shown that spent fuel is a very stable material which is suitable for direct disposal as a waste form in a geological repository. For the prediction of long-term radionuclide release, processes controlling the potential mobilization of radionuclides are investigated. The dissolution of spent fuel has been studied under anaerobic conditions in saline and carbonate-free solutions (e.g. Refs [7–14]) in the absence/presence of corroding container material. It has been found that processes which govern spent fuel dissolution and the corresponding radionuclide release are controlled by a multitude of effects. Radiolysis, especially α-radiolysis, leads to oxidative dissolution. Sorption occurs on the spent fuel itself, on iron corrosion products and on container materials, and solubility and co-precipitation effects take place. Upper limits of oxidative dissolution rates are given by the production rates of oxidative radiolysis products. This limitation leads to a strong decrease in surface-area normalized reaction rates with increasing surface to volume ratio and imposes geometric constraints on the prediction of the spent fuel behaviour in a repository.

The americium concentrations in the solution during spent fuel corrosion were by several orders of magnitude lower than the solubility of $Am(OH)_3(s)$ and are likely controlled by coprecipitation or by sorption processes. Plutonium concentrations may be controlled by Pu(VI) or Pu(IV)(hydr-) oxides. Lowest Pu concentrations were found in the presence of Fe corrosion products.

Cemented waste forms

Full-scale leaching tests of cemented waste forms were started between 1978 and 1989. Full-scale samples having different pore volumes were leached in concentrated salt brines and tap water for periods of up to 20 years. The attacking solutions were analyzed periodically. Recently, experimental findings were evaluated and compared with results of model calculations [15–17].

Leaching behaviour

Leaching behaviour of full-scale samples corresponds well with the findings of laboratory-scale experiments. The leached activity measured in solutions of laboratory-scale and full-scale samples is well reproducible and the ratio of the samples' surfaces to volumes of the leachant can be used as a scale factor. The full-scale leaching experiments confirmed that cemented waste forms do not have a retention capacity for caesium.

Mechanical durability of the waste forms

Mechanical durability of the waste forms, in the sense that no significant formation of cracks or disintegration was observed, is estimated to be 10 to 20 years for cemented waste forms in contact with $MgCl_2$-rich brines. Durability may be longer, if the cemented waste is exposed to NaCl brine, especially in the case of a low pore volume (low W/C). For self-shielded waste canisters, the lid system consisting of a high W/C cementitious product is identified to be the weak point. Radionuclide release from such canisters may occur after 30 to 50 years. However, durability of the high-quality concrete of the cylindrical walls is considerably longer.

Radionuclide release

Cemented waste forms do not retain caesium. Cs release follows a linear time function. Only for short periods, diffusion-controlled transport processes may be relevant. Concentrations of uranium in the attacking solutions were constant for more than 10 years, which can only be explained by assuming that U is controlled by solid phases. Neptunium was measured to be present in concentrations close to the detection limits.

Geochemical milieu of the leachants

One liter of Q-brine has the ability to corrode more than 0.5 kg of cement and NaCl brine of approximately 0.01 kg. In the NaCl brine, the pH raised quickly to about 12 to 13. In Q-brine the pH was buffered at about 8, and only after complete reaction of Mg from the brine did the pH increase depending on the reaction progress. Due to the high Mg concentrations in the solutions (also in the NaCl solutions by Mg release from cement), the carbonate concentrations remain relatively low.

Natural barriers

In general, the application of laboratory experiments to natural conditions causes problems. For this reason, the behaviour of natural radionuclides or chemical homologues of fission products and actinides in groundwaters and solid materials is investigated. The in-situ distribution coefficients (K_a) of these elements between groundwaters and solids are determined. It was possible to obtain information on the type of binding of the elements to the solid matrix by mineralogical characterization and by selective chemical extraction methods.

In-situ K_a values were determined in equilibrated groundwaters and in waters extracted by centrifugation dew from sediments. The total element concentrations were measured in the samples and the amount of trace elements bound to colloidal species was determined [18]. The following properties of the solid matrix were determined: BET surface, mineralogical composition by means of scanning electron microscopy. In order to correlate the elements with certain fractions of the sediments, the mineral phases were determined by x-ray diffraction analyses and by sequential extraction schemes.

In-situ K_a values were determined for the following elements: Cs, Sr, Ba, Ra, La, Ce, Pr, U, Zr, Th and Re. The distribution coefficients are in the same order of magnitude for pore waters and equilibrated waters. Nevertheless, the K_a values show a scatter of about 1.5–2 orders of magnitude. The in-situ K_a values are higher by 2 orders of magnitude than laboratory distribution coefficients. This discrepancy is attributed to the following reason: In the case of K_a the total amount of elements in the solid phase is considered, whereas in laboratory K_d experiments only the amount of surface-sorbed elements is taken into account. In order to determine K_as comparable to K_ds, the amount of trace elements which are bound at the mineral surfaces and which are in direct interaction with the groundwater has to be measured. This can be done by extraction with CH_3COOH at pH = 2.4.

The correlation of the trace elements with the minerals showed that concentrations of Cs, rare-earth elements, U and Th increase with increasing concentrations of Fe and Al in the sediments. Rare-earth elements, U and Th are increased, too, in sediment fractions having increased concentrations of calcite and aluminosilicates, e.g. clinochlore. Cs is correlated significantly with illite and kaolinite and with Ca-containing minerals such as calcite, gypsum, anhydrite, etc. The chemical behaviour of Cs and Sr corresponds to that of K and Ca. Surface sorption (cation exchange reactions), diffusion into interlayers and entrapping into the bulk of the minerals are responsible for the binding of the elements under consideration to clay minerals. A correlation of the rare-earth elements, U and Th with the cation exchange capacity of the sediments could not be observed.

EXTRAPOLATION METHOD

The predictive geochemical modelling of thermodynamic properties of radionuclides in complex natural aquatic systems requires a fundamental thermodynamic database as well as an appropriate thermodynamic model for the excess GIBBS energy of the aqueous phase, valid for a wide range of temperature, (pressure) and chemical composition. Different approaches for calculating activity coefficients in electrolyte solutions have been proposed. Among these the ion interaction approach (PITZER equations) is applicable to highly concentrated aqueous solutions of unlimited complexity. However, accurate model parameters specific for interactions of radionuclide species in trace concentrations are required [19].

Strong association reactions of actinides in concentrated electrolyte solutions, for example, hydrolysis, or carbonate complexation require a combination of the ion interaction approach and association concepts. Weak associations like chloride complexation of tri- or pentavalent actinides can be treated as strong ion–ion interactions.

Based on the available experimental data, comprehensive sets of thermodynamic data (chemical potentials, thermodynamic constants) and model parameters (Pitzer parameter) are derived for tri- and pentavalent actinides. The model is applicable for predicting the major homogeneous and heterogeneous equilibria of curium(III) and neptunium(V) in a wide range of composition. The predictive capability of the model and Pitzer parameters was demonstrated by comparison of the computed predictions with *independent* experimental results.

The database applied is based on the PITZER "data0" file provided with EQ3/6 code and additions made at our institute with regard to uranium [20, 21] and other actinides [22, 23]. Based on the available experimental data, comprehensive sets of thermodynamic data (chemical potentials, thermodynamic constants) and model parameters (Pitzer parameter) for the major homogeneous and heterogeneous equilibria of americium/curium(III) and neptunium(V) could be predicted [24]. For the high pH range which can be expected for glass waste form dissolution in NaCl solutions, PITZER interaction coefficients for silicate and alumina species were incorporated into the database [25].

RESULTS AND DISCUSSION

It cannot be assumed that permanent isolation of radioactive wastes from aquatic interactions in geological formations is possible, either temporarily or spatially, because water is a natural component of every geological site on both the macroscopic and the microscopic scale. The retardation of radionuclide migration, enhanced by aquatic interactions, can be effected by a well-conceived multi-barrier system which includes engineered, geo-engineered and geological barriers. Depending on the time scales under investigation, both the natural environment and the engineered structures will change significantly and an unavoidable uncertainty as regards the future state or evolution of the repository system has to be taken into account.

Radionuclide transport from the repository to the biosphere is part of safety/performance assessment. Transport of radionuclides is correlated to the flow of water (brine), therefore the driving forces and the transport resistance are the key issues [26]. The long-term safety analysis of a nuclear waste repository thus entails advanced knowledge of the aquatic chemistry of the long-lived radionuclides and their migration behaviour with respect to the barriers.

Two limiting types of control of the chemical reactions take place in the repository and the surrounding aquifers: Thermodynamic control and kinetic control [26]. The understanding of chemical thermodynamics is far superior to that of chemical kinetics. The recognition of this fact leads to a larger confidence in predictions of future events, if they are based on thermodynamics. Independently of thermodynamic or kinetic control, the extrapolation of experimental data to those periods of time relevant to the isolation of long-lived radionuclides in repositories involves model calculations based on the best experimental and theoretical data available from various fields of science, such as geology, hydrology, mineralogy, and the aquatic chemistry of radionuclides.

For the systems under consideration in this paper we found that the

- Long-term geochemical milieu in the near-field of radioactive wastes will be controlled by the waste forms.
- Change of pH depends on the composition of the attacking solutions. For example, in a cement system pH will be buffered at about 8 in a concentrated Q-brine (presence of Mg^{2+}), in water or NaCl brines, the pH will increase to about 12–13.
- For HLW glasses in Q-brine the pH will decrease to or below 5 in Q-brine and increase to 8–9 for NaCl brine.
- The source term for fission products depends mainly on their chemical states [1].
- Cs(I) and Sr(II) are released with the same rate as the constituents of the waste form, e.g. Li or B in the case of HLW glass or Ca for cemented waste forms.
- Lanthanides can precipitate as solids, e.g. molybdates or as hydroxides.
- Formation of solid solutions by substitution of lanthanides seems to be possible.
- Concentrations of dissolved actinides, such as uranium, americium and plutonium in the attacking solutions are controlled by solid phases.
- In the cement-Q-brine and NaCl brine, uranium is stable in the hexavalent oxidation state. Computed U(VI) concentrations with $Na_2U_2O_7$ (or schoepite) as the solubility-limiting solid phase agreed well with the experimental findings. Maximum U(VI) concentration is expected to be in the range of 10^{-5} mol/kg H_2O in Q-brine and about 10^{-6} mol/kg H_2O in NaCl brine.
- In the case of Am in HLW glass experiments, the dissolved concentrations measured were significantly lower than predicted. Several mechanisms, such as formation of solid solutions, are possible. Sorption of Am on precipitates of SiO_2 seems to be the reason for lower experimental concentrations.
- Neptunium was measured to be present in concentrations close to the detection limits. Computations resulted in higher concentrations.
- A good agreement between computed and experimental Pu concentrations could be shown. Pu was assumed to exist as Pu(IV).

High-temperature data for important species, the identification of temperature-dependent sorption reactions and K_{sp} data as a function of temperature for the actinide-containing solids are not available. It must be kept in mind that the model is not well defined. Different approaches may be chosen. Nevertheless, computations for a temperature of 25°C can explain the experimental results obtained at 110°C and 190°C, respectively.

Thermodynamic modeling is one of the tools used to describe the characteristics of chemical systems in nature and elsewhere. Models are used in science and technology as tools; they are by choice and necessity incomplete and describe only those aspects of "reality", which the modeller finds to be relevant for the understanding and description of real systems. From this, it follows that modeling may be performed on different levels of sophistication, and necessary elements are approximations of various kinds, based on the perceptions of the problem on hand.

CONCLUSIONS

The examples presented in this paper cannot satisfy completely the demand of long-term extrapolations, but they demonstrate possible approaches. Actual work of the INE shows methods based on experimental and theoretical data and model calculations to extrapolate thermodynamically or kinetically controlled processes.

Thermodynamic models and data concerning radionuclides and other components (waste constituents, rock minerals, canister materials, etc.) in a repository are available:

- Radionuclide solubilities
  - complexation with relevant groundwater constituents
- Characterization of solid phases
  - pure radionuclide phases
  - mixed phases (solid solutions)
  - co–precipitation
- Thermodynamic models and data:
  - Pitzer coefficient for dissolved species in the whole range of ionic strengths and temperatures,
    thermodynamic basis of sorption
- Kinetically controlled processes and non–equilibrium states have to be taken into account:
  - Corrosion of glass and spent fuel
  - Radiolysis
  - Characteristics and stability of colloids
  - Characterization of metastable phases.

Models used in performance assessment are based on empirical data (*not* ab initio models), experiments are necessary to parameterize these models. This fact indicates that these models and data primarily cover that test case they are developed for and an extrapolation of model calculations to systems beyond this frame has to be done with care. In order to improve reliability, the results of model calculations, including the understanding, mathematics, code and data, need to be compared with special experiments that are not used for the determination of model parameters or calibration and with natural analogues. In this context, the terms verification and validation are often used. Some authors use these terms for the process of comparing the results of model calculations with findings of real systems either in the lab-scale or in natural systems. Other authors [27] state that “verification and validation of numerical models of natural systems is impossible. This is because natural systems are never closed and because model results are always non-unique. Models can be confirmed by demonstration of agreement between observation and prediction, but confirmation is inherently partial. Complete confirmation is logically precluded by fallacy of affirming the consequent and by incomplete access to natural phenomena. Models can only be evaluated in relative terms, and their predictive value is always open to question. The primary value of models is heuristic."

Extrapolations of radionuclide migration must confine the unavoidable uncertainty as regards the future state or evolution of the aquatic system. Nevertheless, these uncertainties remain and cannot be solved by laboratory experiments. They mainly include the rate or frequency of natural processes which act on the system and human activities in the future. Also, the degree of validation of models and data gives rise to uncertainties. Some important statements are given by the National Research Council of the American Commission on Geoscience, Environment and Resources [28]: Data and models are vital for two purposes:

- to understand the history and present characteristics of the system, and
- to predict the possible future behaviour.

Well known principles can be used to estimate or to set bounds on the behaviour of a site, so that its likely suitability as a waste repository can be evaluated. But increased knowledge may lead to a greater humility as regards one's ability to fully understand the phenomena involved. The key task for performance assessment modelling is to separate the significant uncertainties and risks from trivial ones. The treatment of uncertainties in long-term extrapolations deserves distinguished concern.

Besides this more philosophical treatment of models for the long-term extrapolation, radioactive waste disposal and performance assessment is an urgent need. The collective opinion of OECD/NEA and IAEA [29] summarizes the state-of-the-art in safety assessment methods by a number of interrelated elements, beginning with scenario development, model development, etc. An important aspect of safety assessment is an iterative feedback between these elements. The collective opinion reads:

Recognize that a correct and sufficient understanding of disposal systems is a basic prerequisite for conducting safety assessment.

Note that the collection and evaluation of data are the major tasks on which further progress is needed.

Acknowledge that significant progress in the ability to conduct safety assessment has been made.

Acknowledge that quantitative safety assessments will always be complemented by qualitative evidence.

Note that safety assessment methods can and will be further developed as a result of ongoing work.

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THE EXTRAPOLATION OF SHORT TERM OBSERVATION TO TIME PERIODS FOR ISOLATION OF LONG LIVED RADIOACTIVE WASTES (INDIA)

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Abstract

The work presented covers different parts of a repository system, such as near and far field aspects. Investigations are reported for the degradation of HLW glass, for the corrosion of container materials, for changes of geochemical environment in geological repositories, and for the thermo-mechanical behaviour of granitic host rock. Extrapolation methods are developed and applied for temperature and stress development in the host rock and for the radionuclide transport through a fractured system.

INTRODUCTION

Strategies for the management of high level waste in India involves:

- Its immobilization in borosilicate matrices
- Interim storage for a period of about 30 years
- Ultimate disposal in deep geological repository.

Borosilicate matrices of suitable compositions have been formulated and characterised for their suitability under repository conditions. After the period of interim storage, the disposal strategy involves a multibarrier approach consisting of the secondary container, backfill and host rock. A suitable sealing mechanism for this repository has also been conceived.

While working towards this integrated approach including long-term scenario of repository conditions, various components of this system have been individually studied in detail. Although most of these studies have been carried out on short time frames, the data generated can be amenable for extrapolation to geological time frames. Details of the work in this direction involving major components are:

Degradation of waste form (glass)

Depending upon the reprocessing procedures adopted, compositions of high level wastes vary. Part of the high level wastes presently stored are sulphate bearing whereas most of it are non-sulphate bearing. Sodium borosilicate composition (IR-110) has been developed for non sulphate waste accommodating 27% waste oxide along with 35.6% SiO_2, 6.9% B_2O_3, 14.7% Na_2O, 9.6% MnO and 6.2% TiO_2 as glass forming additives. As sulphate is non-compatible with sodium Borosilicate matrix, lead borosilicate formulation (WTR-62) has been developed for sulphate bearing high level waste. This contains 25% waste oxide, 30% SiO_2, 10% B_2O_3, 25% PbO and 10% Fe_2O_3.

It is necessary that vitrified waste product should withstand aqueous attack with minimum release of activity to the surrounding in case of accidental contact with water in underground repository where it will be buried for several thousands of years. With this objective, leaching studies were carried on these two types of glasses under aggressive leaching conditions.

Corrosion of container material

The proposed storage programme for waste immobilization involves storage of vitrified waste in stainless steel canisters. The SS canisters will be placed inside an overpack made of carbon steel. The carbon steel overpack will be emplaced with bentonite clay as backfill. In course of the long duration of storage, water may seep through the rocks to the bentonite surface and after absorption can result in swelling. In such an eventuality, there is a possibility of attack on the carbon steel containers. Since carbon steel and stainless steels are in contact with each other, there is a chance of galvanic attack as well. Hence, it was decided to study the corrosion behaviour of carbon steel and stainless steel separately and in galvanic contact. The experiments conducted were of exploratory nature that could provide guidelines for further studies.

Changes in the geo-chemical environment

Study of sorption behaviour of various radionuclides of interest in the high level waste, on to the backfill and the host rock material using groundwater were undertaken. Behaviour of long lived radionuclides like Am-241, Eu, etc. as well as fission products like Cs-137 and Sr-90 with regard to their retention and retardation behaviour have been studied.

Thermomechanical behaviour of host rock

Heat generating nuclides in high level radioactive waste dissipates the heat in surrounding rock mass when emplaced in a geological repository. Rocks having high thermal conductivity and very low coefficient of expansion are always preferred as host medium. In course of time, the heat-induced stresses develop in the near field, compressing the rocks, resulting in opening/closure of the existing fractures. The presence of moisture in the rocks may further expand the voids, causing micro fracturing. If rock is heated to high temperature it may result in its spalling near the heat source. The orientation of fracture/joint planes with respect to direction of stresses may behave differently along the slip planes. All these near field effects in long time periods gradually affect the far field and may cause change in over all effective porosity and permeability of rock mass, facilitating groundwater flow towards the repository. This may also affect the integrity and stability of the whole multi-barrier system of the repository. To study the near field effects with respect to thermo-mechanical behavioural changes in rockmass, it is essential to determine the thermal and mechanical properties of host rocks such as thermal conductivity, Coefficient of thermal expansion, Specific heat and Young's Modulus of Elasticity, Poisson's ratio, compressive strength, tensile strength and shear strength, etc.

After knowing these basic properties, the rocks are subjected to varying stresses, under confined/unconfined, wet/dry and elevated temperatures (pre-heating and during heating) conditions to evaluate the variations in thermomechanical parameters during smaller duration.

The short term data so generated on thermo-mechanical attributes on laboratory core samples of host rocks, as well as the data generated through in-situ experiments on host media, can be used for long term extrapolation/prediction on behaviour of repository rock medium with respect to rock stability, rock matrix/structural changes, groundwater flow and radionuclide migration. This is achieved by thermo-mechanical modelling of the repository rockmass. In-situ experiments to study thermo-mechanical behaviour of host rock (granite) have been studied in an abandoned mine nearly 700 meters below ground level. Predicted temperature profiles have been verified with experimental values to validate the model.

Migration of radionuclides

Radionuclide migration is the movement of radionuclides through the fluid media either through physical flow of the fluid or through diffusion in the fluid medium. The primary inputs needed for evaluation of migration of radionuclides include fluid velocities, diffusion coefficients, and retardation coefficients on the solid phases through which or about which the nuclides in the fluid have to migrate. The other inputs are leaching characteristics of the wasteforms and the inventories. Presence of backfill material such as clay which modify the flux of radionuclide output to the groundwater are equally important.

The fluid flow directions and magnitude of velocities vary over a wide range at the same physical depth from the ground surface due to several factors and it is usually preferable to employ measured values. Even if direct flow velocity determinations cannot be carried out easily, it is possible to compute them using laboratory determined hydraulic conductivity values coupled with field estimated effective porosity values and hydraulic head/gradient through known relations.

EXPERIMENTAL

1. Degradation of waste form

For estimating the long term chemical durability of vitrified waste, leaching studies were carried out. During these studies, high surface area for glass was achieved by crushing the same to –16+25 mesh size particles and boiling distilled water was used as a leachant. SA/V ratio was kept at 0.209 cm^{-1} in these experiments. Studies were also conducted on the pellets of WTR–62 by using boiling distilled water as the leachant. Pellets of size 1" × 1/2" were taken in 200 mesh SS cloth. ISO method was followed and leachants were analyzed for their Na content by flame photometry.

Since the vitrified waste product would ultimately be buried in a deep geological repository, it was found necessary to conduct leaching studies using groundwater from the probable repository site. Accordingly, groundwater was collected from the site near Kalapakkam at the depth of 85 meters. This groundwater was analyzed for Na, Ca, Mg, Cl, SO_4, K, Pb, Fe, etc. It was observed that water was alkaline having a pH of 8.6, with Na and Cl content of 710 and 910 ppm respectively (Table 1). One-gram glass particles of –16+25 mesh size were subjected to 100 ml of groundwater at ambient, 50^0C and 100^0C for a month as per ISO procedure. Because of high sodium in the groundwater itself, amount of sodium reported in the leachate could not be analysed and leach rates were evaluated on weight loss basis alone.

Table 1. Composition of groundwater from repository site near Kalpakkam

Element	**Na**	**Ca**	**Mg**	**K**	**Cl**	**SO_4**	**Si**
Conc. (ppm)	710	28	60	35	910	70	3

Some work on leaching under repository conditions was also carried out on glass formulation IR-110 for over 1000 days. Three separate PTFE cells were taken wherein glass, glass+ granite, and glass+granite+rust are taken to simulate repository conditions. In all these experiments, glass grains of –16+25 mesh size was taken and distilled water was used as a leachant. These experiments were carried at 70^0C and SA/V ratio was kept at 1.083 cm^{-1}. The leachant was removed periodically, filtered and taken for analysis of boron after making up the volume. MCC-1 test procedure was followed and the leachants were analyzed using ICP-AES system.

2. Corrosion of container material

Corrosion behaviour of candidate canister materials, carbon steels and stainless steel was studied in bentonite–groundwater slurry. Immersion testing, galvanic corrosion testing and electrochemical techniques (linear polarization, impedance spectroscopy and noise) were used. Coupons were used for immersion testing in bentonite–groundwater slurry (5 gm: 100 ml) at room temperature (28–30°C) and at 60°C. The overall duration was 7 days with continuous stirring for 8 hours in 24 hours. Galvanic tests were carried out for carbon steel–SS couple with area ratio of unity. The galvanic current was recorded with a zero resistance ammeter. Periodic corrosion rates were measured using linear polarization technique once in every 24 hours. Electrochemical impedance spectroscopy was also performed on carbon steel periodically to study the condition of the surface. For electrochemical experiments EG & G 273 a potentiostat was used along with required hard- and software. Electrochemical noise was studied with two identical samples used as electrodes while the potential noise was picked up with a saturated calomel electrode (SCE). Current and potential signals were recorded at sampling rate of 1 Hz. with PCL 208 AD/DA converter. All potential values were referred to SCE.

3. Evaluation of geo-chemical environment in geological repositories

Studies concerning the sorption of Am^{3+}, Cs^{+} and Sr^{2+}on backfill materials included bentonite from Kutch region of India, and those of Cs^{+} and Sr^{2+} on pink granite rock from Rajasthan, India. Actual borehole water from one of the candidate sites was used for these studies. Batch sorption technique was utilized to evaluate the distribution coefficients (K_d) with varying parameters such as time, pH, amount of sorbate and sorbent. The local bentonite and site water samples were characterised using ICP-AES, ion chromatography and spectrophotometric techniques.

4. Thermomechanical behaviour of host rock

In situ experiments were carried out and extrapolated to verify the predicted temperature and stress profile due to decay heat. To simulate the decay heat the multi-heater array was chosen. Thermo-mechanical experiments were carried out in an underground chamber of Mysore mine at KGF over a period of one year. Four heaters each simulating the immobilised high level radioactive waste overpack of 2.0 m length and 0.355 m in diameter were used in the experiment. All the four heaters were energised to heat output of 2 kW (each) emplaced in a square geometry with center to center distance between heaters equal to 2 m. Number of thermocouples and stress-meters were installed to monitor the temperature and stress distribution consequent to continuous heating of rockmass.

EXTRAPOLATION METHOD

Temperature and thermal stress prediction using thermo-mechanical in-situ experimental observations

The main purpose of the experiment was to validate the theoretical model developed for the above-mentioned pitch, array and heat output of the heaters as described in the above section.

The following thermal and mechanical values were used for the Amphibolite host rock in the numerical model:

Thermal conductivity = 2.261 W/m^{0}C   Poisson's Ratio = 0.21

Specific heat capacity = 920.7 J/kg ^{0}C   Young's Modulus = 70.456 Gpa

Density = 3000 kg/m^3 Linear thermal coefficient = 1.13×10^{-5} /^{0}C

In order to extrapolate the temperature values for extended period of time and at greater distances, a mathematical model has been developed. For this the multi-heater array has been reasonably approximated by a single point source of heat output of 8 kW. The near field temperature variations were recorded as given in Table 2.

Table 2

Distance from outer periphery	Maximum rise in temperature	Time
Inside the heater layout	120–140^{0}C	220 days
0.5 m	88–110^{0}C	215 days
1.0 m	70–65^{0}C	210 days

Temperature prediction

A computer code was written for prediction of temperature due to a point source with decay function as $Q(t) = Q_e \exp(-At)$. Following equation given by Crouch and Mclain (1978) and also used by Stephansson et al. (1991) was used:

$$T = \frac{Q_e}{4\pi K\, r} \exp\left[\frac{-r^2}{4kt}\right] \mathrm{Re}\left[w\left(\sqrt{At} + ir/\sqrt{4kt}\right)\right] \quad \text{With} \quad w(x) = \frac{2ix}{\pi} \int_0^\infty \frac{\exp\left(-t^2\right)}{\left(x^2 - t^2\right)} dt, \ \mathrm{Im}[x] > 0$$

Re[x] = real part of x

Im[x] = imaginary part of x

$i = \sqrt{;-1}$

r: distance between source and observation point

t: time after source release

K: thermal conductivity

k: thermal diffusivity

T: temperature

Output was obtained upped 5000 years and for distance up to 100 metres for both decaying and non-decaying Case. Values of the input parameters are given below. Generally the experimental observations on temperature distribution matched with that of predicted ones in the heater mid-plane, i.e. a plane at a depth of 3.3 m from the floor of the chamber.

Input parameters:

Point source output	8.0 kW	Density	3000.0 kg/m^3
Decay constant	7.3265e–10 /s	Sp. heat capacity	920.7 J/kg/^{0}C
Thermal conductivity	2.261 W/m^{0}C		

Temperature variation

For non-decaying source, the temperature value is maximum (53.85^{0}C) at a distance of five metres and decreases with increasing distance. The peak value is computed at 500 years for all the distances.

For decaying sources with decay constant of 7.7e–10 s^{-1}, for a given distance the temperature values increase for a certain period and then decrease after that. Overall values show a decreasing trend with increasing distance. The peak temperature values are obtained after shorter time for a distance of 5 m, the peak value of 24^{0}C is obtained in less than a year while for a distance of 10 m, and the peak value of 5.75^{0}C is obtained after 10 years.

Maximum thermal stress calculations

Thermal stresses for maximum temperature change (T_{max}) can be obtained by the following formula

$$\Delta P_{max} = K_B . \beta . T_{max} \qquad \text{With} \qquad K_B = \frac{E}{3(1-2\nu)}$$

$\beta = 3 \cdot \alpha$	α: Linear thermal expansion coefficient
K_B: Bulk modulus of elasticity	β: Volumetric coefficient of thermal expansion
ν: Poisson's ratio	E: Young's modulus of the host rock
T: Maximum temperature change	

For calculation of maximum thermal stresses, following thermal parameters values corresponding to the host rock have been used:

(i) $\alpha = 1.13\text{e}{-5}/^0\text{C}$ (ii) $K_B = 40.492$ GPa

Table 3 lists the maximum stress (ΔP_{max}) corresponding to maximum temperature change (T_{max}).

Table 3

Distance from the source (meters)	Time, (years)	CASE 1: WITHOUT DECAY Max. thermal stress, ΔP_{max} (Mpa)	CASE 2: WITH DECAY Max. thermal stress, ΔP_{max} (Mpa)
5	500	73.915	33.195
10	500	37.109	7.897
20	500	17.974	3.316
30	500	11.536	2.529
50	500	6.389	1.54
100	500	2.556	0.924

Maximum thermal stress variation

Results from the multi-heater experiment indicate that the maximum thermal stress is around 30 Mpa with decay which is half to one third of the value obtained from the numerical model developed to validate the experiment.

Maximum thermal stress values calculated from the mathematical model indicate that maximum stress values decrease with increasing distance from the source for both decaying and non-decaying source as can be seen from the tabulated results. The variation follows the same trend as in the case of temperature.

Radionuclide transport through a single fracture and dispersion with adsorptive removal through the surface of the cylindrical fracture

The numerical computations of radionuclide transport and dispersion through a single fracture (cylindrical) can be modelled taking into account the adsorptive removal at the cylindrical inner surface of the fracture are presented. The computations are carried out for three radionuclides significant from the high level solid waste management in deep geological repository of granite/basalt type. The results show that while the fission product radionuclides of relatively short half life (high radioactive decay rate coefficient) decreases with distance along the fracture flow length rapidly, the medium half life nuclide (relatively lower radioactive decay coefficient compared to short lived fission product radionuclides like ^{137}Cs or ^{90}Sr) do not decrease as rapidly with flow distance. The magnitude of decrease is also a function of the adsorption equilibrium coefficient, Ka.

Computations base on the following mathematical formulation. The dispersion transport solution with radionuclide adsorption at the internal surface of the fracture of width B is taken as

$$\frac{c}{c_0} = e^{\frac{-\lambda x}{u'}} \cdot e^{\frac{-(y-r)^2 \cdot u'}{4 \cdot Ky' x}}$$

λ = radioactive decay rate coefficient
Co = initial concentration of the radionuclide at the beginning of the fracture

Parameters in flow direction through the fracture	**Parameters normal to the flow direction**
x = distance along the fracture	y = distance normal to the flow direction
u = fluid velocity through the fracture	u' = radionuclide velocity through the fracture
	Ky'= retarded dispersion coefficient for the radionuclide in the normal direction to the flow
	B = width of the cylindrical diameter, B
	r = radius of the fracture = B/2

The hydraulic conductivities of geological media like granite/basalt are very poor and are characterized by low fluid velocities of the order of 1.0 m/y. Unless the media are of very much fractured nature (large individual grain size) and do not show any great effective porosity, the fluid velocities can rarely reach the order of 1.0 m/d. For the computations in this note we will assume fluid velocities characteristic of a fractured rock with single fracture for simplicity and impermeable rock otherwise.

Table 4 presents a summary of the numerical values of the parameters used in the computations. The parameter values chosen are typical for granite/basalt rock matrices. Table 5 gives summery of numerical values of concentrations of ^{137}Cs for an initial flux of 10^4 Bq/m^{2}s at x = 0.0 and corresponding initial concentration. This shows that an equilibrium adsorption coefficient on aerial basis of about 2 m. The numerical computations for the medium half life nuclide ^{241}Am which shows that the concentrations are higher than those for shorter lived radionuclides provided the Ka, the equilibrium adsorption coefficient on aerial basis is of the same order.

Table 4. Summery of typical numerical values of the parameters

Parameter	**Numerical values with units**
Fluid velocity, u	3.17 E – 08 m/s
Width or diameter of fracture, B	0.001 m
Eq. Adsorption coefficient on areal basis, Ka	10 m
Diffusion coefficient in fluid, K	1.0 E – 08 m^2/s
Initial flux, Co	1.0 E + 04 Bq/m^2 s
Total fracture length (maximum, x)	10 m
Distance normal to flow direction, y	0 to 10 m
Half life	^{90}Sr (28y); ^{137}Cs (33y); ^{241}Am (460 y)

Table 5. Sensitivity analysis for radionuclide fluxes at y = 0.0 and varying x for different values of Ka for ^{137}Cs

Parameter	**Concentrations along the flow direction, x (Bq/m^3)**		
	x = 2.0 m	x = 6.0 m	x = 10.0 m
Ka = 1.0 m	1.5 E + 08	3.4 E – 04	7.7 E – 16
Ka = 2.0 m	4.7 E + 02	2.6 E – 21	≤ 1.0 E – 40
Ka = 3.0 m	1.1 E – 03	≤ 1.0 E – 40	≤ 1.0 E – 40
Ka = 4.0 m	2.3 E – 09	≤ 1.0 E – 40	≤ 1.0 E – 40
Ka = 5.0 m	4.5 E – 15	≤ 1.0 E – 40	≤ 1.0 E – 40

RESULTS AND DISCUSSION

1. Degradation of waste form (glass)

Leach rate on weight loss basis at the end of 70 days was 6.8×10^{-6} g/cm^{2}d for WTR-62 and 2.1×10^{-4} g/cm^{2}d for IR-110 leach rate on Na loss basis after 925 days was 2.5×10^{-5} g/cm^{2}d. Groundwater was found to be more corrosive than distilled water as the leach rate after one month of leaching in boiling distilled water was 1.8×10^{-5} g/cm^{2}d as against 2.84×10^{-5} g/cm^{2}d in boiling groundwater. Leach rate at ambient temperature and at 50^{0}C was 3.9×10^{-6} g/cm^{2}d and 8.5×10^{-6} g/cm^{2}d for the same period of one month. t was observed that leaching is less in presence of granite. Leaching of glass was found to be high where rust was in conjunction with the granite.

Thus, it can be seen that both IR-110 and WTR-62 have an acceptable leachability as can be seen from the studies carried under different conditions. Groundwater sample was found to attack the glass than distilled water owing to very high sodium content in it. Leaching is less under granite atmosphere as silica saturation is reached in the leachate. The presence of rust enhances the corrosion of the glass as silica is removed from the system owing to the formation of iron silicate. Since leaching has to be continued till leach rates get stabilised, the final leach rate forming the source term is under evaluation.

2. Corrosion of container material

Corrosion studies revealed that, carbon steel corroded with a rate of 8.46 mpy (0.21 mmpy) in bentonite-groundwater slurry at room temperature and at a rate of 13.7 mpy (0.35 mmpy) at 60^{o}C. At room temperature, the rate was higher than that in distilled water (3.31 mpy or 0.084 mmpy) and tap water (3.71 mpy or 0.094 mmpy) . However at 60^{o}C, the carbon steel corroded almost with the same rate in both the distilled as well as tap water (distilled water 13.41 mpy or 0.34 mmpy; and tap water 12.38 mpy or 0.31 mmpy). Corrosion rate of stainless steel was very low, 0.02 mpy (0.005 mmpy). Periodic corrosion rate measurements showed the following trend over the period studied (7 days). The initial rates were very high but gradually reduced to low value. Average galvanic noise current between carbon steel–carbon steel and carbon steel–stainless steel also varied in similar fashion. Potential changes were not significant in case of carbon steel. It remained in the range of –700 to –800 mV. During the course of experiments it was found that, stirring of the slurry has a profound effect on the corrosion rate. Corrosion rates were measured in stirred condition after taking reading in still condition. The same technique was followed in linear polarization measurements as well as in the electrochemical noise measurements. Corrosion rate under stirred condition was higher than in still conditions.

Polarization experiments on stainless steel did not show active passive behaviour but showed low anodic current near open circuit potential (ocp). Addition of bentonite reduced the open circuit potential (ocp) but increased the tendency for pitting. In groundwater there was a tendency for metastable pit formation in the potential range 200 mV to 400 mV while the pitting potential was close to 450 mV. In presence of bentonite, metastable pits are formed in the potential range –100 mV to 100 mV and 200 mV to 400 mV; the pitting potential remaining same.. Sensitized stainless steel showed low pitting tendency in the lower potential ranges but higher anodic current. Samples exposed for 7 days indeed showed pits on the surface. Grain boundary etching of the stainless steel was not found in 10 days exposure time.

Corrosion rate of carbon steel and stainless steel is low at room temperature but is appreciable at higher temperature. Corrosion of carbon steel decreased with time. The decrease in corrosion rates is due to the formation of a film on the surface. The nature of the film is still under investigation. It is not very stable mechanically and hydrodynamic conditions are important for its stability. The groundwater has high concentration of chloride ions (>900 ppm); the other major constituent being sodium ions. Bentonite contains $Na_{0.3}(AlMg)_2Si_4O_{11}(OH)_2.4H_2O$. It appears that bentonite generates some organic compounds which are specifically adsorbed on the carbon steel surface. This leads to decrease in the corrosion rate . Stirring damages the film and thus increases the corrosion. Increased anodic current and pitting tendency is direct consequence of increase in ion concentration particularly the chloride ions.

The findings of the corrosion tests can be summarised as follows:

- Corrosion rates of carbon steel is low at room temperature but increases with temperature.
- Corrosion of SS 304 is low in bentonite–water slurry.
- Galvanic coupling of carbon steel with SS 304 increases the corrosion of the former.
- Corrosion rates reduce drastically with time. This reduction is due to specific absorption. To know long term behaviour longer duration must be tried.
- Corrosion of carbon steel is sensitive to hydrodynamic conditions.
- SS 304 will undergo pitting if exposed to bentonite–groundwater slurry.
- Inter granular corrosion was not found on sensitized stainless steel sample exposed for ten days.

3. Evaluation of geochemical environment in geological repositories

Sorption of Am, Cs^+ and Sr^{2+} on bentonite

Sorption studies have been based on batch sorption technique with varying parameters involving time, pH, amount of sorbate and sorbent etc. The K_d values have been determined by using the equation

$$K_d = \left|\frac{A_i - A_e}{A_e}\right| \cdot \left|\frac{V}{W}\right| \quad (ml/g)$$

where A_i and A_e are activities of radionuclides in solution initially and after equilibration. V is the volume of solution (ml) and W the weight of the sorbent (g). Sorption of Am^{3+}, Cs^+ and Sr^{2+} on bentonite. With an aim to fix the pH of the solution so that after equilibration with bentonite, the final pH does not reach in the range, where Am^{3+} will get hydrolysed and precipitated, bentonite to water ratio was increased. With a ratio between 1:200 to 1:20, keeping initial pH at 2.9, 3.9, 5.0 and 6.1, the equilibrium pH were measured and found to be between 3.7 to 7.2 (pH 2.9), 6.6 to 8.1 (pH 3.9) and nearly between 7.0 to 8.0 (pH 5.0 and 6.1) respectively. To achieve a reliable sorption data for actinides on bentonite, the initial pH should not be taken more than 6.0 and a bentonite to water ratio of 1: 200. Later on at increased pH and with more bentonite the sorption data should be generated and compared with extrapolated data from experiments done at lower pH. In the case of Cs and Sr problems of precipitation etc. do not arise even up to pH ~9.

K_d values of Am^{3+} at initial pH varying between 2.9 to 6.1 were measured, keeping the bentonite to water ratio of 1:400. Similar experiments were performed in order to determine K_d values of Cs^+ and Sr^{2+} at initial pH varying between 2 to 10.0 at a bentonite to water ratio of 1: 20. The K_d value of Am^{3+} is found to be very high, 1948 ml/g, even at the equilibrium pH of 3.2. These values of Am^{3+} sorption on bentonite are higher as compared to those with Cs^+ and Sr^{2+}. In general, the uptake of Am, Cs and Sr increase with increasing pH of the equilibrated solution. In the case of Cs there is a regular increase in the uptake even up to a pH of 9.9, whereas in the case of Sr, there is an increase up to about pH 9 and then at pH 9.8 increase in uptake is very sharp. At such high pH (9.8) the increased sorption could be due to the cumulative effect of normal sorption and the formation of $SrCO_3$ precipitate. The increase in bentonite to water ratio between 1:400 to 1:40 at an initial pH of 2.9, the K_d of Am remained almost constant 2024 ± 79 (±4%). However, in the case of Cs and Sr, while changing the bentonite to water ratio between 1:60 to 1:6.6, the K_d values of both the metal ions were observed to increase.

$K_{d\ Am}$ data were measured at various Eu(III) and (Cs + Sr) concentrations in the range of 10^{-8} to 10^{-2} M. In the case of Eu, the Kd of Am remained almost constant up to a concentration of 1×10^{-5} M, then it decreases. In the case of Cs + Sr, even at 1×10^{-8} M, the Kd of Am decreases to almost half to that with ^{241}Am tracer alone and then it slowly decreases up to $\sim 1 \times 10^{-4}$ M of Cs + Sr, later on it decreases drastically. At 1×10^{-2} M concentration of these metal ions the decrease in Kd values as compared to that for ^{241}Am tracer alone is 27 and 4 times respectively for Eu and Cs + Sr. It is worth noting that, even at a concentration of 1×10^{-2} M (which is the expected total rare earth concentration in the HLW solution), the Kd_{Am} is quite high suggesting that if at all Am^3 + or any other trivalent actinides get leached out, it will be sorbed by bentonite. The Kds of Cs and Sr with their varying concentrations in the range of tracer to 10^{-2} M. were found to decrease with increasing metal ion concentration. Even under the extreme conditions, i.e. 1×10^{-2} M of the metal ion, the sorption of Cs and Sr is high.

The effect of cations such as Na^+, K^+, Mg^{2+} and Ca^{2+} on the sorption of Cs^+ and Sr^{2+} on bentonite was studied by taking the nitrate salt of these metal ions in the concentration range of 0.01 to 0.5M. The bentonite to aqueous phase ratio was maintained at 1:20. In general, the sorption of Cs^+ and Sr^{2+} on bentonite decreased with increasing concentration of each of the above competing metal ions. It has been observed that the ability of the cations to depress the sorption of Cs^+ follows an order $K^+ > Ca^{2+} > Mg^{2+} > Na^+$ and in the case of Sr^{2+}, the order is Ca > Mg > K > Na. It could be inferred that for an efficient sorption of Cs^+ and Sr^{2+} on bentonite, the higher concentrations of complementary cations should be avoided.

Sorption of Cs^+ and Sr^{2+} on granite

The study has also been carried out for the sorption of Cs^+ and Sr^{2+} by pink granite. In general, the uptake of Cs and Sr by granite rock (Kd value ~ 20 and 2.6 respectively) is much lower than that for bentonite (~1100 and 222 respectively). The kinetics of uptake of Cs by granite has shown that the Kd increases up to about 3 hrs. and then it remains almost constant.

The change in granite to water ratio (1:66 to 1:5) had practically no effect on the sorption of Cs or Sr. The effect of pH, initially in the range 6.9 to 9.1, on the uptake of Cs and Sr was investigated. The equilibrium pH was found to vary between 8.1 to 8.9. The Kd_{Cs} showed a decreasing trend while Kd_{Sr}, an increasing one with increase in equilibrium pH. The Kd values for the sorption of Cs and Sr by granite at pH 8.0 and granite to water ratio of 1:20 decrease with increasing carrier concentration.

CONCLUSIONS

Long term behaviour of vitrified waste product may not be a predominant barrier considering geological time scales. However, for time periods spanning initial 1000 years leaching from the vitrified product shall contribute the major source term for migration of radionuclides. It is essential that the source term be computed based on stabilized leach rates only, especially under geochemical environment.

The primary and the secondary containers are more for handling and transportation prior to disposal and their effectiveness as a barrier for disposal can at best be considered for initial 50–100 years. However during this period its effectiveness as a barrier shall have predominant effect on the leach rates.

Backfill materials and the geochemical environment have a predominant role for retention and retardation of radionuclides specially the long-lived actinides. Backfills like bentonite have a special role in the disposal scenario on account of their swelling behaviour, which helps in the sealing of the repository. It is noted that migration of actinides through bentonite is highly pH dependent. Besides, sorption of actinides on to these backfills should also consider their different valency states at temperatures ranging between 80–100^{o}C.

Long term prediction based on short-term thermo-mechanical behaviour of host rock can be well correlated. However, our co-relations are based on single point source and the computer code has to be modified to take into account the situation wherein point sources are distributed in the domain. The effect of these heat sources could be computed using the principle of superposition. Also similar long-term study for temperature and stress prediction will be simulated using finite element method.

Radionuclide transport model studied through a single fracture and dispersion with adsorptive removal through the surface of the cylindrical fracture need to be extended to the case of multiple fracture with connectivity between the individual fractures.

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