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Proceedings from the technical workshop on near-field performance assessment for high-level waste held in Madrid October 15-17, 1990

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PROCEEDINGS FROM THE TECHNICAL WORKSHOP ON NEAR-FIELD PERFORMANCE ASSESSMENT FOR HIGH-LEVEL WASTE HELD IN MADRID OCTOBER 15-17, 1990

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ABSTRACT

This report contains the proceedings of "Technical Workshop on Near-Field Performance Assessment for High-Level Waste" held in Madrid October 15-17, 1990. It includes the invited presentations and summaries of the scientific discussions.

The workshop covered several topics:

- Post-Emplacement Environment
- Benchmarking of Computer Codes
- Glass Release
- Spent-Fuel Release
- Radionuclide Solubility
- Near-Field Transport Processes
- Coupled Processes in the Near-Field
- Integrated Assessments
- Sensitivity Analyses and Validation

There was an invited presentation on each topic followed by an extensive discussion.

One of the points highlighted in the closing discussion of the workshop was the need for international cooperation in the field of near-field performance assessment. The general opinion was that this was best achieved in smaller groups discussing specific questions.

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TECHNICAL WORKSHOP ON NEAR-FIELD PERFORMANCE ASSESSMENT FOR HIGH-LEVEL WASTE

This Workshop was convened to review and compare approaches of near-field performance assessment (PA) for high-level waste (HLW) disposal. The objective was to establish a technical consensus of the credibility of current models and to guide needs for further research.

The near-field (engineering barriers) and the far-field (site) represent the two key subsystems in the overall multiple-barriers strategy for nuclear-waste isolation. Recent international forums have focused on identifying and resolving technical issues regarding far-field PA: Based on these successes, a parallel appraisal of near-field PA was warranted.

The Workshop was intended for researchers in near-field PA, with particular emphasis on integrated source-term modelling. Subordinate topics included were:

* modelling the post-emplacement environment of the near-field (including both waste package and disturbed zone of surrounding rock)
* modelling of waste form-groundwater interaction
* assessment and use of solubilities for radionuclide-bearing phases
* transport phenomena within the near-field
* mass-transfer analyses of engineered barrier systems
* benchmarking/validation of computer codes for near-field PA

This workshop was not intended as a permanent forum. The need for, and organization of, such a continuing forum for near-field PA was addressed within the context of the Workshop.

Opening sessions were devoted to separate presentations regarding the status of national and multinational programs. These were followed by invited presentations that systematically covered the technical issues of near-field PA specifically relevant to source-term evaluation. Topical areas included glass and spent-fuel performance, and solubility of radionuclides, mass-transport, and validation/benchmarking of predictive models. Holistic aspects and approaches to assessment were emphasized. Each technical presentation was accompanied by an extended period of open discussion that was summarised. A Summary Session, the final day, drew together the conclusions and recommendations from the participants for the Workshop.

Organizers: Mick Apted, Intera Sciences, Denver, Colorado, USA, Patrik Sellin, SKB, Stockholm, Sweden, and José Gago, ENRESA, Madrid, Spain. This Workshop was conducted in cooperation with the Nuclear Energy Agency (NEA).

OPENING OF THE MEETING

It is my pleasure to welcome all the participants in this workshop on Near-field performance assessment for a high-level waste repository.

During these days you will be examining the state of the art in this area and will for sure establish a technical consensus on the credibility of current models to assess the performance of a system of the unique characteristics we are dealing with.

You will also interexchange information on the programs and knowledge of the countries here represented, providing orientation and guidelines for the R+D to be developed in the future.

I would like to emphasize the big effort that is being devoted to performance assessment at an international level, and the importance given to this task in the OECD/NEA, CEC and IAEA Programs.

The inflexion point in the area of performance assessment happened to occur, in my opinion, at the symposium held about a year ago in Paris, which was organized by the three organizations I previously mentioned. This symposium was the opportunity to put together of the thoughts by all the different countries and organizations. From then onwards, different workshops on near-field, far-field, biosphere, integrated models, uncertainty and sensibility analyses, scenarios, etc., are taking place which will state the applicability of the performance assessment to the different tasks and phases of our work, and which will help in establishing common criteria to be applied in different countries.

I consider the task of converging and agreeing on methodologies for the different countries, as well as that of establishing common tools and criteria for their application to all the possible situations, as one of the most importance and necessary to progress in the difficult task of demonstrating ourselves, firstly, and the society later, that the disposal systems we are designing are, and will stay, safe during the large period of time these wastes will remain active.

This task, to which most of you are dedicating a big effort is of primary importance, and I hope a remarkable progress will be achieved after these days of your stay in Madrid.

Once again, and on behalf of ENRESA, and after spanish organizations involves in this task, I welcome you all and hope you will enjoy the company of your foreign colleagues, you will enjoy also this city and its citizens, who are friendly to visitors and welcome them with their kindness and good humour. I Hope.

We can start the sessions ... Thanks,

Aurelio Ulibarri
Engineering and Project Director
ENRESA

PERFORMANCE ASSESSMENT PERSPECTIVES WITH REFERENCE TO THE PROPOSED REPOSITORY AT YUCCA MOUNTAIN, NEVADA

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INTRODUCTION

The near-field environment of geologic repositories for high-level nuclear waste (HLW) encompasses the interface between engineered waste containment structures and the geologic surroundings. Near-field fluxes of heat and mass, fields of radiation and stress and the effects of these fluxes and fields on the physical and chemical characteristics of the system are critical to the performance of the geologic repository. The relations among transient and heterogeneous thermal, hydrologic, physical, chemical and radiologic phenomena over the large time and space scales of a geologic repository are incompletely understood. Simplified mathematical and statistical models, which are generally required in present-day performance assessments of HLW systems, can not be expected to represent the complex interactions in detail. These models are justified in part on the basis of conservatism in assumptions and parameters and sensitivity and uncertainty analyses. They must also be supported by comparisons with more detailed theoretical and experimental analyses that are capable of identifying and quantifying significant synergistic effects and assessing the conservatism of the simpler models. The purpose of this paper is to review the general physical and chemical features of the HLW near-field environment. Examples are drawn from selected theoretical, experimental and field analyses of thermal, hydrological, mechanical and chemical phenomena relevant to performance assessments of the proposed repository at Yucca Mountain, Nevada, U.S.A. The consequences of the environmental characteristics for waste isolation and their significance for performance assessments are the focus of other contributions to this volume and will be addressed only generally in this paper.

HEAT FLUX AND TEMPERATURE

Heat in the HLW near-field environment is generated by radioactive decay of waste elements and their daughter products and drives many hydrological, mechanical and chemical processes. The heat generation rate or heat load depends on the quantity of waste material and its nuclear composition. The latter is a function of the initial composition of the nuclear material, its burn-up history in nuclear reactors, the reprocessing history and its age. The temperatures attained in the repository environment depend on the ambient temperature, the heat load, the spatial and temporal configuration of the heat source(s) and the rate and direction of heat transfer. Heat transfer can occur by convection, conduction and radiation in solid and fluid phases and its rate is governed by the thermal and hydrologic characteristics of the system. Endothermic and exothermic chemical reactions, particularly vaporization and condensation of water, also affect heat flow and temperature in the near-field.

Numerical thermal analyses of the proposed repository system at Yucca Mountain (e.g. O'Neal et al., 1984; Johnson and Bauer, 1987; Johnson et al., 1989) generally assume that conduction is the principal heat transfer mechanism although other processes have been treated implicitly. For example, although fluid flow and heats of vaporization were not treated explicitly in the models of O'Neal et al., (1984), a temperature-dependent equivalent bulk thermal conductivity that accounts for heat transfer by conduction, natural convection and thermal radiation was employed for air gaps in the near-field environment. For a vertical waste package reference configuration, O'Neal et al., (1984) calculated that maximum temperatures of 236° and 188°C were achieved in less than 20 years at the borehole wall and in the host rock 1 meter beyond the borehole wall, respectively. The calculated temperature in the near-field (1 meter from the borehole) decreased rapidly to approximately 150°C at 100 years, but it exceeded 100°C for over 1000 years. Explicit treatment of fluid fluxes and phase changes in the near-field can have a strong effect on the results of thermal modeling as described in the following section.

FLUID FLOW AND THERMOHYDROLOGY

Fluid flow driven by the natural hydrologic gradient or other ambient forces is modified in the near-field both by thermal effects, which may lead to buoyancy driven flow, vaporization and/or capillary pressure gradients and by differences in permeability or other hydrologic characteristics between natural and introduced or modified materials (e.g. Chapman and McKinley, 1987). In turn the fluids may significantly affect the heat flow and chemical reactions associated with fluid phases can alter the environment. Recent field and laboratory studies and calculations related to the Yucca Mountain site show that interactions among hydrologic, thermal and chemical phenomena can have strong effects on the characteristics of the near-field environment related to nuclear waste isolation.

The proposed repository horizon at Yucca Mountain is approximately 200 m above the groundwater table, but it is far from dry. A typical rock at Yucca Mountain with porosity of 11 to 14% and water saturation of 40 - 70% (e.g. DOE, 1988) contains more water than low porosity rocks in many hydrologically saturated sites. In this partially saturated environment, capillary and adsorption forces draw water into the small pores and crevices and the larger pores and open fractures are filled with gas. The suction pressure, the permeabilities for gas and liquid phases, the thermal conductivity of the fractured rock and the mass transport properties are all functions of the degree of hydrologic saturation.

Several numerical models for coupled fluid and heat transport in the unsaturated tuff of the proposed Yucca Mountain repository have been generated (e.g. Tsang and Pruess, 1987; Nitao, 1988; White and Altenhofen, 1989; Pruess et al., 1990a,b). In the computations of Pruess et al., (1990a,b), mass and energy balance equations were solved numerically to account for: **a)** heat transfer by conduction and by convection of gas and liquid phases; **b)** mass transport due to the force of gravity, phase and capillary pressures on fluids and binary diffusion of water vapor and air; and **c)** energy and mass transfer due to water vaporization and condensation. The effects of fracture permeability were modeled explicitly using an idealized fracture configuration and implicitly using an effective continuum approximation. The modeled temperatures in the near-field were found to depend strongly on the mobility of liquid water along fracture surfaces. Results of calculations assuming immobile fracture water are similar to those that neglect discrete fractures. They give a maximum temperature of 260°C at the waste emplacement borehole boundary after approximately 10 years, which corresponds well to the thermal effects calculated by O'Neal et al., (1984). In contrast, water mobility on the surfaces of high permeability fractures permits development of a stable heat pipe through vapor outflow and liquid inflow, which is an effective heat transfer mechanism. The maximum temperature calculated for these conditions is limited to 100°C in a heat-pipe zone that extends from the borehole surface to several meters into the rock.

Thermohydrologic field experiments in the G-Tunnel at Rainier Mesa, Nevada in unsaturated tuff similar to the repository horizon at Yucca Mountain demonstrate a redistribution of moisture due to thermal perturbations induced by an electric heater (Ramirez et al., 1989; Buscheck, written communication, 1990; Ramirez, written communication, 1990). Moisture movement was dominated by vapor flow and its rate increased with fracture density. Water condensation in cooler regions at a distance from the heat source can lead to conditions of increased saturation favoring gravity driven flow of water in fractures. Measurements from an array of thermocouples in the vicinity of the heater showed a zone of nearly constant temperature at about 95°C that persisted for an extended period of time. This effect would be characteristic of heat-pipe phenomena.

Recent laboratory studies on the hydrologic consequences of heating tuff samples show that the presence of fractures has an important effect on variations in the permeability (e.g., Lin and Daily, 1984; Moore et al., 1986; Daily et al., 1987; Lin and Daily, 1989). Unfractured tuffs have a permeability on the order of 1 microdarcy independent of heating or saturation/desaturation cycles. In contrast, samples with fractures have a greater permeability parallel to the fracture direction (e.g. 1000 microdarcies). With heating (with or without dehydration) the fracture permeability was observed to decrease by approximately three orders of magnitude to values similar to unfractured tuff. The permeability changes were accompanied by mechanical cohesion of the fracture and are attributed to smoothing of fracture asperities by dissolution and fracture healing by precipitation of silica on surfaces. In the Rainier Mesa field tests, however, gas permeability was found to increase slightly as a result of the heating test (Ramirez, written communication, 1990), which may be a consequence of partial drying of the rock.

These detailed studies illustrate the complex interactions among thermal, hydrologic, chemical and mechanical phenomena that would affect the near-field hydrology and transport properties at a Yucca Mountain repository.

STRESS AND STRAIN

The near-field environment is subject to regional lithostatic, hydrostatic and/or atmospheric stress fields that are modified by excavations and other engineered structures and by induced effects such as thermal expansion and phase changes. Anisotropies in the stress field may be expected due to anisotropic tectonic and lithostatic forces, thermal gradients and anisotropy and spatial variations in materials. In many repository settings, a transition may be expected over a relatively short time period from atmospheric to hydrostatic to lithostatic pressure on waste packages as the repository resaturates and/or the rocks creep or otherwise strain in response to regional forces (e.g. Chapman and McKinley, 1987). Swelling of clays in backfill material can also impose large forces on waste packages, which may be comparable to lithostatic forces. The stress field can affect the mechanical and structural integrity of the engineered system and the hydrologic characteristics of the site.

The principal lithostatic stress on the highly fractured welded tuff in the proposed repository horizon at Yucca Mountain is vertical at 10 MPa or less and the horizontal to vertical stress ratio is 0.55 to 0.65 (DOE, 1988). Borehole stability is of concern at Yucca Mountain because an air gap may provide a hydrologic barrier between the waste containers and the host rock and because borehole wall collapse could affect the mechanical loading on the waste packages or their retrievability (e.g. DOE, 1988). An additional concern is that cristobalite, a dominant mineral at the repository horizon, undergoes a phase transition with a volume increase of approximately 5% at approximately 225°C (Glassley, 1986), a temperature which may be attained in the immediate near- field.

Johnson et al., (1989) have generated finite element continuum models and discrete element discontinuum models of thermomechanical strain in the fractured near-field environment at the proposed Yucca Mountain repository. Temperatures calculated in the continuum models were similar to those of O'Neal et al., (1984). Stresses calculated in the continuum models were used as boundary conditions for the discrete element models of strain in idealized discontinuous blocks and fractures surrounding the waste emplacement borehole. Compressive stresses at the borehole wall were lower in the discrete element model (e.g. 2 MPa) relative to the continuum model (e.g. 80 MPa) because block displacements redistribute the stress. All calculated strains were small relative to the proposed 5 cm air gap.

Mineral compressibilities are generally negligible under pressure conditions expected for nuclear waste repositories, so variations in pressure would have insignificant effects on mineral properties. In contrast, pressure variations can have large effects on fluid phases in the near-field environment (such as during operations and/or thermal periods). The vapor-liquid phase relations for water depend strongly on pressure, as well as the solubilities of volatile and potentially reactive species in the fluid phases. For example, variations in the partial pressures of volatile species (e.g. CO_2) are more important than variations in the total fluid pressure in the Yucca Mountain environment, where hydrothermal effects in the near-field may result in only small pressure transients on the fluid phases up to approximately 0.2 MPa from the ambient pressure of 0.1 MPa (e.g. Pruess et al., 1990a).

GEOCHEMISTRY

The natural mineral and fluid compositions in geologic settings considered for HLW repository sites are in approximate steady states resulting from long evolution toward chemical equilibrium. The near-field geochemistry is perturbed from ambient conditions by variations in temperature and pressure, introduction of foreign materials (including air), increases in mineral surface area and reactive site density, variations in fluid flow, radiolysis and consequent chemical reactions. Changes in water, gas and solid phase compositions and masses in the near-field can affect hydrologic and mass transport characteristics, alteration of the waste package and waste form materials and waste element speciation and solubility. Thus, the performance of a repository system can depend strongly on the near-field geochemistry.

An understanding of the ambient site geochemistry is required to address near-field perturbations. The site geochemistry offers an enormous buffering capacity that will moderate chemical disturbances. Controls on the ambient geochemistry would be expected ultimately to govern properties of the near-field environment. Understanding these controls provides a basis for predictive modeling of near-field effects. Furthermore, the site geochemistry poses initial and boundary conditions for performance assessment modeling of the near-field.

In characterizations of both site and near-field geochemical systems, relations among some species can be described by mass action equations representing chemical equilibrium. Chemical equilibrium offers a powerful predictive capability as well as constraints on kinetic descriptions of irreversible processes. Nevertheless, some critical thermodynamic data are dubious, including data for the properties of secondary mineral solid solutions and aqueous species at elevated temperatures. Furthermore, metastable or unstable (i.e. disequilibrium) conditions are common, particularly in low temperature systems, for some oxidation-reduction reactions (e.g. Lindberg and Runnells, 1984) and under transient physical conditions such as those in the HLW near-field environment. In general, differences in rates among individual reactions lead to states of partial equilibrium in geochemical systems. Reactions that are not at equilibrium progress at rates that depend strongly on temperature and the degree of disequilibrium and the rates of heterogeneous reactions depend on the properties of phase boundaries, such as mineral-solution interfaces.

Mass transfer calculations that account for partial equilibrium and reaction kinetics in gas-water-rock interactions have provided geochemical models related to the Yucca Mountain site and near-field environment (e.g. Kerrisk, 1983; Ogard and Kerrisk, 1984; Delany, 1985; Arthur and Murphy, 1989). The aqueous silica concentration and the CO_2 pressure have been shown to be particularly important in controlling the solid phase assemblage and the aqueous solution composition. At present these models are limited principally by the lack of thermodynamic and kinetic data and calculations of time-dependent processes are further hampered by the difficulty in realistically characterizing reactive surfaces in geologic environments.

At Yucca Mountain, silicic tuffs (70-80% SiO_2; Byers, 1985) are variably vitric, devitrified to an assemblage of silica minerals and alkali feldspar or altered to the silica-rich zeolites, clinoptilolite and mordenite or to analcime at depth (e.g. Bish and Chipera, 1989). The groundwater is a dilute, oxidizing, sodium bicarbonate solution rich in dissolved silica. Its precise chemistry is incompletely understood because of the difficulty in obtaining uncompromised samples from the unsaturated medium(e.g. Yang et al., 1988). Aqueous silica concentrations in excess of cristobalite saturation are observed in tuffaceous aquifers at Yucca Mountain (e.g. Kerrisk, 1987). The high silica contents are generated by reaction of infiltrating meteoric water with siliceous volcanic glass (e.g. White et al., 1980). This is accompanied by incongruent precipitation of clinoptilolite, a zeolite with important sorptive characteristics (e.g. Ames, 1964). In the proposed repository horizon and hence in the near-field environment at Yucca Mountain, the tuffs are devitrified to alkali feldspar, cristobalite and quartz. Here smectite is the dominant aluminosilicate alteration phase, occurring in abundances up to 5% (Bish, 1988). In lower volcanic units at Yucca Mountain primary glass has been altered to analcime kaolinite rather than clinoptilolite. This mineralogic change, which is associated with the disappearance of cristobalite with depth, is consistent with a decrease in the activity of aqueous silica (e.g., Kerrisk, 1983).

In saturated repositories the introduction or generation of a gas phase would be a transient phenomenon, which could nevertheless lead to significant chemical changes (e.g. oxidation or dehydration of mineral species). In contrast, the Yucca Mountain site is expected to remain partially saturated with water. The gas phase in the vadose zone there is primarily water-saturated air containing excess CO_2 relative to the atmosphere. Gas chemistry analyses show substantial variability in the CO_2 content in space and time (Yang, written communication, 1988; Thorstenson et al., 1989). The maximum observed CO_2 content of the unsaturated zone gas phase corresponds closely to the CO_2 content for gases calculated to be in equilibrium with saturated zone waters. The partial pressure of CO_2 in the gas phase has a strong effect on the pH of the coexisting groundwater, which in turn affects aqueous speciation, solubilities and mineral stabilities (e.g. Arthur and Murphy, 1989).

Elevated temperatures in the near-field at Yucca Mountain are expected to lead to a number of important geochemical variations. Rates of alkali feldspar dissolution and growth of secondary phases such as smectite, clinoptilolite, silica minerals and/or calcite would be accelerated. Volatilization of water will initially tend to purge the dissolved CO_2 affecting solution pH and will ultimately lead to precipitation of "salts" including silica in the near-field dehydration zone. Recent thermodynamic analyses for smectites (Ransom, written communication, 1990) and clinoptilolites (Bowers and Burns, 1990) have quantified their decreasing stability with increasing temperature and decreasing aqueous silica content. In addition, the swelling capacity of uncompacted smectite has been shown to be dramatically and irreversibly decreased by alteration in a water vapor environment at temperatures above 150°C (Couture, 1985). Field evidence for temperature induced changes can be obtained by regarding the natural environment at depth as an analog of the near-field environment (e.g. Apted, 1990). Observations at Yucca Mountain include the transitions with increasing depth from clinoptilolite to analcime to albite and from smectite to ordered illite/smectite to illite. The clay mineral data have been interpreted to give thermal profiles with temperatures ranging up to 300°C for an extinct hydrothermal system at depth at the north end of Yucca Mountain (Bish, 1989).

Experimental studies of the hydrothermal reaction of tuffs and natural waters from Yucca Mountain at 90° to 250°C (e.g. Knauss and Beiriger, 1984; Knauss et al., 1984, 1987; Knauss, 1987) show evidence for dissolution of primary minerals, precipitation of secondary phases and variations in water chemistry. Secondary clay minerals, zeolites, cristobalite and calcite have been observed. Experiments in which CO_2 loss occurred showed more extensive secondary mineralization and particularly more calcite precipitation than in pressurized closed-system experiments. Water chemistry variations were generally modest and achieved approximately steady-state conditions in long-term experiments. The aqueous silica concentration was observed to increase substantially at elevated temperatures corresponding to the increased solubility of silica minerals. The water chemistry in selected experiments was reasonably represented as a function of time with partial equilibrium and kinetic reaction path models of the water-rock interactions (Delany, 1985). Application of the results of these experiments to the near-field environment at Yucca Mountain must be judicious because the high temperatures, high pressures and short time scales of the experiments may lead to unrepresentative results.

Reaction rates are also likely to be accelerated in the near-field because of increases in surface area and reactive site density due to localized fracturing or disaggregation of host rocks during excavation. This may promote a variety of geochemical processes prompted by increased temperature or other perturbations. Sorption of radioelements on a larger number of reactive sites or coprecipitation of radioelements with secondary phases may be affected.

Predicting the geochemical effects of the introduction of engineered materials in the near-field environment requires research that spans the engineering and geoscience disciplines. Stability in the repository can be enhanced by use of engineering materials that are stable in the natural environment, such as copper in a low sulfur, reducing environment or by introduction of materials in the near-field that react geochemically to improve isolation (e.g. Langmuir, 1987). A variety of metal alloys which are inherently unstable in contact with oxidizing water are being considered as container materials for the Yucca Mountain repository (DOE, 1988). Although corrosion of these materials may be slow, it would consume oxidants in the near-field environment and oxidation of spent fuel would provide a large additional reducing potential. Therefore, corrosion of container materials and/or spent fuel may lead to locally reducing conditions in the near-field despite the prevailing oxidizing nature of the geologic setting. Localized reducing conditions could be promoted by near-field hydrologic effects and phase variations. Gas flow from the near-field driven by vaporization of water is predicted to be away from the near- field in all directions (Pruess et al., 1990a, Tsang and Pruess, 1987) and would tend to purge air containing O_2 from the near-field environment. Because the vapor pressure of water at temperatures above 95°C exceeds the hydrostatic pressure of less than 0.1 MPa at Yucca Mountain, the gas phase in the near-field would tend to be dominated by H_2O. Diffusion of air toward zones of relatively high water vapor pressure could reintroduce oxygen to the near-field (Tsang and Pruess, 1987). Local fluctuations of reducing and oxidizing conditions in the near-field due to an unstable hydrologic regime could also induce secondary chemical effects such as the formation of colloids (e.g. Buddemeier and Hunt, 1988; McCarthy and Zachara, 1989). Corrosion cells, in which oxidation (e.g. of metal containers) and reduction (e.g. of water) occur at different points, can also lead to significant spatial variations in the geochemistry (e.g. pH) of the near-field environment (e.g. Walton, 1989).

Radiolysis also has important effects on the geochemistry of the near-field environment. For Yucca Mountain, analyses by Van Konynenburg (1986; written communication 1990) indicate that only gamma and neutron radiation would be significant outside the containers. Gamma radiation dose rates may be as high as 10^4 rad/hr and the relative neutron doses would be minimal. Likely radiolytic effects are fixation of gaseous N_2 as nitrogen oxides which could produce NO_2- and NO_3- ions and equivalent amounts of H^+ ions in the aqueous phase, thus influencing pH. Net radiolysis of liquid water would lead to production of H_2 and O_2; radiolytically produced H_2O_2 should decompose to H_2O and O_2 in the presence of catalysts such as metals, oxides or aqueous species.

CONCLUDING REMARKS: NEAR-FIELD PERFORMANCE ASSESSMENT

In performance assessments of radionuclide release from geologic HLW repositories, radionuclide source term models based on near-field characteristics are generally coupled to hydrologic flow and transport models for the far field. The understanding of the near-field environment must be sufficient to provide defensible limits for the source term. Release of radionuclides from the near-field may be limited by numerous complex processes including: **a)** the rate of degradation of the waste form or the engineered barriers; **b)** the solubility of primary waste forms or secondary phases that incorporate waste elements; **c)** transport of radioelements or other reactive species through components of the near-field environment or the waste package, such as the packing or the air gap; and/or **d)** the inventory of the waste species. In general, either flux conditions (e.g. based on dissolution rates) or concentration conditions (e.g. based on solubilities) must be constrained for each radionuclide of interest in near-field performance assessment models.

Detailed analyses of physical phenomena affecting repository behavior are required to support performance assessments, particularly for the near-field environment where manifold thermal, hydrological, mechanical and chemical processes are coupled in a complex manner. These analyses can identify important processes and support development of a complete spectrum of performance scenarios, which includes the exceptional processes and events in the evolution of a HLW repository system. These, rather than the average behavior, are likely to make the greatest contributions to the release of radionuclides (e.g. O'Connell, 1990). Detailed analyses are also required to provide justification for the conservatism of assumptions and parameters in performance assessment models.

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DISCUSSION ON POST EMPLACEMENT ENVIRONMENT

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On the chemical aspects of near-field performance discussion was initially centered around a diagram from work by Lindberg and Runnells of calculated Eh based on analytical data for redox couples against values of calculated Eh measured in the field using on electrode. Dr Murphy used this diagram in his presentation to illustrate the point that redox couples (as well as many other reactions) are frequently out of equilibrium with one another in natural waters. Geochemical systems are commonly in a state of partial equilibrium.

However, it was agreed that it is difficult to make electrode measurement in field conditions, and such experimental data cannot fairly be used to test the models and equilibrium data. It was further pointed out that if kinetic factors are important in determining redox values for certain cases. There are reaction path codes available that could be used to simulate these systems (However, there is still the question of availability of kinetic parameters for such models).

The discussion later returned to the question of reliability or availability of thermodynamic data for modelling purposes, particulary for complex mineral systems such as those relevant to Yucca Mountain described in the presentation. In this case, the dataset is incomplete, and the stability of minerals under near-field conditions is not firmly established. At this point the necessity for a complete database for silicate minerals, as far as performance assessments are concerned, was questioned. However, it was noted that there are natural analogues of the Yucca Mountain systems, where uranium is present in a rock as uranyl silicate minerals. Complex mineral systems are often not in equilibrium at low temperatures, and differences in stabilities between similar minerals are small, so data for specific phases may be unnecessary. Effort should perhaps be directed towards modelling incongruent dissolution and improving modelling of complex mineral transformations in clays.

Another aspect of the chemistry that was briefly discussed was the effect of far-field groundwater on near-field materials, with particular focus on the buffering capacity of bentonite. Canadian work has shown that such perturbations should not affect the canister performance, since the corrosion behaviour is dominated by chloride concentrations rather than pH.

Bentonite performance featured strongly during the discussion session, since it is clearly of wide interest amongst the participants. On the physical behaviour side, the question of resaturation times was discussed in some detail. A number of experimental results were cited which showed that the process is critically dependent on the permeability of the host rock, because of the high suction pressure of dehydrated bentonite. The hydrologic consequences of heating bentonite were discussed, following the results relating to tuff presented in the paper (Lin and Daily). Results were quoted that suggested the permeability of bentonite deceases, following such treatment.

The question of the relevance of short-term transient effects (such as repository heating) to the overall safety assessment was discussed in some detail. Changes to the physical properties in the near-field, although they occur over relatively short time scales, may have important effects to nuclide migration in the longer term. For example, the reduction of porespace in bentonite may reduce transport of colloids later. (The permanence of such changes to the physical properties can perhaps best be demonstrated by natural analogues.)

Other transients discussed included the effects of operating a repository in naturally saturated, reducing rock. The introduction of oxygen into the system, and perhaps the drying out of the rock, during the operations period, might lead to permanent changes in the physical properties.

Caution should however be exercised when interpreting results such as the ones quoted on bentonite clay. In the steam/swelling experiments of Couture 1985, in which swelling capacity was irreversibly reduced, the clay was not compacted, and in short-term experiments where the clay had been compressed, such decreases in swelling capacity were not seen.

A further comment on the problems of reaching a satisfactory understanding of the effects of repository heating was that perhaps we should consider longer surface storage, so heat fluxes have decayed to low levels prior to emplacement. However, in the case of Yucca Mountain the high temperature may provide an advantage in terms of decreasing water content of rock. Also at lower temperatures other chemical effect, due to introduction of foreign materials, may occur which require equal investigation.

WHAT DO WE KNOW ABOUT NUCLEAR WASTE GLASS PERFORMANCE IN THE REPOSITORY NEAR FIELD?

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Borosilicate glass waste forms will contain about 99% of the highly radioactive isotopes extracted by reprocessing from spent nuclear fuel. The glass phase provides stability for intermediate storage and transport. During geological disposal the glass waste form is one of many barriers against possibly harmful radionuclide release to the biosphere. The relative significance of glass as a barrier depends technically on the interdependency of reactions and mass transfer within the overall geologic and engineered barrier system but it depends also on the public's conception of safety. It may be considered safe if dispersed radionuclides do not exceed an acceptable dose limit or one may require permanent waste isolation in within the engineered barrier system or near field, i.e. to always know were the radionuclides are. If for example, as in the PAGIS project, the performance of repositories is assessed by calculating maximum-dose-to-future-standard-man, it can be shown that the near field and in particular the waste form characteristics has almost no effect on the calculated results [Cadelli et al. 1988]. Parameters controlling mass transfer in the far field (advection, dispersion/diffusion, sorption/desorption) appear more significant. However, if radionuclides are dispersed over the geosphere the containment imperative is violated (dilution is no solution to pollution!). Consequently, studies on near field performance assessment may become essential for demonstrating repository safety.

In order to assess the long-term ability of vitrified waste forms to immobilize radionuclides the corrosion mechanism and the effect of other near field components (steel container, overpack, backfill, host rock etc.) were studied by large experimental programs. Modeling has been identified as a key for using experimental results for predicting the glass' future behavior. Incessant interplay between pre- or postdictions and correction of the models by experimental data is a chief characteristic in modeling. Confidence in modeling results can only grow if models represent a major fraction of experimental data and experience, both conceptually and quantitatively. Nevertheless, agreement of model and experiment is not sufficient in the context of long-term predictions, because the problem of scaling from experimental to geologic time frames remains unsolved. This gap can only be closed by reference to natural analogue systems. In the following the current status in understanding and modeling of glass corrosion is briefly reviewed. Despite the general inte- rest in radionuclide release data, the paper is focussed on the corrosion kinetics of the glass phase because (1) glass corrosion has a major impact on the overall solution chemistry in the near field and, hence, indirectly also on radionuclide solubility limits and (2) the glass phase dissolution data are a direct measure for the release of soluble nuclides.

PROCESSES INVOLVED IN GLASS DISSOLUTION

The need to dispose nuclear waste glass has attracted significant attention to the long-term aspects and the mass balance of the glass/water reaction. Extensive experimental data bases were generated on the chemical durability of few reference glass compositions and, in addition, large generic studies were performed on the durability of hundreds of glass compositions to identify best glass compositions and study the effect of waste and frit variation. The worlds most studied glass is probably the COGEMA produced glass R7T7. One can only estimate the number of different corrosion experiments with this glass, definitely being more than 2000. Experiments were performed in many European states, applying conditions of national disposal concepts varying from granitic groundwater to clay water or saline brines from room temperature to temperatures well above 300°C.

Today, many aspects of the corrosion mechanism appear to be clear. However, care should be given to the notions 'mechanism' and 'clear'. In the literature, the term 'mechanism' sometimes refers to individual processes and sometimes to complete reaction networks, with one or the other process being release rate determining at a given time. In the context of the present paper, only the latter meaning is used. Also in a strict way, a mechanism can never be understood completely, as any mechanistic study is bound to an infinite search for solutions to problems which appear on the surface of an otherwise 'clear' picture of the mechanism.

Many of the details described below are scientifically interesting but may finally turn out irrelevant to the overall glass performance. However, the parameter and processes critical for long-term prediction can only be identified on a detailed knowledge of the interdependency of the various processes. The paradox in current understanding is that many processes can be described to a certain depth by physical-chemical laws whereas the most relevant question of long-term rates can only be described in an empirical way.

Release to solution

The reaction of glasses with aqueous solutions is usually interpreted as a result of two apparently independent processes: initial diffusional controlled alkali release and dissolution of the glass matrix itself [Schröder 1953, Zagar et al. 1960, Douglas et al. 1967, Doremus 1975]. The initial reaction shows a square root of time dependence for the alkali release, and it is described as an ion exchange (interdiffusion Na^+/H_3O^+ or Na^+/H^+) process [Doremus 1975] or as a result of water diffusion into the glass network [Smets and Lommen 1982]. Surface analyses have shown that not only the alkali ions but also network former elements such as boron or, under acid conditions, even Nd are subject to this interdiffusion process [Scholze et al. 1982].

The diffusion of water and/or H_3O^+ at the glass surface involves the hydrolytic cleavage of glass network bonds as does network dissolution. Several recent observations support that network dissolution and alkali ion exchange are governed by similar processes. Transmission electron microscopy of leached alkali-silicate glass surfaces has shown that gel layers were formed which are highly porous and contain phase separated water and silica spheres [Bunker et al. 1984]. High amounts of molecular water in the gel layer were determined by infrared transmission spectroscopy [Aines et al. 1986, Ernsberger et al. 1983]. The presence of free water molecules is probably a result of the condensation of silanol groups by the reaction [Scholze 1977] $2\,\text{–Si-OH} \rightarrow \text{–Si-O–Si} + H_2O$. Silanol groups may have been produced prior to this reaction by ion exchange or by network hydrolysis. It has been shown by leaching alkali silicate glasses in $D_2{}^{18}O$ that the ratio of the surface uptake of oxygen to that of hydrogen is greater than one [Baer et al. 1984]. This was interpreted as an indication for the predominant role of hydrolysis and condensation of glass network bonds for the initial release of alkali ions, hence, matrix dissolution and initial alkali release appear to be governed by similar processes.

Under idealized conditions (no surface layers, no accumulation of dissolved material in solution) matrix dissolution would be governed by a linear rate law. In reality constant rates are seldom observed, because the pH of the solution changes in the course of the reaction, silica accumulates in solution ('saturation effects') and surface layers may become diffusion barriers. In the absence of saturation effects and surface layers, i.e. during the course of the initial reaction, the reactivity of the glass matrix is correlated with the thermodynamic stability of a hypothetical mixture of glass component oxides and silicates with respect to hydrolysis and complexation in solution (hydration theory) [Paul 1979]. An improved model for calculating the Gibbs free energy of hydration has recently been incorporated into the geochemical code EQ3/6 [Bourcier 1989, 1990a]. This model replaces the initial mechanical mixing model by an ideal solid solution model. For a wide range of glass compositions, e.g. window glasses, medieval glasses, basalt glasses and nuclear waste glasses, there appears to be a linear relationship of the calculated Gibbs free energy of hydration and the logarithm of the corrosion rate [Plodinec et al. 1982]. Also the pH-dependence of the initial reaction rate with a maximum glass stability at about pH 8 can be described by the hydration theory. Alternatively to hydration theory, the initial dissolution reaction and its pH-dependence may be explained by surface adsorption models. Various authors have described a correlation between reaction rates of simple and complex oxide phases and the pH-dependent degree of adsorption of H^+or OH^- at specific surface sites as assessed by potentiometric surface titration [Furrer and Stumm 1986, Blum and Lasaga 1988, Guy and Schott 1989].

In static leach tests it is observed that the corrosion rate of the glass matrix decreases with time because of saturation effects of silicic acid in solution, and this decrease can be described mathematically by a first order dissolution mechanism [Grambow 1983, Barkatt et al. 1985]. An attempt was made to describe the initial corrosion rate and the saturation effect, similar as mineral/water reactions, in terms of transition state theory. According to this theory the irreversible detachment of an activated surface complex is rate limiting. The activated complex is a surface configuration of atoms in transition to become a solution complex. The shortcoming of transition state theory is that the stoichiometry of the activated complex cannot be directly observed. Recently, based on results from acidimetric and alkalimetric titration of surface sites on a basalt glass and on correlation of degrees of surface protonation with reaction rates, it was suggested that the stoichiometry of the activated complex equals the composition of network formers in the glass (for a basalt glass under acid conditions $Si_{0.68}Al_{0.22}Fe_{0.11}(OH_2)_{3.7+3.7}$) and the reaction order of 3.7 is given by the average valency of network formers [Guy and Schott 1989]. However, such stoichiometry is incompatible with transition state theory because this theory is valid only for elementary reactions and only structural units with real and not fractional atoms participate in such reactions. Alternatively, by reference to the observed effect of silica saturation on reaction rates it was suggested [Grambow 1985] that the precursor of the activated surface complex is a ($-Si(OH)_3$) group attached to the glass surface. Its concentration and, hence, the reaction rate were assumed to be controlled by local equilibrium conditions involving hydrolysed and nonhydrolysed bonds in the reaction zone. The occurrence of dynamic surface equilibria may explain the above mentioned linear relationship between the logarithm of the glass corrosion rate and the Gibbs free energy of hydration of the glass phases. The more negative the hydration free energy, the more the surface equilibria are shifted to the side of the products (formation of hydrolysed bonds), the higher is the concentration of activated surface complexes and the corrosion rate. A general rate equation for glass dissolution was derived which describes for a given reaction progress, ξ, the effect of glass composition and pH [Grambow 1985]. In the most simple case the rate r_m is given by

$$r_m = k_+ (1-\exp(-A^*(\xi)/RT))$$

where k_+ is the forward rate constant and A^* is the affinity for the rate limiting reaction. It is important to distinguish the affinity of the rate limiting reaction from the affinity of the overall glass/water reaction. The glass phase itself cannot reach equilibrium with the solution because the overall affinity of the glass water reaction remains high for long periods of time [Bourcier 1990a, Advocat et al. 1990] when the affinity of the rate limiting reaction approaches zero. It was suggested [Grambow 1985] to describe the rate limiting reaction as

$$SiO_2 + 2H_2O \rightarrow H_4SiO_4$$

For this reaction the rate equation is given by

$$r_m = k_+ (1 - (a_{H_4SiO_4} / K^*))$$

K* is the 'saturation concentration' of silica. Implicitly, this equation implies that glass corrosion rate is limited by the solubility of a silica polymorph. One must keep in mind that k+ is only constant at constant pH. Hydration theory allows to estimate the magnitude of the forward rate constant. Typical forward rate constants of nuclear waste glasses are in the order of 1 g/m^2d (0.3 μ/d) at 100°C. The equation appears to be rather simple but the time dependence of the release of soluble glass constituents becomes quite complicated, because mass transfer rates in the near field and additional reactions must be considered which consume or produce silicic acid (hydrolysis of silicic acid, dissolution of silicates from the host rock, precipitation of silicates, etc.). Therefore, the equation must be integrated numerically, simultaneously solving mass balance and mass action equations.

Bourcier [1989] has suggested that the affinity term is related to the composition of the glass surface alteration layer ('gel layer') rather than to a SiO_2 polymorph. Hence, glass corrosion rates would slow down when the solution is saturated with respect to the surface layer. However, the composition of the surface alteration layer changes considerably with time, water flow rate and S/V. For example, in a soxlet test with iron-containing glasses silica deficient surface layers will be enriched with large quantities of Fe [Grambow 1984]. The solubility of the layer would be close to the solubility of iron oxyhydrates. The glass corrosion rate should decrease, when iron is saturated but actually, reaction rates are unaffected by FeOOH saturation.

The understanding and quantification of corrosion processes under silica saturated conditions is a prerequisite for the long-term performance prediction of nuclear waste glasses exposed to conditions typical for a repository. Some authors [Wallace et al. 1983, Mendel et al. 1984, Zavoshy et al. 1985] consider leaching to cease, when silica is saturated in solution, but from a theoretical point of view this seems to be unlikely, because glasses are thermodynamically unstable with respect to an assemblage of alteration products [Grambow 1985, Dibble et al. 1981]. Tests performed at temperatures well above 100°C show that glass corrosion continues with a low rate despite silica saturation [Fullam 1980, Freude et al. 1985, Grambow 1985, Conradt et al. 1985]. If a limiting silicic acid concentration in solution has been accumulated, the reaction rate may slow down by as much as a factor of 1000. Present state knowledge allows to distinguish two long-term rate controlling processes: (a) the slow formation of stable secondary alteration products such as zeolites, acting as a sink for silica and providing a residual (or 'contextual' [Advocat et al. 1990]) affinity of reaction or (b) if the affinity of the rate limiting dissolution step becomes zero at saturation, the rate limiting step may change and, maybe, the initial alkali ion exchange/water diffusion process becomes dominant again. There is some evidence for case (b), as long-term glass corrosion in salt brines between 110 and 190°C follows a square root of time law (yet unpublished data). Studies on the long-term corrosion rate will remain an important field of future studies. "Long-term modeling cannot simply consist of extrapolating such an experimental rate law" [Advocat et al. 1990].

Altered surface layers

The reaction of glass with water leads to the formation of surface layers. Three major processes control layer formation, (1) the hydration of the glass surface, interdiffusion (Na^+/H^+) and ion exchange, (2) reprecipitation of crystalline or amorphous reaction products growing from supersaturated solutions and (3) pseudomorphic replacement of the glass phase by less soluble reaction products remaining on the surface during reaction ('in situ' precipitation). Initial layers form by hydration/ion exchange. These layers exhibit diffusion profiles for hydrogen, water and alkali elements and there is a smooth transition from the outer surface to the unaltered glass phase. It is either within the whole volume of this layer or at its outer surface, where the actual glass dissolution reaction occurs. Therefore, this layer or its outer surface is sometimes called 'reaction zone'. In contrast to some binary alkali silicate glass compositions, due to their contents of Al, Fe, Zr, REE and actinides, all nuclear waste glass composition show layers formed from low soluble material (processes (2) and/or (3)). The layer forming material is often amorphous, and may be called a 'gel'. Crystalline phases may grow within the amorphous layer. At high temperatures (i.e. 200°C), crystallinity increases. Layer composition can be described in terms of the thermodynamics of mineral solubility, sorption equilibria and coprecipitation. The fine structure of the layer may involve the kinetics of mobility within the layer (diffusion of reactants etc.). Layer composition depends both on glass and on solution composition and can be calculated by means of geochemical codes (see below).

Typically, a multi-layered structure forms, with the layer formed by process (1) being closest to the pristine glass and reprecipitated layers form at the interface to the solution. Layer formation is always associated with structural reorganization of glass network bonds. As shown by glancing angle EXFAS, Fe^{3+}, commonly tetrahedrally coordinated in the glass phase, assumes octahedral coordination of Fe-silicate minerals within less than an hour of corrosion [Greaves 1990].

There has been a discussion as to whether or not the surface layers are protective, i.e. decrease the rate of corrosion [Malow 1982, Chick et al. 1984, Barkatt et al. 1981, Clark et al. 1983, Grambow et al. 1984, Lanza 1985]. In some cases, it could be shown experimentally that the surface layer had no effect on the leaching process whereas in other cases the reaction rate decreased in the presence of a surface layer [Grambow et al. 1984]. In the general case, transport processes within the surface layer may contribute to or control the glass/water reaction rate. This will occur when the transport of silica from the glass/water interface to the bulk solution is slower than the rate of silica release from the glass. Slow transport would result in higher activities of silicic acid at the glass surface than in the bulk solution. The effect of a concentration gradient on the leach rate r_m was calculated in a simple way by a combination of the above described rate equation with Fick's first diffusion law. Using the diffusion coefficient D and a surface layer thickness L, the quotient $(D/L)K^*/k+$ gives a criterion, whether or not transport processes control the reaction rate. This quotient is similar to the parameter α of Murphy et al. [1989]. Diffusion is rate controlling if the quotient is smaller than unity. In all cases where surface layers act as a diffusion barrier, the mechanical integrity of the layer and its adherence to the glass phase must be studied.

Parametric description of glass corrosion behavior

By considering the interdependence of the various reactions and processes and their control by external parameters one can describe the reaction behavior of a large class of glass compositions under varying experimental or field conditions. This allows also to distinguish favorable glass compositions and disposal conditions from unfavorable ones. The following parametric description of glass corrosion behavior is based on a qualitative assessment of the interdependence of processes described above, referring to typical borosilicate nuclear waste glass compositions in contact of solutions at about 90°C (if not otherwise stated). Quantitative interpretation of these relationships can only be made by modeling.

(1) **Water diffusion:** For all nuclear waste glasses, initial alkali release/water diffusion is of minor importance [Grambow 1983]. It plays a more prominent role under acid than under alkaline conditions and is favored by low temperature conditions [Guy and Schott 1989].

(2) **Temperature:** At high temperatures, due to high reaction rates, transport processes of silica in the surface layer are important and surface reactions at lower temperatures. Resulting from the change in the rate controlling step, activation energy changes with temperature [Guy and Schott 1989]. The temperature at which transport control changes to surface reaction control can be calculated from the above mentioned quotient $(D/L)K^*/k+$ and the temperature dependence of D and k_+. This interdependence only applies to the initial reaction, far away of silica saturation in the bulk solution. The layer thickness L and the diffusion coefficient D can either apply to the growing surface layer or to the thickness of a near field barrier. Under saturated conditions the relation is invalid, because there is no more gradient in silica concentrations across the surface layer.

(3) **pH:** The pH value has a major impact on radionuclide solubility. Often, for example in the case of Pu, solubility limits are not specific to glass corrosion, but, at the same pH, similar solubility can be observed for example in dissolution tests with spent fuel [JSS 1988]. With respect to kinetics, pH influences mainly the initial reaction rate, saturation and concomitant low reaction rates will occur at all pH values [Grambow 1983]. Under acid conditions, the initial reaction rates are fast and silica transport becomes important. Consequently the apparent activation energy of the initial reaction is as low as expected for transport control [Grambow 1983]. Guy and Schott [1989] have shown that below pH 2, reactions are controlled by transport of silica in a diffusion boundary layer (solution phase adjacent to the glass phase). Under neutral or slightly alkaline conditions, glass stability is at its maximum and slow reaction rates are associated with high apparent activation energies typical for surface reactions.

(4) **S/V:** The thickness of the various layers are affected in different ways by the ratio of the sample surface area to the solution volume (S/V). Initial alkali release yields no significant contribution to long-term release. The growth of the hydrated layer is only slightly affected by changes in the S/V ratio. Layer thickness is typically in the range of a few tenth nm. The growth of layers formed from low soluble material is strongly affected by S/V. Layer thickness ranges from a few nm (at very high S/V) to mm size. It is often (not always) possible to mechanically remove the layers. Thick layers resulting from tests at low S/V are often of low density and show apparent enrichment of Fe, Zr etc. At high S/V ratios (S/V>1000 m^{-1}), only thin surface layer form in laboratory time scales and silica transport control in the layer does not occur. Initial alkali release becomes a significant contribution to the overall alkali release. Silica saturation will be reached immediately. But even if the solution concentration of silica achieves an equilibrium value, this value may be subject to change, because the reaction does not cease and the pH could become more alkaline. Surface layers are of high density and are rich in silica and the enrichment of Fe etc. is not as pronounced as under low S/V conditions. A constant rate of release of soluble elements may be observed if second-

ary alteration products would form. Alternatively, if resumption of reaction control by ion-exchange does occur, the release rate may decrease with the square root of time.

(5) **Flow rate:** With high groundwater flow rates similar results are expected than for small S/V values. However, steady state conditions will be achieved, balancing the accumulation of dissolved silica in solution with dilution by flowing water. Steady state conditions become disturbed if the growing surface layer is a diffusion barrier. Therefore, solution concentrations of soluble elements decrease with time. The release of sparingly soluble glass constituents is controlled by the groundwater flow rate, but it is not proportional to flow rate, because the steady state pH changes with flow rate [Grambow et al. 1987].

At groundwater flow rates sufficiently high to prevent silica saturation, release rates of soluble glass constituents are independent on flow rate. At lower flow rate, release is controlled by the amount of glass which must be dissolved to reach silica saturation and, hence, release rates are proportional to flow rate. [Mendel 1984]. At even lower flow rates Si-saturation is always ensured and rates are again independent on flow and are governed either by diffusion in the near field, by secondary phase formation or by selective alkali-ion exchange/water diffusion in the glass network.

(6) **Glass composition:** If glass compositions contain Mg, diffusion coefficients for silica in the surface layer are often lower than for glass compositions free of Mg and, hence, silica transport becomes more important [Grambow and Strachan 1984]. If glass compositions have a high molar ratio of Al/Si (>0.5), secondary alteration products could form which prevent silica saturation to occur or to persist. In the latter case, reaction rates may increase, if solubility limits of an aluminum silicate mineral such as analcime is exceeded [Van Iseghem et al. 1988].

In most natural groundwaters, glass corrosion produces alkaline solutions (pH>8). Glass compositions with low Na/B ratios yield lower pH values than glasses were this ratio is high. This is because the dissolved boron will buffer the solution.

Glass compositions with very high Na/Si ratios may never reach silica saturation in solution if the increase in solution pH is faster than the accumulation of silica.

(7) **Groundwater composition, salinity:** If the solution contains sufficient $MgCl_2$ (>0.1 m) as in high saline brines, than acidification will occur, because Mg-silicate phases form by production of HCl. Acid conditions will lead to high release rates of actinide elements [Grambow et al. 1990a]. Due to their initial silica contents, granitic groundwaters are often beneficial to glass corrosion.

The solubility of silica is strongly influenced by salinity. For example, in $MgCl_2$ dominated brines, amorphous silica solubility is about 20 times less than in deionized water.

(8) **Interdependency of radionuclide release data:** The release of some glass constituents depends on the release of others. For example, under acid conditions, the release of trivalent actinides may be controlled by the release of molybdenum (formation of REE(or actinide)-molybdates). But if the solution contains high concentrations of Ca, Ca-molybdates (Powellite) will form and actinide concentrations will only be limited by dissolution kinetics [Grambow et al. 1990b].

(9) **Effect of waste package components:** If a glass product interacts with groundwater in the presence of corroding iron canisters, silica will be sorbed on iron corrosion products. Silica saturation will not be achieved, if the rate of iron corrosion is faster than the rate of glass corrosion.
If the glass corrodes in the presence of clay buffer materials, various cases may be distinguished:
(a) The equilibrium concentration of silica with respect to the clay phase is higher than the concentration required for decreasing the reactivity of the glass phase. This situation is beneficial for glass stability and was observed for bentonite [JSS 1987].
(b) the clay equilibrium concentration of silica is lower than the respective value for glass saturation effects, as observed for example with illitic and some smectite clay compositions [Godon et al. 1990].

The large number of possibly interdependent reactions (many hundreds of complexation, hydrolysis and precipitation reactions) can only be considered in the frame of computer programs, as will be described below.

GEOCHEMICAL MODELING OF GLASS DISSOLUTION

Modeling of glass corrosion is a relatively new field of research. Similarities between glass corrosion processes and rock/water interactions suggest the application of geochemical models. A large driving force for model development was the need to use thousands of experimental data generated by new analytical techniques for the prediction of the reaction behavior of multicomponent glass phases under a variety of environmental conditions. Modelling allows to consider information from other research fields, especially from solution, solid state and interface thermodynamics. It also places the problem of glass/water reactions into the general context of rock/water interaction, thus allowing a larger fraction of the scientific community to participate in the evaluation of research results. However, no model (and no theory) is complete and it is always a simplification of the real world. Purpose guides the distinction between relevant and irrelevant phenomena and processes. The viewpoint of long-term performance assessment of waste form behavior, i.e. the need to evaluate the build-in future of these solids, introduces a new aspect into modeling which less common in geochemistry. Straight forward deterministic (mechanistic) modeling of the reaction behavior would yield meaningless results because one may always overlook details, which could become important in the long run. Therefore these modeling efforts have to be backed up by pragmatic models, which give worst case (conservative) interpretation of the uncertainties in known data and processes and which replaces unknown reaction behavior of certain components by conservative estimates of the final states.

Geochemical models have already been applied successfully to many corrosion tests of nuclear waste glasses and to the alteration of basaltic glasses in the geochemical environment. Computer codes include EQ3/6 [Wolery 1983], PHREEQE [Parkhurst et al. 1980], DISSOL [Crovisier et al. 1989] and SOLMNEQ [Kharaka et al. 1973]. The reaction behavior is simulated by various degrees of simplifications. No model considers the initial or long-term ion exchange/water diffusion. Glass corrosion behavior is always described in terms of a mechanism which is based on congruent glass network breakdown. This is acceptable as long as the S/V ratio is lower than 1000 m^{-1}, and as long as detailed knowledge on the mechanism of the long-term reaction is lacking. Some studies do not consider reaction kinetics but only describe the reaction path [Savage 1986, Bruton 1988, Grambow et al. 1990a]. This approach allows to study the effect of the extent of glass corrosion on solution pH, surface layer formation by precipitation of secondary phases (in some cases also of solid solutions [Bourcier 1989, Crovisier et al. 1989]. Geochemical reaction path models were also used to consider, simultaneously with glass dissolution, reactions with the host rock, clay backfill or with iron canisters [JSS 1987, 1988, McGrail et al. 1990].

Some models combine reaction path calculations with kinetic concepts [Grambow 1985, Bourcier 1990, Advocat et al. 1990]. Ideally, a kinetic model would have to describe the magnitude of the initial reaction rate, the decrease of reaction rates by saturation effects, the kinetics of precipitation of secondary alteration products and of diffusion processes in formed surface layers. Present models generally neglect precipitation kinetics (except of the model by Bourcier [1990]) and only few models consider diffusion in surface layers [Grambow 1987]. The time dependence of the reaction is commonly calculated after the reaction path has been determined with fair accuracy. One single reaction path model is valid for various calculations of reaction kinetics, as long as only the solution volume, the sample surface area or the flow rate of solution is changed. New reaction path calculations are required when changes in temperature, glass or initial solution composition are made, or when additional system components such as bentonite or steel corrosion products are added to the reaction system.

Reaction path modeling

The reaction path is constrained by the initial glass and solution composition, the solubility of alteration products, the stability of solution species, and environmental parameters such as temperature, the composition of the gas phase (CO_2), sample surface area and solution volume, and by the presence of additional waste package components. Open system calculations differ considerably from calculations for closed systems. In a closed system, reaction progress is associated with an accumulation of dissolved material in solution, whereas in an open system the mass transfer

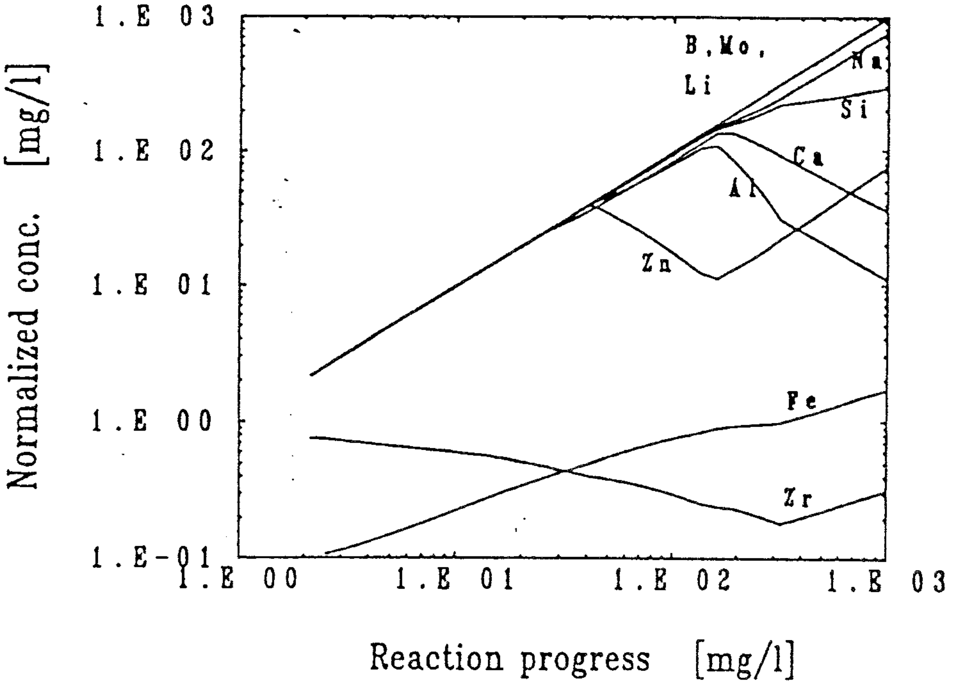

Figure 1: Results of reaction path calculations for the glass R7T7 in deionized water. Calculated solution concentrations were normalized to the glass composition.

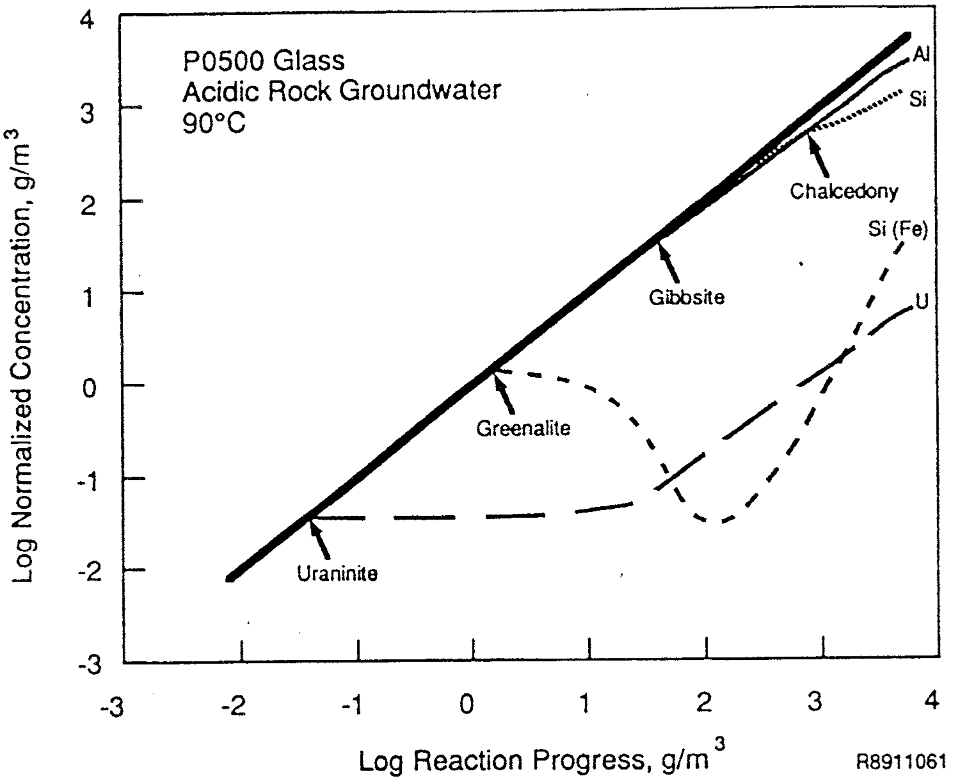

Figure 2: Results of reaction path calculations for glass corrosion in the presence of corroding iron canisters.

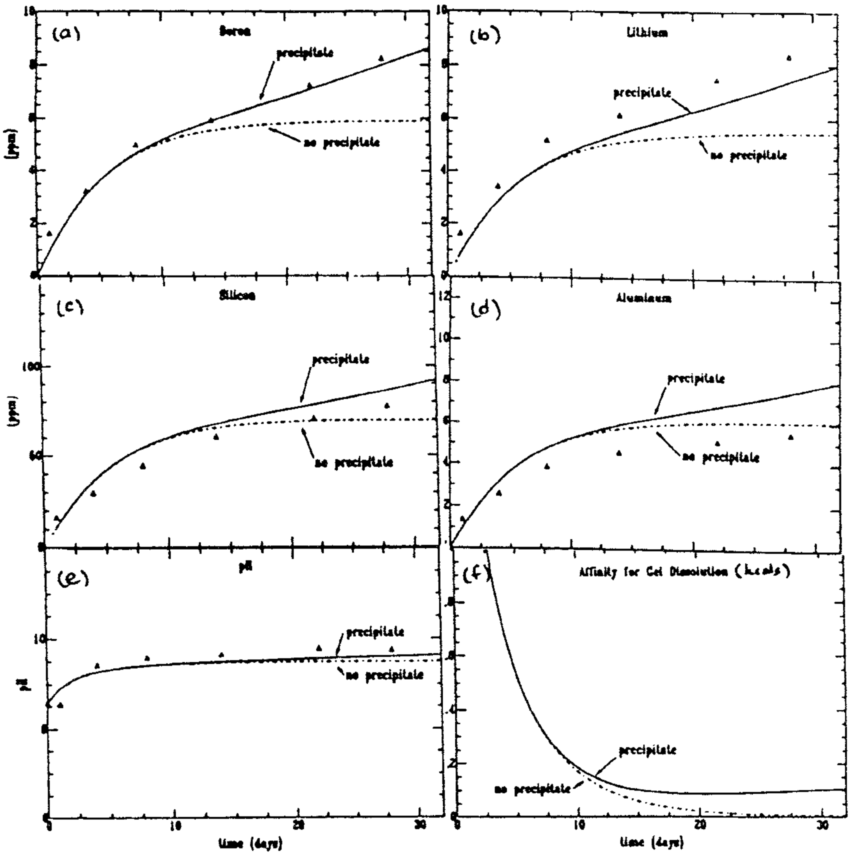

Figure 3: Comparison of experimental data for the corrosion of the glass SRL-165 at 150°C in ionized water with data calculated with EQ3/6 on the basis of the concept of' surface layer dissolution affinity' [Bourcier 1990]

from the glass to secondary alteration products may occur under conditions of constant solution composition.

Calculated results depend significantly on the thermodynamic data base for the solid phases, for solution species and for activity coefficients. In particular the thermodynamic data are uncertain for temperatures well above room temperature and/or in highly saline solutions (ionic strength >3M), or for trace elements, such as the constituents of radioactive waste. Different results are obtained if only the thermodynamically most stable phases are allowed to form or if the formation of metastable phases is considered. Also, the results are different if or if not solid solution formation is considered. From the point of view of a prediction of release to solution, solid solutions are important in particular for the trace components of the glass. Coprecipitation can occur much before individual solubility limits of the trace component are exceeded. Instead, release of major glass constituents could just as well be simulated by the individual precipitation of two idealized end members as by their solid solution. Coprecipitation of radionuclides has not yet been described in the context of glass corrosion models.

At present, a realistic reaction path cannot be determined from first principles but requires empirical knowledge on metastable phase formation. The model includes a set of empirically based assumptions concerning the formation of metastable phases and the congruency of the dissolution reaction. Typically, leach solutions are supersaturated with respect to stable phases such as goethite (FeOOH) or the clay minerals nontronite or chlorite. Modeling can only attempt to match experimental data if the calculations either exclude the phases supersaturated in the experiments or provisions are taken for considering precipitation rate laws. The identification of the true reaction path for the dissolution for a given glass and a given set of experimental conditions is quite complicated and requires frequent comparison of model and experimental results.

As an example, Figure 1 shows the results of reaction path calculations for the nuclear waste glass R7T7 in deionized water at 90°C. The calculated solution concentrations are normalized to glass composition and are plotted versus the amount of glass reacted per unit volume of solution. Solid solution formation was neglected. Idealized phases predicted to precipitate along the reaction path are $ZrSiO_4$, $Fe(OH)_3(am)$, $Nd(OH)_3$, gibbsite ($Al(OH)_3$), analcime ($NaAlSi_2O_6$), montmorillonite, and SiO_2. In reality some of these phases may actually be end members of solid solutions.

The effect of waste package components on the glass dissolution behavior can only be modelled, if their reaction behavior with silica is known. In case of iron canisters, silica may either be sorbed on iron corrosion products (critical parameters are the specific surface area of the products and the ratio of iron to glass corrosion rates) or specific iron silicate phases will form. The latter was assumed by McGrail [1990]. The authors accounted for the effect of iron by simply changing the molar ratio Fe/Si of the dissolving glass phase to values higher than in the glass. The results of this work are shown in Figure 2. The calculations predict the formation of greenalite, preventing silica saturation to occur.

Reaction kinetics – Modeling with GLASSOL

Long-term predictions require modeling of the time dependence of the glass water reaction. A principal difficulty arises from the fact that most (if not all) rate constants are determined empirically. All models use experimentally determined forward rate constants instead of the less accurate values which could be estimated from hydration theory. In the case of EQ6, the time dependence of the reaction can be described using either a transition state rate law or an empirical rate expression. The build-in solid solution option was used to calculate the effect of reaction progress on the dissolution affinity of a surface layer [Bourcier 1990]. The calculated results were significantly influenced by the precipitation kinetics of a nontronite solid solution. As can be seen from Figure 3, if precipitation kinetics was considered (using a fitted rate constant) good agreement could be obtained between calculated and measured time dependence of reaction. Slow formation of nontronite would be the driving force of a long-term reaction and this process would also be compatible with the observed [Grambow 1987] nontronite supersaturation of many leach solutions. EQ3/6 does not consider rate control by the transport (diffusion) of reactant or product species. Hence, the code cannot describe the effect of growing surface layers as a transport barrier on the reaction rates. In many cases it is sufficiently accurate to neglect this effect but, in particular in tests with flowing leachants surface layers may be an important transport barrier.

Reaction rates cannot be calculated with the PHREEQE code. Therefore, the code was modified to provide an output which can be used for the calculation of reaction kinetics. A code, GLASSOL, was developed to interpret this PHREEQE output in terms of kinetics [Grambow 1987]. The effect of the growth of a surface layer as a barrier to silica transport is considered. The reaction rate and the time increment between two steps of the reaction path model are calculated using the activities of ortho-silicic acid from the output of PHREEQE and a set of kinetic parameters determined experimentally. The silica saturation concentration is determined experimentally, using data from tests performed at high S/V values. Because the activities of silicic acid calculated by PHREEQE are constrained by the sum of all reactions consuming silica (i.e. precipitation of silicates, sorption or hydrolysis of silicic acid), the effect of such reactions on the dissolution kinetics of the glass matrix is considered implicitly in GLASSOL. The diffusion coefficient of silica in the surface layer was determined from the best fit of the model to experimental data, in particular to the data from flow experiments.

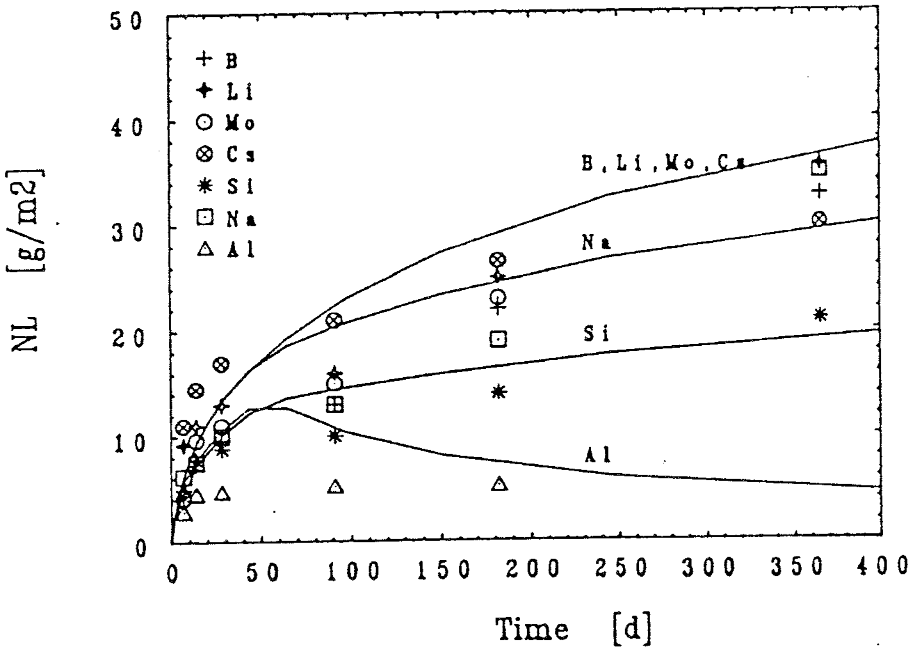

Figure 4: Comparison of experimental and calculated (PHREEQE/GLASSOL) normalized mass loss data of various elements from the glass R7T7 during corrosion in static tests (90°C, SA/V = 10 m^{-1}, deionized water)[Grambow 1987]

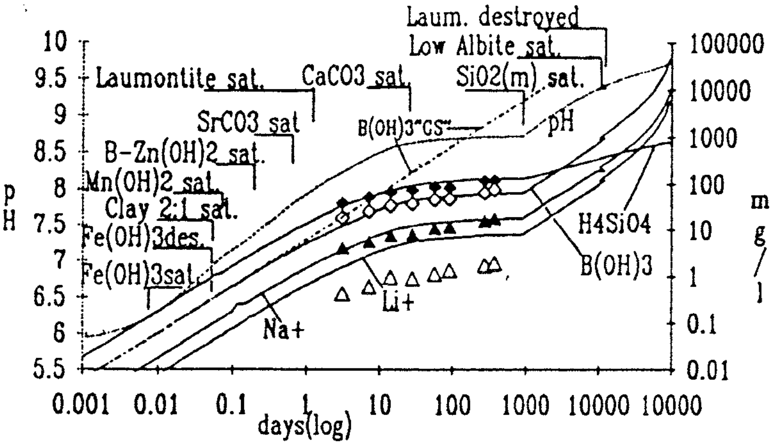

Figure 5: Calculated (DISSOL) and measured [Fillet 1987] elemental concentrations for corrosion of R7T7 glass at 100°C and secondary products when calculating reaction affinity to SiO_2. 'GS' refers to overall affinity concept [Advocat et al. 1990]

A comparison of modeling and experimental results is shown for R7T7 glass in deionized water under static conditions. Solution data and calculated curves are contained in Figure 4. The calculated time dependence of glass corrosion is based on the reaction path model described in Figure 1. The calculated curves deviate by less than 20% from the average value for the Si, B, Na, Li, Mo and Cs data. For the release of Al the deviation between theory and experiment is larger (as much as a factor of 2).

Corrosion of R7T7 glass was also modelled for 100°C (10 m^{-1}) with the code DISSOL [Advocat et al. 1990]. Alteration products considered were hydroxides, carbonates, silicates, aluminum silicates, zeolites and phyllosilicates. The compositions of the latter phases were calculated as a function of reaction progress using the solid solution model CISSFIT. Two cases were considered, (1) one with the dissolution affinity given by the affinity of the overall glass water reaction and (2) another with the affinity being controlled by the reaction SiO_2 *2 H_2O -> H_4SiO_4 similarly as in PHREEQE/GLASSOL. A comparison of calculated and experimental results is given in Figure 5. For case (1) only the boron curve is shown, indicating no match with the data. In contrast, for case (2) the agreement of calculated and experimental data was in an average less than 10%. It could be shown that, except of the zeolite 'dachiaridite', none of the phases would consume sufficient silica to allow resumption of glass corrosion after the reaching silica saturation.

Whether dachiaridite will form is not known. But in case of the glass SAN-60 there is experimental evidence that the formation of another zeolite (analcime) leads to an increase of the reaction rate with time. The reaction was modeled with PHREEQE/GLASSOL and the results also predicted an acceleration of glass corrosion due to the formation of analcime [Van Iseghem et al. 1987]. This agreement of model results with a complex experimental reality shows on the one hand that even in the absence of full scale real solid solution models and a complete set of alteration phases, current models are able to represent general dissolution trends to a high degree of detail and, on the other hand, open new fields for experimental investigations ('does dachiaridite form?').

Due to the dominant role of SiO_2-saturation, the groundwater flow rate and the accessible solution volume play an important role for the corrosion kinetics of nuclear waste glass. Depending on the flow rate and saturation concentration the release of soluble glass constituents is independent of or proportional to the flow rate [Mendel 1984]. The program EQ3/6 allows clear distinction between open and closed system calculations. At the time being, this option has not been used to model glass corrosion behavior. In the case of PHREEQE/GLASSOL the application of open system conditions to glass corrosion was considered within the GLASSOL code [Grambow 1987]. This was possible because, with respect to solution composition, the reaction path in a static test is similar to a sequence of steady states for varying ratios of reaction rates to flow rates. The effect of flow rate has been considered in GLASSOL by the equation

$$dC_G/dt = r_m\, S/V - C_G\, F/V$$

where F is the volumetric flow rate, C_G is the amount of glass reacted (expressed in units of concentration in solution), and r_m is the corrosion rate. The flow test experiments were performed with the R7T7-glass using the MCC-4 test procedure [MCC 1983]. The effect of flow rate was calculated, using the same reaction path model and rate constants that was used for static leaching of the glass. Calculated and

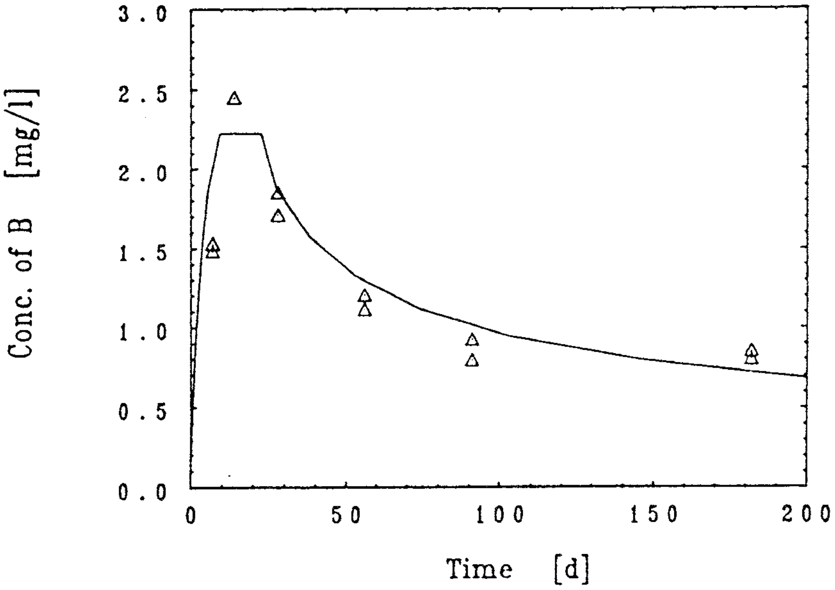

Figure 6: Comparison of experimental and calculated (PHREEQE/GLASSOL) solution data of boron, resulting from corrosion of R7T7 glass in tests with flowing water (90°C, SA/V = 10 m^{-1}, deionized water at 2.9 ml/d) [Grambow]

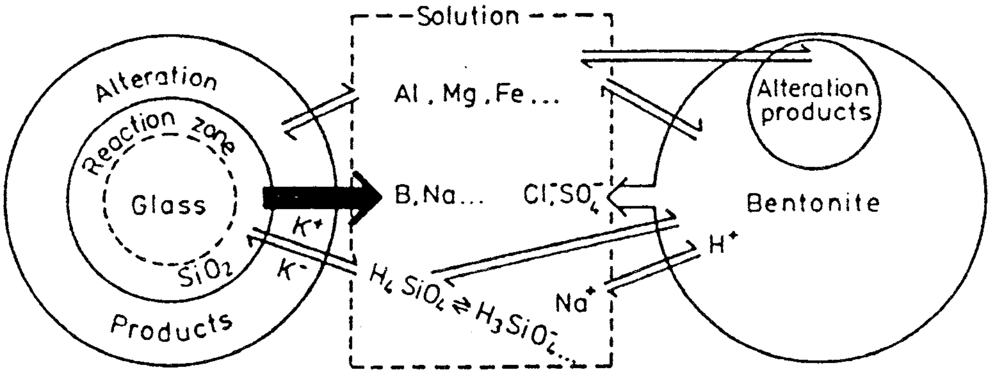

Figure 7: Interdependence of the various reactions in the glass/bentonite/water system.

experimental B solution concentrations (flow test 2.9 ml/d) are shown in Figure 6. The data show the typical maximum in solution concentration [Mendel 1984]. It occurs after a reaction time of about 14 days which is similar to the solution residence time in the leaching vessel. The curve deviates by less than 20 % from the measured data.

For the presence of clay backfill the interdependence of the various reactions is described in Figure 7. Until now, modeling of the clay/ glass/water system was only performed for bentonite (MX-80, mainly Na-montmorillonite) and R7T7 glass using the PHREEQE/ GLASSOL code [Grambow 1987, JSS 1987,1988]. The mass balance equations have been simultaneously solved. Ion exchange equilibria were calculated considering competition of Na, K, Cs, Mg, Ca, and H -ions for surface sites. Exchange constants and cation exchange capacity were determined experimentally. Modeling results for the corrosion of the a radioactive glass of R7T7 composition (S/V = 1100 m^{-1}) in the presence of 4 g of bentonite in 30 ml of solution are shown in Figure 8 together with experimental data [JSS 1988]. Rate and stability constants were the same as those used for modeling the glass reaction behavior in deionized water (Figures 4 and 6). At this high S/V ratio silica saturation with respect to the glass surface is achieved almost instantaneously, similar as in the absence of bentonite. For glass corrosion at S/V = 10 m^{-1} the effect of the presence of bentonite was modelled for various clay/water ratios.The calculated effect of bentonite/water ratio on glass corrosion is shown in Figure 9. Small amounts of bentonite increase the initial release from the glass (a pH effect), whereas large amounts of bentonite appear to be beneficial (promotion of silica saturation). The observed and calculated trends are specific to bentonite clay and cannot be considered representative of other clay/water systems. Experiments have shown that some smectite clays dramatically enhance glass corrosion by keeping silica concentrations low [Godon and Vernaz 1990]. These clay compositions controlled the solution concentration of silica to values much lower than required for saturating the glass surface, thus maintaining a high dissolution affinity. Consequently, also the effect of the clay/water ratio on glass corrosion was inverse of that shown in Figure 9. Modeling of the effect of clay compositions other than bentonite has not yet been performed.

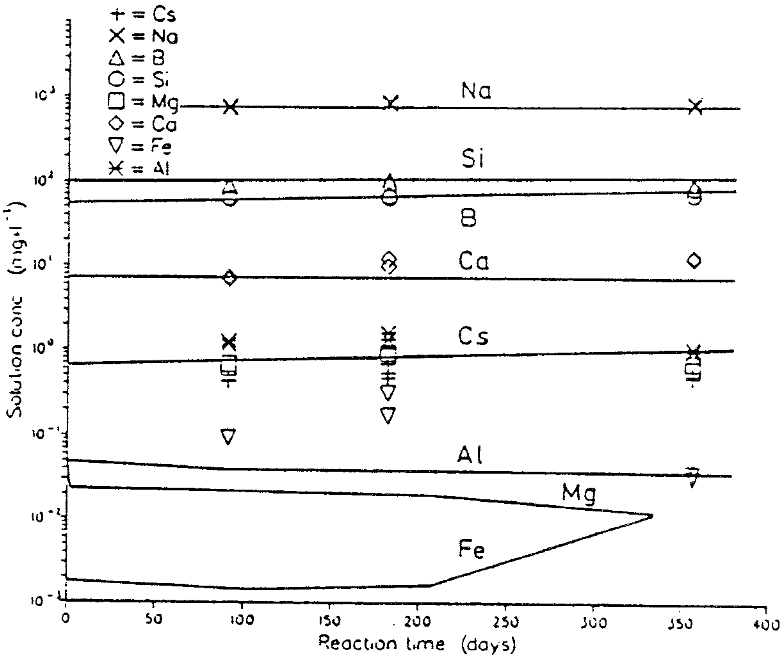

Figure 8: Comparison of modelling results and experimental data for the corrosion of the α radioactive glass of R7T7 composition (S/V = 1100 m^{-1} in the presence of 4 g of bentonite in 30 ml of solution [JSS 1988].

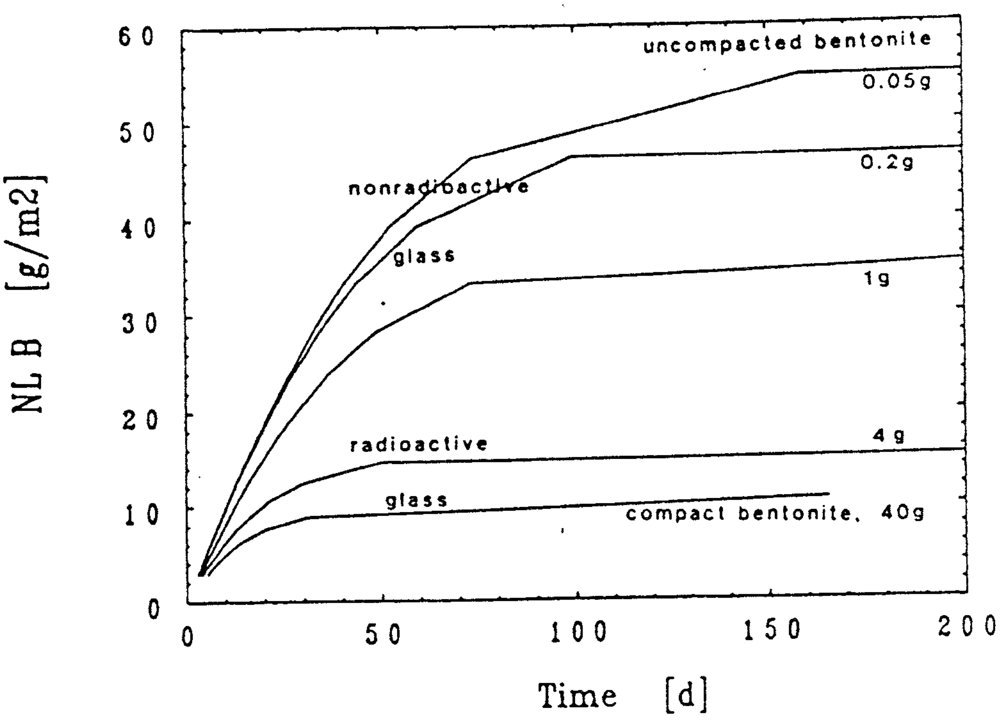

Figure 9: Calculated effect of bentonite/water ratio on glass corrosion.

VALIDATION PROCESS FOR THE MODELS

Before models can be used to predict long-term materials performance, there must be sufficient confidence in the degree of understanding and quantification of the corrosion mechanism. All models are based on a combination of theoretically sound concepts with semi-empirical to purely empirical parameter. The general treatment of mass transfer by reaction path modeling and of kinetics by a transition state rate law has a sound theoretical basis. On the other hand, the meaning of the term 'silica saturation' is still not well understood and saturation effects may alternatively be described by the dissolution affinity of a surface layer. A model which "explains" a single set of data cannot be considered confirmed, because different models may fit the same data and the lack of sufficient precision may not allow distinction between "good" and "better" or "right" and "wrong" models. The validity of the EQ3/6 based 'surface layer affinity model' cannot yet being assessed, because the model was only applied to data of a single experimental setup. The validity of the GLASSOL model was assessed by comparing calculated results to an extensive experimental data base. This data base includes different glass compositions and a wide range of experimental conditions (Table 1).

For the condition of each corrosion test, the model was used to calculate solution concentrations and pH, as well as normalized elemental mass loss and surface layer thickness. The temperature of all tests was 90°C. For each glass composition a separate set of kinetic parameters were determined from the experiments. The parameters remained unchanged within the studied range of S/V values, flow rates and groundwater compositions. The same list of potential alteration products (a detailed description of this list is given in ref. [Grambow 1987]) was used for all glass compositions.

Table 1: Summary of conditions used for experimental validation of GLASSOL at 90°C, typical solution volume: 30 mL

Glass	Solution	final	S/V	flow	time	system
R7T7	DI,GW,SI	7-9	10-10000	0-3	3-365	BE,MAG
SRL-131	DI,BA,	SI7-10	10	0-15	28-1400	
PNL-76/68	DI	7-9	10	0-14	28-365	
SM58	DI	7-9	10-100	0	1-365	
SAN60	DI	7-9	10-100	0	1-365	
MW	DI	7-9	10, 1320	0	7-365	

GW=granite water, SI=silicate water, DI=de-ionized water, BA=basalt water, BE=bentonite, MAG=magnetite

For the soluble glass constituents such as Na, Li, B, Mo and Cs, and for Si the calculated results usually deviated by less than 30% from the results of solution or surface analyses. Due to limited thermodynamic data, discrepancies were larger for sparingly soluble elements such as Fe, Mg and Al. A detailed comparison between the data and the model is given in the references [JSS 1987, 1988, Grambow 1987, Grambow and Strachan 1988, Zwicky et al. 1989].

The fit of soluble element and silica release data shows that some general aspects of the reaction path (i.e. of solution chemistry and of mass transfer relations) and of the kinetic constraints are represented by the model in a reasonable manner, even without considering details of the reaction. A better agreement of experimental and modeling data will probably be obtained if some of these 'details' are considered, i.e., solid solution formation, degree of crystallinity of phases, alkali ion exchange, sorption phenomena in the surface layer, and the formation of colloids or polynuclear complexes in solution.

The long-term reaction rate controlling process constitutes the major uncertain and not at all validated aspect of all present models. Various cases (continued water diffusion/ion exchange, zeolite formation as driving force etc.) have been proposed, but at the time being, long-term predictions cannot be based on these mechanism. Instead of the deterministic modelling approach, the only thing which can be done for performance assessment are pragmatic worst case calculations using linear long-term rate laws.

Due to the long times involved agreement of modeling and experimental data is not sufficient to allow strong long-term predictions. Long-term trend may not be visible in short-term laboratory data. It has been suggested to use natural analogues, in particular basalt glasses, to test hypothesis concerning long-term glass dissolution processes [Lutze et al. 1985].

Preliminary analysis of rate controlling processes for seawater altered basalt glasses have shown that the same general concepts (forward reaction rate, silica saturation) used to describe nuclear waste glass corrosion can be used to describe the alteration in the natural environment [Grambow et al. 1985]. The uncertainty in the determination of reaction rates on natural samples did not yet allow to infer a long-term rate law with strong confidence. Nevertheless, significant observations helped to validate significant aspects in the overall picture of glass corrosion. Fractured basalt glass shards and hyaloclastite surfaces of closed fractures are apparently altered to the same degree as more open fractures. Thus, silica-saturated conditions are reached in most samples. This observation is of paramount importance, because it gives evidence that the surface area of all fractures in a nuclear glass monolith must be considered when calculating release under saturated conditions. Also, the enhancement of glass corrosion by zeolite formation is confirmed by natural samples.

EVALUATION OF THE LONG-TERM GLASS PERFORMANCE

The GLASSOL model was used to predict the performance of a typically fractured COGEMA glass monoliths of R7T7 composition, for periods of time up to 10^5 years at 90°C in a granite repository [Grambow et al. 1988]. Because there is uncertainty in the empirical parameters, such as the silica saturation concentration or the long-term rate, and especially because the process controlling the long-term reaction rate at silica saturation is still not well understood, a set of results was calculated for which parameters and bounding assumptions were varied. The calculations were performed for flowing groundwater (1L/yr/canister) under the assumption that no major sink for silica is present (i.e. that iron corrosion products or smectites with low equilibrium concentration of dissolved silica are absent). In Figure 10, four alternative cases are compared. Only soluble elements were considered.

Case (a) is for the forward rate of reaction and describes a hypothetical case which will not be exceeded even with an infinite volume or flow rate of groundwater or an infinite sorption capacity of iron corrosion products. The actual release will always be less than these extrapolated values. Case (b) is calculated with the same rate constants as used for modelling experimental data (Figures 4, 6 and 8). Almost all experimental data justify confidence that the release will not be higher. The curve is dominated by the constant long-term rate of $2.5 \cdot 10^{-3}$ g/(m^2d). The plateau is given by the saturation concentration of silica. Acceleration of reaction rates by silica consuming dachiaridite [Advocat et al. 1990] cannot be excluded with absolute confidence, but there are no experimental data support this possibility. Cases (d) and (e) are calculated for glass/-water reactions which eventually stop after reaching silica saturation. These cases are calculated as a bounding condition, to account for the possibility that the long-term rate may decrease with time by an unknown rate law. In Case (d) the reaction rate is governed only by the groundwater flow rate and by the solubility limit of silica with respect to the glass surface. Case (e) describes the release when a 1 m backfill barrier of bentonite is present which limits the transport of silica away from the glass surface with a diffusion coefficient of 10^{-11} m^2/sec. For the reference temperature of 90°C, a lower release than that given by the curves (d) and (e) respectively, cannot be substantiated.

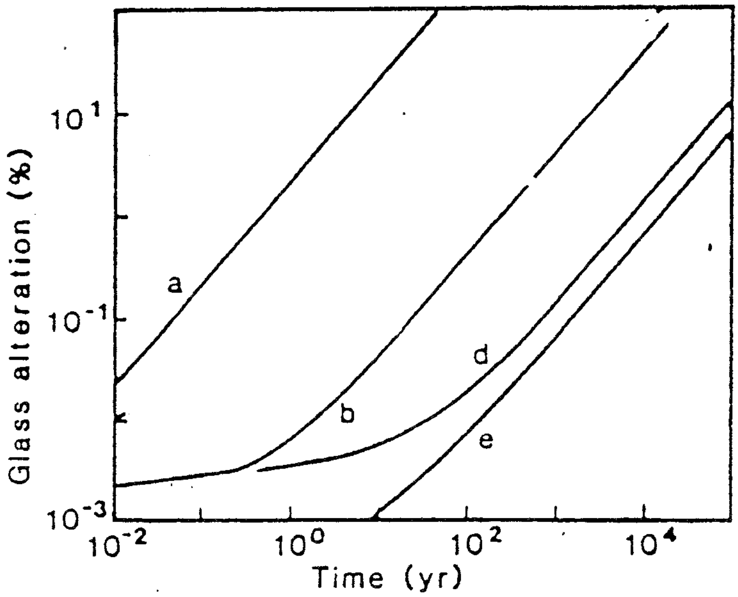

Figure 10: Long-term -prediction of glass alteration. Limiting cases described in the text.

Conclusions

Provided that silica consuming engineered barrier materials are absent one can conclude from Figure 10 that

(1) Uncertainties in the forward rate constant can be important to model experimental data but they are irrelevant for long-term predictions.

(2) Maximum possible uncertainties by a factor of 2 in the magnitude of the silica saturation concentration would only yield corresponding uncertainties in the initial plateau in curve (b) and in the position of bounding case (d).

(3) Because the long-term rate law is unknown, long-term glass stability can only be assessed with a factor of 100 of uncertainty at groundwater flow rates of 1L/yr/canister. This factor is given by the differences between the curves (b) and (d,e).

(4) Increasing groundwater flow rate and lower temperatures (due to an expected decrease in the long-term rate) would decrease the gap between the bounding cases (b) and (d).

(5) A flow rate dependent life time of the glass canister is expected, when the long-term rate becomes too low to determine the release. However, at very low flow rates, silica diffusion into the near field may become rate controlling.

(6) 1 m of bentonite may be of important for retention of radionuclides but does not effect the kinetics of glass degradation at a flow rate of 1L/yr/canister.

If silica consuming materials are present, the upper limit of release is given by the forward rate. With forward rate control complete glass degradation is expected within few hundreds of years, hence, the glass phase cannot contribute to waste isolation. Critical parameters are the reaction rate of dissolving materials (i.e. of iron canisters), the sorption or precipitation capacity of the material (specific surface area, mass ratio glass/barrier material). With the low reaction rates of iron canisters under reducing conditions (ca. 2cm/1000 yr) iron canister corrosion cannot prevent silica saturation to occur [JSS 1988]. However, under oxidative conditions with high iron corrosion rates glass corrosion rates may remain very high. Glass corrosion rates will also be significantly effected by the equilibrium concentration of silica with respect to clay buffer materials. If this concentration is lower than the saturation concentration with respect to the glass surface, saturation may never be achieved. Consequently, it is highly recommended to use only high silica clay buffer materials or to provide additional sources for high silica solution concentrations within the engineered barrier system.

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DISCUSSION ON GLASS RELEASE

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This topic includes several aspects: identification of glass dissolution parameters, geochemical modelling of the solid/solution interaction and validation of models. Such aspects must be well understood to carry a credible performance assessment of the glass durability (and the associated release/retention of radionuclides of interest) in near-field conditions.

From the review presentation of Bernd Grambow and the discussion that followed amongst the attenders, it can be stated that:

- Mechanisms of glass dissolution are now fairly well known. The role of silica dissolved in solution seems crucial for the rate of corrosion. However, from the performance assessment perspective, the exact significance of "saturation effects", and thus of the long-term corrosion rate of the matrix, remains unclear. Very few experiments are thought to be actually directly useful, because they deal with too short periods of time and research efforts should hence be devoted to this subject in the future. Long-term experiments, in carefully and relevant conditions are needed.

- Natural analogues (notably basaltic glasses) can be very useful for giving hints on the long-term behaviour of the nuclear glass. They show in particular the major importance of alteration products. We should now focus on the behaviour of trace radionuclides with respect to these secondary phases and specify both the mechanisms involved (sorption, incorporation in the lattice, co-precipitation, etc) and the corresponding solid/solution partition coefficients. The "retention" of radionuclides in the near-field is also concerned with the alteration products of the canister corrosion (iron(oxi)hydroxides) which will likely play a dominant role. Models describing quantitatively such partition phenomena are still lacking and would be a research priority.

- If one refers to some experiments, the role of bentonite (engineered barrier) may be of prime importance in acting as a geochemical sink for silica thus promoting continued dissolution of the glass, even on the long-term. However, such a statement should be put into perspective because the effects seems to vary from one type of clay to another and also the effect could be rapidly limited by the saturation of the trapping sites.

- Geochemical models presently developed seem to describe quite conveniently the glass/solution interaction, in particular in terms of reaction path. Nevertheless, the modelling of the glass performance in complex geochemistry of the near-field (which includes coupling with transport through the engineered barrier) has still to be performed.

- The individual effect of various parameters (temperature, pH, S/V, flow rate, etc.) is quite well identified. But, many phenomena are independent and the overall role of these parameters should be clarified.

SOURCE TERM MODELS FOR THE RELEASE OF RADIONUCLIDES FROM USED NUCLEAR FUEL

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1. INTRODUCTION

The environmental and safety assessment of used nuclear fuel disposal in an underground vault requires information concerning the rates at which radionuclides will be released from the fuel elements after groundwater breaches the fuel cladding and contacts the fuel. This information is provided by the source term model.

Experimental studies on used-fuel dissolution have shown that the release of radionuclides from used fuel depends largely on the location of the radionuclides within the fuel element. Three main release mechanisms, which operate on different time scales, have been identified (Johnson and Shoesmith, 1988).

First, there is the rapid release of soluble fission products (e.g., cesium and iodine) from the fuel/cladding gap as soon as groundwater penetrates the fuel cladding. Second, there is the leaching of fission products (e.g., cesium, iodine and technetium) from the fuel grain boundaries. Third, there is the very slow release of radionuclides from the fuel matrix due to the dissolution of the UO_2 grains. The dissolution of the fuel controls the release of the major fraction of the radionuclide inventory. This does not mean, of course, that the radionuclide releases from the gap and grain boundaries are not important contributors to the calculated doses and/or risks (cf., Fig. 1).

The source term model describing radionuclide releases from used fuel should represent all three release mechanisms. In mathematical terms, such a model defines the boundary conditions at the fuel/buffer interface needed to solve the mass transport equations describing the migration of radionuclides away from the fuel/groundwater interface, through the engineered barriers (e.g., clay buffer) and into the host rock.

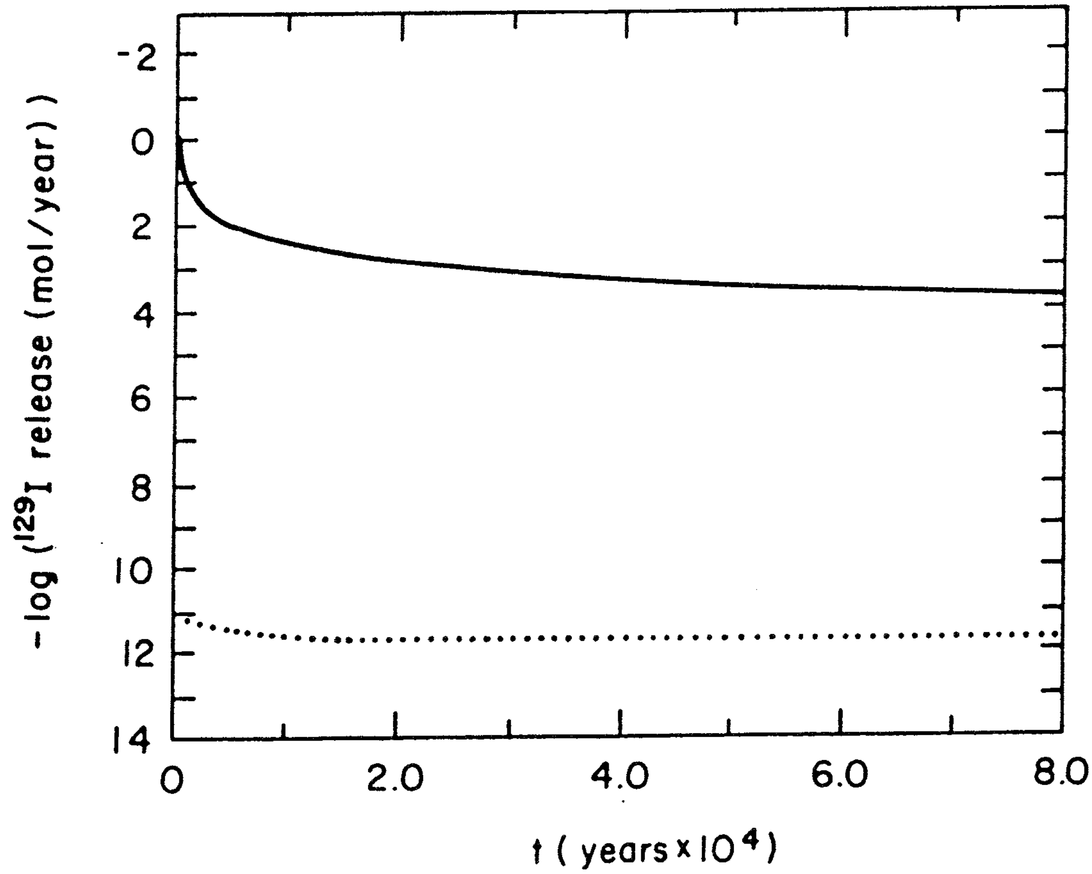

Figure 1: An example of the instant-release (——) and the congruent- release (......) source terms for ^{129}I release from used fuel as a function of time (Garisto et al., 1989).

The source term model used in the Canadian Nuclear Fuel Waste Management Program (CWMP) consists of three components: (i) an instant-release model, representing both the gap and grain-boundary releases; (ii) a long-term release model, representing the congruent release of radionuclides due to dissolution of the fuel grains; and (iii) a model for the release of activation products from the Zircaloy cladding. The objective of this paper is to describe the radionuclide source term model used in the CWMP and to identify key areas that require further research. In addition, alternative approaches for determining radionuclide source terms will be briefly discussed.

2. MASS TRANSPORT MODEL

Before describing the CWMP source term model, it is necessary to summarize the mathematical equations used to model the migration of radionuclides through the buffer material surrounding the fuel containers. The mass transport of radionuclides in the buffer is modelled using a one-dimensional diffusion equation

$$\frac{\partial C_i}{\partial t} = \frac{D_i^B}{R_i^B} \frac{\partial^2 C_i}{\partial x^2} - \lambda_i C_i \qquad (2.1)$$

where C_i is the pore-water concentration of radionuclide i in the buffer, D_i^B is the effective diffusion coefficient of radionuclide i in the buffer, R_i^B is the capacity factor of radionuclide i in the buffer, i.e., the retardation factor times the porosity, and λ is the decay constant of radionuclide i. The justification for a one-dimensional model has been given by Garisto and LeNeveu (1989) and will not be repeated here.

For convenience, we have only presented a simple version of the mass-transport equation. Thus, Equation (2.1) it only valid if the convective flow velocity in the buffer is negligible and if radioactive buildup, i.e., the creation of radionuclide i due to the decay of its parent, are not important. This latter process, for example, must be included in the description of 226 Ra transport through the buffer (Garisto and LeNeveu, 1989).

To solve Equation (2.1), boundary conditions must be specified at the fuel/buffer interface ($x = 0$) and the buffer/rock interface ($x = L$). The $x = 0$ boundary conditions are defined by the radionuclide source term model. Since the CWMP source term model does not explicitly give (see following sections) the radionuclide fluxes at $x = 0$, these are calculated from the solution of Equation (2.1).

The $x = L$ boundary condition determines, explicitly or implicitly, the rate of mass transfer across the buffer/rock interface. Various exit boundary conditions can be used: (i) $C_i = 0$ (swept-away boundary condition), (ii) use of mass transfer coefficients, i.e., the flux across the buffer/rock interface is proportional to the concentration at $x = L$; and (iii) continuity of flux and concentration at $x = L$. The latter boundary condition is more difficult to apply since, in this case, Equation (2.1) must be solved simultaneously with the equation used to describe mass transport of radionuclides through the host rock. The exit boundary condition depends on the properties of the host rock, e.g., the $C_i = 0$ boundary condition applies if the host rock is permeable to water flow. Further discussion of these options is beyond the scope of this paper.

3. THE INSTANT-RELEASE MODEL

The short-term release of fission products has been the subject of extensive study (Stroes-Gascoyne et al., 1987). These studies show that fission product release from both the fuel/cladding gap and grain boundaries can contribute to release in the short term. Fission products that would be released instantly include I, Cs, Tc, ^{3}H and ^{14}C (Garisto et al., 1990; Oversby, 1987; Apted et al., 1987).

In our model, we treat both gap and grain-boundary radionuclide inventories as instant-release fractions (IRFs), i.e., the fractions of the total used-fuel inventory for given radionuclides that are available for fast release when groundwater contacts the used fuel. This conservative approximation neglects the difference between the kinetics of release from the gap and from grain boundaries (Garisto et al., 1990). We use this approximation because it is difficult experimentally to separate the individual release contribution of the gap and grain boundaries. Furthermore, only sparse experimental data are available on the chemical nature and quantities of grain-boundary constituents and their rates of release (Johnson and Shoesmith, 1988).

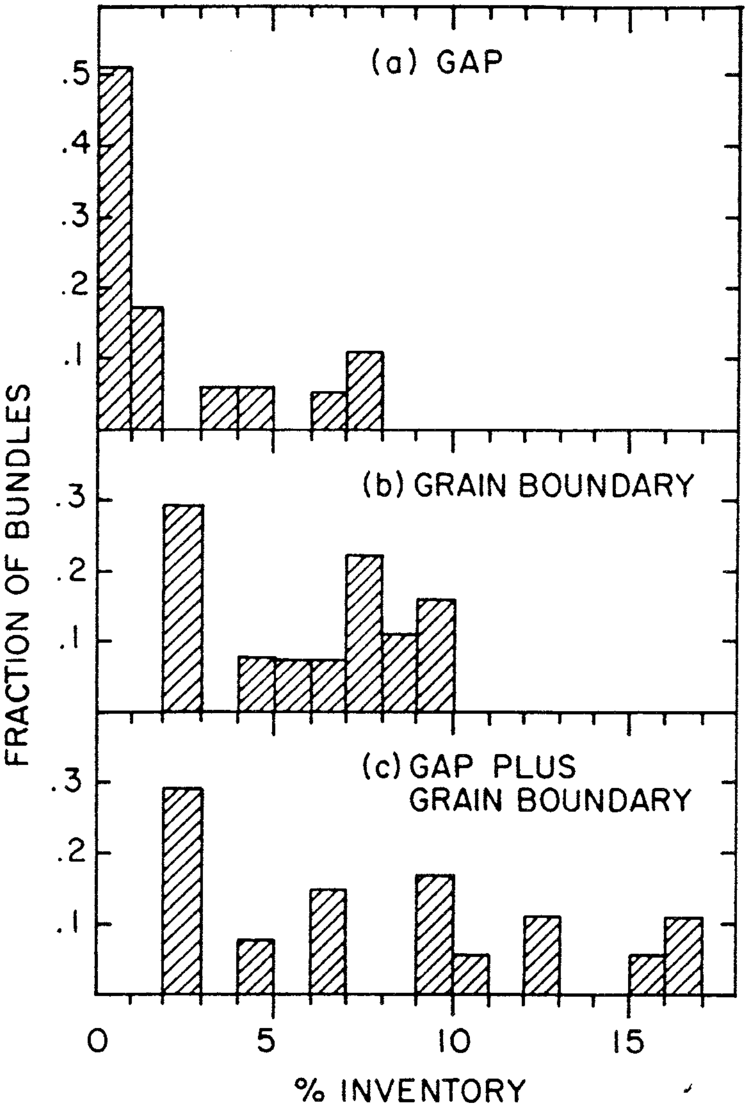

Figure 2: Distribution of (a) Gap, (b) Grain-Boundary and (c) Gap plus Grain-Boundary Inventories of Cesium and Iodine in Used Fuel Bundles (Garisto et al., 1989).

3.1 The Instant-Release Source Term

The instantly released radionuclides are assumed to dissolve in the groundwater immediately upon container flooding (see Section 5) and reach uniform concentrations inside the container (LeNeveu and Johnson, 1986; Apted et al., 1987). For this model, the instant-release source term is obtained by first solving the diffusion equation (2.1) with the boundary condition

$$\varepsilon_c V_c \frac{\partial C_i}{\partial t} = I_i(t_c)\delta(t) - \lambda_i \varepsilon_c V_c C_i + D_i B \frac{\partial C_i}{\partial x} A_c, \qquad x = 0 \qquad (3.1)$$

where $I_i(tc)$ is the inventory (per container) of radionuclide i at the time of container failure, ε_c is the void fraction of the container, V_c is the volume of the container, A_c is the surface area of the container, and $\delta(t)$ is the Dirac delta function. The instant-release source term, $G_i(t)$, is given by the equation

$$G_i(t) = - D_i B \left. \frac{\partial C_i}{\partial x} \right|_{x=0} A_c (IRF)_i \qquad (3.2)$$

The instant-release source term is proportional to $(IRF)_i$, which depends on both the gap and grain-boundary inventories of radionuclide i in the used fuel and the aqueous chemistry of the radionuclide. Gap and grain-boundary inventories are strongly dependent on the fuel power history (see Fig. 2). Estimated distribution functions for IRFs are shown in Table 1 (Garisto et al., 1990).

Table 1. Parameter distribrution functions for instant-release fractions.

Radionuclide	Distribution	μ (%)	σ (%)	Cutoffs (%)
^{135}Cs	normal	8.1	1.0	1.2 – 25
^{129}I	normal	8.1	1.0	1.2 – 25
^{99}Tc	normal	6.0	1.0	1.2 – 25
^{14}C	uniform	–	–	1 – 25
^{3}H	uniform	–	–	30 – 40

Figure 1 shows $G_i(t)$ for ^{129}I release from used fuel, calculated using $(IRF)_I$ = 1.2%. The instant-release flux drops sharply at short times and decreases gradually at long times due to depletion of the ^{129}I inventory in the container. The instant-release source term for ^{129}I is much larger than the ^{129}I source term due to the solubility-controlled dissolution of the fuel matrix (calculated with a UO_2 solubility of 10^{-10} mol/kg).

3.2 Possible Improvements in Modelling Short-Term Release of Radionuclides from Used Fuel

A more realistic source-term model for the short-term release of radionuclides from used fuel could be derived if appropriate data were available. In particular, more reliable data on the distribution of the radionuclides between the gap, grains and grain boundaries, and the chemical form of fission products in the fuel are required. This information could decrease significantly the uncertainty in the IRFs, many of which were derived by simplistic, chemical-analogy arguments (Garisto et al., 1990).

In addition, kinetic data on the leaching of radionuclides from grain boundaries would allow us to treat the gap and grain-boundary releases separately in the source-term model, thus eliminating the considerable conservatism in the current instant-release model. Several experimental approaches that could lead to a mechanistic understanding of grain-boundary release have been suggested by Grambow (1989) (e.g., studies of fragmented and powdered fuel, studies of water penetration into the fuel, and surface area measurements).

Instantly released technetium is potentially an important contributor to the calculated doses from a repository (Garisto and LeNeveu, 1989). The technetium release model could be improved by measuring the dissolution kinetics of metallic alloys that have a similar composition to the Ru-Mo-Tc-Rh-Pd inclusions found in grain boundaries.

4. THE MODEL FOR UO_2 MATRIX DISSOLUTION

4.1 Solubility-Limited Fuel Dissolution Model

Radionuclides will be released from used fuel as the fuel matrix dissolves. As previously mentioned, this relatively slow process controls the release of the major portion of the radionuclides present in used fuel. A solubility-limited dissolution model can be used to determine the rate of used-fuel dissolution. In this model, the dissolution rate of the used UO_2 fuel is limited by the solubility of UO_2 if the mass-transport of dissolved uranium through the buffer is slow and if UO_2 is the thermodynamically stable uranium solid (Garisto and Garisto, 1986).

A solubility-limited dissolution model is considered appropriate for the CWMP because reducing conditions are expected to prevail in the vault. Moreover, studies of the dissolution of UO_2 in the presence of the alpha-radiolysis products of water indicate that, for radiation fields comparable to those at a used-fuel surface, oxidation will not proceed beyond the U_3O_7 stage (Sunder et al., 1990).

It is emphasized that a solubility-controlled radionuclide release model may not be valid if UO_2 (or U_4O_9) is not the thermodynamically stable uranium solid in the vault environment. For example, the oxidation of UO_2 to U_3O_8 would disrupt the fluorite structure of the fuel, with the possible concurrent release of radionuclides. In this case, the solid transformation rate would control the release of radionuclides rather than the transport of dissolved uranium away from the fuel/buffer interface. Possible approaches to modelling the long-term release of radionuclides from fuel under oxidizing conditions are discussed in Section 4.4.

In the solubility-limited fuel dissolution model, the transport of dissolved uranium is described by the equation

$$\frac{\partial C_m}{\partial t} - \frac{D^B_m}{R^B_m} \frac{\partial^2 C_m}{\partial x^2} + \lambda_m C_m = 0 \qquad (4.1)$$

where the subscript μ is used to denote parameter values for the used fuel matrix (i.e., uranium). This diffusion equation is solved with a flux boundary condition at the fuel/buffer interface ($x = 0$)

$$- D_m^B \frac{\partial C_m}{\partial x} = \alpha_m(C_m^s - C_m(0,t)) \qquad (4.2)$$

and a flux boundary condition at the edge of the vault (x = L)

$$- D_m^B \frac{\partial C_m}{\partial x} = K_m C_m \qquad (4.3)$$

C_ms is the solubility of the used-fuel matrix, α_m is the dissolution rate constant for UO_2, and K_m is the mass transfer coefficient for transport of dissolved uranium across the buffer-rock interface. K_m depends on the hydrogeological conditions in the rock adjacent to the vault/rock interface and may therefore have different values in different regions of the vault.

The dissolution rate of the used fuel, $F_mU(t)$, is calculated from the solution of the diffusion equation using the expression

$$F_m^U(t) = - D_m^B \frac{\partial C_m}{\partial x} \bigg|_{x=0} Ac \qquad (4.4)$$

radionuclide source term, $F_{im}(t)$, due to the solubility-controlled, congruent dissolution of the fuel matrix is proportional to $F_m^U(t)$

$$F_{im}(t) = (I_i(t) / I_m)\ F_m^U(t) \qquad (4.5)$$

where $I_i(t)$ is the inventory of the radionuclide in the used-fuel matrix, and I_m is the inventory of the used-fuel matrix. This congruent release model is supported by long-term leaching experiments (Johnson, 1982; Johnson et al., 1982) that show equal fractional dissolution rates of all radionuclides at long times, i.e., the radionuclide release is controlled by the extent of dissolution of the UO_2 grains. However, congruency is expected only under conditions where saturation concentrations of radionuclides are not reached in solution. If these saturation conditions are attained, then a congruent model may not be completely valid due to precipitation of some radionuclides.

For example, if the dissolution rate of the UO_2 is fast enough that the plutonium concentration near the fuel exceeds the solubility of PuO_2(am), then the plutonium in solution could precipitate, and the rate of release of plutonium would be lowered. In our source term model, precipitation of uranium, plutonium, neptunium, thorium and technetium is considered. The solubility-limited release of a precipitated radionuclide is calculated using the same equations (with radionuclide-dependent parameters) that are used to model the dissolution of the fuel matrix.

4.2 Individual Radionuclide Solubilities

The long-term source term model requires, as input, the solubilities of the UO_2 matrix and other radionuclides as a function of the groundwater conditions in the vault. The solubilities of uranium, neptunium, plutonium, thorium and technetium in the vault are discussed in detail by Lemire and Garisto (1989).

The solubility of the used-fuel matrix is a critical parameter in our source term model. The thermodynamic data used to calculate the solubility of the UO_2 is, for the most part, fairly reliable. Thus, one of the largest uncertainties in the calculation of the UO_2 solubility is the composition of the aqueous solution in contact with the fuel ("contact water"). Dissolved salts can influence solid solubilities by complexation, and by affecting the chemical equilibrium constants (ionic strength and/or specific ion effects) needed to calculate the solubilities.

The reference groundwater in the CWMP is primarily a solution of sodium chloride, calcium chloride and sodium sulphate (Gascoyne, 1988). However, the water contacting the used fuel must first pass through the buffer. Consequently, the composition of the contact water may be quite different from the reference groundwater. The characteristics of the contact water will depend strongly on the ion exchange capacity of the buffer, on the minor components of the buffer material, and on the number of pore volumes that have passed through the buffer prior to container failure (Lemire and Garisto, 1989, Appendix A).

Figure 3 shows the distribution of calculated uranium solubilities for 40000 sampled contact waters at 100°C. More than 85% of the cases resulted in total uranium solubilities of less than •10^{-8} mol/kg at 100°C. Less than 3% of the cases, at 100°C, resulted in total uranium solubilities greater than• 10^{-6} mol/kg. The high-solubility cases were traced to sampled waters in which U_4O_9 was dissolved oxidatively to form uranium(VI) complexes (Lemire and Garisto, 1989). These data show the importance of redox conditions in controlling the UO_2 solubility and, hence, the overall extent of fuel dissolution. These results are consistent with used-fuel dissolution studies. For example, in used-fuel leaching experiments measured uranium concentrations are generally below 10^{-7} mol/kg under mildly reducing conditions and generally higher under oxidizing conditions (Stroes-Gascoyne et al., 1989; Rawson et al., 1987; Werme and Forsyth, 1987).

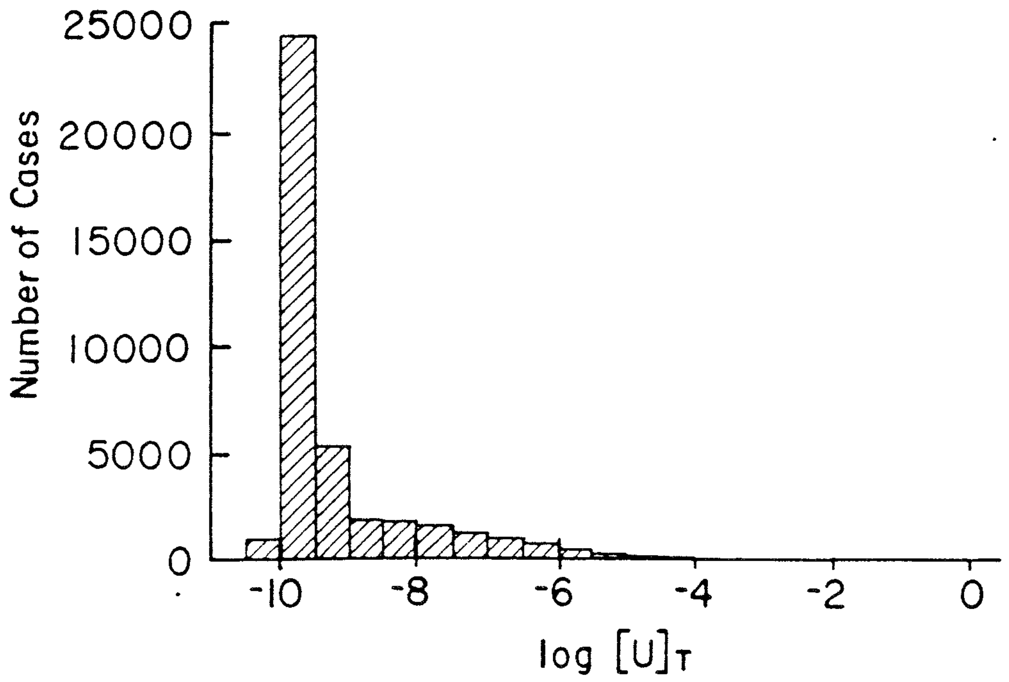

Figure 3: *The Distribution of the UO_2 Solubility (mol/kg) in Contact Waters (Based on 40 000 Sampled Contact Waters) at 100°C (Lemire and Garisto, 1989).*

4.3 The Effect of Precipitation on the Long-Term Release of Radionuclides from Used Fuel

In solubility-limited dissolution models, the rate of fuel dissolution is controlled by the mass transport of dissolved uranium species away from the fuel/groundwater interface. An undesirable property of these models is that any phenomenon that decreases the concentration of the dissolved uranium, e.g., adsorption and precipitation, will increase the mass transport of uranium through the buffer and, hence, increase the rate of fuel dissolution and the radionuclide source terms.

Of particular concern for the source term model is the possibility that a uranium-containing solid may precipitate downstream from the dissolving fuel. Such precipitation could occur if the UO_2 solubility varies from location to location in the vault, because of, for example, temperature or redox-potential gradients. Redox-potential gradients have been used to explain uranium ore deposition (Langmuir 1978).

The enhancement of the fuel dissolution rate due to precipitation (the "enhancement factor") has been investigated using both analytical (Garisto, 1986; Garisto and Garisto, 1988a) and numerical (Garisto and Garisto, 1986, 1988b) methods. Quantita-

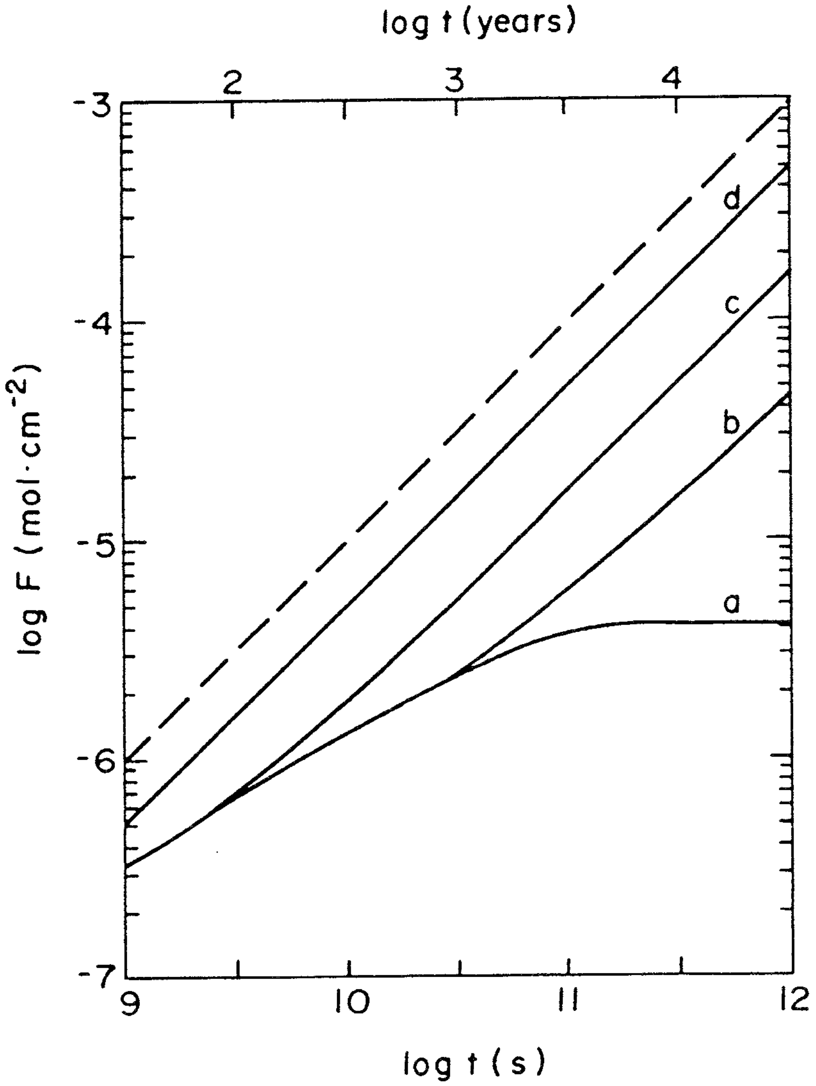

Figure 4: Cumulative release flux as a function of time (Garisto and Garisto, 1986): (a) no uranium precipitation in the buffer;(b),(c), and (d) uranium precipitates at 20, 5 and 1 cm,respectively, from the fuel buffer interface. The dashed line represents release into an infinitely dilute system.

tive estimates of the release enhancement factor have been derived for fuel dissolution under probable disposal vault conditions (Garisto and Garisto, 1986; Garisto and LeNeveu, 1989) and are shown in Figure 4.

These studies show that the enhancement factor is small (1) at short times. For finite system geometries (e.g., the fuel/buffer system), the enhancement factor increases with time and approaches a constant value in the asymptotic $t \rightarrow \infty$ limit. Thus, precipitation of uranium-containing solids in the buffer limits the release of uranium (and of other coprecipitates) into the host rock, but enhances significantly the dissolution rate of the used fuel, thereby increasing release rate of other radionuclides (Garisto and LeNeveu, 1989).

The enhancement factor depends strongly on the magnitude of the solubility gradient near the fuel/buffer interface (Garisto and Garisto, 1986; Apted et al., 1989). Further work is required to derive realistic estimates of the magnitude of this solubility gradient and its time dependence.

4.4 Alternative Models for the Long-Term Release of Radionuclides from Used Fuel

We consider two types of modifications to the long-term release model: (i) improvements to the existing model and (ii) development of kinetic models that are valid under both reducing and mildly oxidizing conditions.

The solubility-limited dissolution model (within its range of validity) could be significantly improved by using time-dependent parameters to describe the evolution of the contact groundwater (e.g., the groundwater composition and redox potential).

Under conditions where UO_2 is not the thermodynamically stable solid (e.g., oxidizing conditions), the solubility-limited dissolution model is not valid and kinetic data are required to describe the fuel dissolution. These data could be obtained empirically from leaching experiments. However, the extrapolation of such data to long times is questionable (Wuertz and Ellinger, 1985).

A fundamental understanding of both the characteristics of used fuel and the underlying chemistry governing the fuel dissolution process are required to make predictions over very long periods of time. For example, in our laboratories, electrochemical methods are being used to determine the rate-limiting steps in the oxidation of UO_2, and to measure their rates in different groundwaters (Johnson et al., 1988). However, it has not yet been demonstrated that kinetic data obtained from experiments on unirradiated UO_2 would be directly applicable to used fuel (Shoesmith et al., 1989). Thus, it may be important to also carry out similar experiments with UO_2 doped with α-emitting radionuclides (mimicking the behaviour of used fuel after hundreds of years of storage).

Because of the difficulties with the experimental approaches, it is also necessary to develop theoretical models for the long-term release of radionuclides from used fuel that include the effect of α-radiolysis. At present, we can estimate upper bounds for the effect of α-radiolysis on the fuel dissolution rate, using the energy spectrum of α-particles emitted from used fuel (Garisto, 1989). If we assume that (i) the effective surface area of a fuel pellet (including cracks) is 5 times the geometric surface area, (ii) the surface-to-volume ratio is independent of time, and (iii) each mole of radiolytic H_2O_2 dissolves one mole of UO_2 (a conservative assumption since H_2O_2 can react with groundwater species or decompose before reaching the fuel surface), then we estimate that the fractional fuel dissolution rate is about 2×10^{-7} per day. Surprisingly, this estimate is in agreement with observed long-term fractional release rates (Grambow, 1989; Johnson and Shoesmith, 1988). These kinetic rates are 6 to 7 orders of magnitude larger than the solubility-limited fuel dissolution rate calculated using a UO_2 solubility of 10^{-10} mol/kg (Garisto and LeNeveu, 1989).

Finally, it is interesting to note that, in contrast to solubility- limited models, the radionuclide source terms calculated using a kinetic model are not affected by precipitation of a uranium-containing solid.

5. RADIONUCLIDE RELEASE FROM ZIRCALOY CLADDING

Zircaloy-4 is a highly corrosion-resistant material (uniform corrosion rate <0.01 µm/a). Thus, the cladding could provide an additional barrier to radionuclide release from the fuel after failure of the container (Pescatore et al., 1989). However, experimental data are required on localized failure mechanisms (e.g., hydrogen-induced cracking, crevice corrosion, and stress-corrosion cracking) to eliminate uncertainties regarding possible early cladding failure (Santanam et al., 1989). In the absence of these data, we have conservatively assumed cladding failure immediately upon breach of the container.

Irrespective of the time of cladding failure, contact with groundwater will lead to corrosion of the cladding and to the eventual release of activation products contained in the cladding. The zirconium oxide film is typically coherent and tightly bound to the underlying Zircaloy. Thus, as the corrosion front moves through the metal, most activation products are expected to be incorporated into the growing ZrO_2 film. The activation products would subsequently be released into the groundwater as the ZrO_2 film dissolves.

In the source term model, we assume that the release of activation products is determined by the dissolution rate of the ZrO_2 film. This rate depends on the solubility of ZrO_2 and the rate of diffusion of zirconium species through the buffer. Thus, the release of activation products from the cladding can be described using the same equations (see Section 4.1) that are used to model the long-term dissolution of used fuel.

To calculate the cladding source term, we require data on the solubility of ZrO_2 and the retardation factor of dissolved zirconium species in the buffer. There are very few data available for zirconium solution species. However, the aqueous chemistry of zirconium is similar to that of thorium (Baes and Mesmer, 1976). Thus, the zirconium data needed for the cladding source term model are taken to be equal to the corresponding thorium data. This approximation should not lead to serious errors in the calculated risk factors since the cladding source terms are relatively small.

6. SUMMARY

In this paper we have described the conceptual and mathematical framework of the radionuclide release model used in the CWMP and discussed the assumptions used in its derivation. The model includes the fast release of fission products from the fuel gap and grain boundaries, the long-term release of radionuclides due to the dissolution of the fuel grains, and the release of activation products from the Zircaloy cladding. The model can account for the power history of the fuel bundles, the geochemistry of the contact groundwater, and the precipitation of radionuclide solids. Finally, improvements to the model have been suggested, and alternative fuel dissolution models have been briefly discussed.

ACKNOWLEDGEMENTS

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DISCUSSION ON SPENT FUEL RELEASE

Discussion leader: Timo Vieno

Gap and grain boundary releases: The significant nuclides in the gap are I and Cs. Tc is present at the grain boundaries, but not in significant amounts in the gap. Data is needed on the inventory fractions of I, Cs and Tc at the grain boundaries of LWR fuel. There are difficulties in determining the chemical forms and inventories of C-14 in the gap and at the rain boundaries.

There was some discussion whether there is a need and the data to distinguish between gap and grain boundary releases. It was concluded that in some scenarios there might be a need to distinguish between these two, but at present there are not good enough data and models.

Mechanism of fuel dissolution: The key factor is redox potential on the fuel surface, not in the bulk solution. If reducing conditions prevail on the fuel surface, release from the fuel is congruent and governed by the solubility of uranium in reducing conditions which results in rather low release rates.

There was some discussion whether water chemistry has any effects on the fuel degradation rate when oxidizing conditions prevail on the fuel surface. It was concluded that fuel degradation is governed by α-radiolysis and the effects of water chemistry on the fuel degradation rate are minor. Water chemistry has, however, a significant influence on the behaviour of nuclides in the near-field and their release rates into the geosphere.

It was noted that the mechanism of fuel dissolution may not be very crucial for the overall performance of a disposal system. Nevertheless, to build up confidence in performance analyses we should be able to understand and explain the degradation mechanism of spent fuel in groundwater.

Estimation of effects of α -radiolysis: There was a concern that scoping calculations based on the α-activity, the fuel surface area, G-values, and on the assumption that 1 mol of UO_2 is oxidized by 1 mol of H_2O_2 will result in too conservative estimates. The water volume affected by α-radiolysis on the surface of partly oxidized fuel is difficult to estimate. The presence of other materials than UO_2 should be taken into consideration, too.

Natural analogues: The role of natural analogues was emphasized. On the other hand, it was noted that natural analogues are aggregated outcomes of many coupled processes, and, therefore, it is difficult to isolated the mechanism of a single process – like UO_2 degradation – from natural analogues.

MOX fuel: In some countries there will be a need to model releases from spent MOX fuel, too.

SOLUBILITY AND SPECIATION STUDIES FOR NUCLEAR REPOSITORY PERFORMANCE ASSESSMENT

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ABSTRACT

Solubility and speciation data are important in understanding aqueous radionuclide transport through the geosphere. They define the source term for transport retardation processes such as sorption and colloid formation. Solubility and speciation data are useful in verifying the validity of geochemical codes that are part of predictive transport models. Radionuclide solubility studies in groundwaters from a repository region will provide limits on radionuclide concentrations in these waters. Meaningful thermodynamically defined solubility studies must satisfy four criteria: (1) solution equilibrium conditions, (2) effective and complete phase separation, (3) a well-defined solid phase, and (4) knowledge of the speciation/oxidation state of the soluble species at equilibrium. Results from solubility and speciation experiments of $^{237}NpO_2^+$, $^{239}Pu^{4+}$, and $^{241}Am^{3+}/Nd^{3+}$ in J-13 groundwater (from the Yucca Mountain region, Nevada, which is being investigated as a potential high-level nuclear waste disposal site) at three different temperatures (25°, 60°, and 90°C) and pH values (6, 7, and 8.5) are presented.

ESSENTIAL PHENOMENA CONTROLLING AQUEOUS RADIONUCLIDE TRANSPORT

Gaseous and aqueous transport are two principal mechanisms of radionuclide transport from a potential nuclear waste repository to the environment. Aqueous radionuclide migration through the geosphere is controlled by several chemical and physicochemical phenomena, including the dissolution rate of the waste package, formation of secondary solids, radionuclide complexation in the solution phase, and sorption processes on the geomedia. These processes are interconnected and depend strongly on each other.

Solubility describes the concentration of radionuclides in the aqueous phase. It is controlled by the formation of solubility controlling secondary solids that are in equilibrium with soluble species. The soluble species in turn can form solution complexes by reacting with ligands that are present in the groundwater. Complex formation is dependent on the oxidation state and charge of the radionuclide in the solution phase, as well as the nature and the amount of potentially complexing ligands present in the groundwater. The electrical charges of the solution complexes can vary widely. Detailed knowledge of the species and associated charges are very important for understanding their sorption on the geomedia. Differently charged species adsorb differently. Understanding of sorption processes is also very beneficial in understanding colloidal transport. Colloid transport can be seen as a special form of aqueous transport in which colloidal polynuclear radionuclides and radionuclides that attach themselves to suspended solid material can be transported.

APPLICATIONS OF SOLUBILITY AND SPECIATION DATA

Solubility studies of radionuclides yield good estimates of upper most radionuclide concentrations in groundwaters from the region of potential waste repositories. Such measurements will provide upper concentration limits because the secondary steady-state solids formed can still change from a higher to a lower free energy, which would result in lower solution concentrations. These changes may be very slow and may require very long or even infinite experimental times, which we do not have.

Model Verification, Data Base Validation, and Risk Assessment

Data derived from solubility studies are important for validating geochemical codes that are part of predictive radionuclide transport models. Such codes should be capable of predicting the results of solubility experiments. Furthermore, agreement between geochemical calculations and experimental results can validate the thermodynamic data base used with the modeling calculation.

To predict behavior at higher temperatures, data bases used for modeling calculations must contain data on thermodynamic functions at elevated temperatures. To date, many of these data are unavailable and are therefore estimated by extrapolation from lower temperature data. Agreement between modeling calculations and experimental results would also validate such estimates, whereas significant discrepancies would identify the need for data base improvement. Improvements can be made by filling the gaps with generic experimental data.

In addition, experimental solubility data also provide the source terms or the starting concentrations for experimental sorption studies. To be valid, sorption studies should be conducted at or above the solubility limit because only soluble species can be transported and participate in the sorption process.

SOLUBILITY MEASUREMENTS FOR THE YUCCA MOUNTAIN PROJECT

Concept

The concept of solubility and speciation measurements has been discussed and illustrated [1]. Meaningful thermodynamically defined solubility studies should satisfy four criteria: (1) equilibrium conditions, (2) accurate solution concentrations, (3) a well-defined solid phase, and (4) knowledge of the speciation/oxidation state of the soluble species at equilibrium. This study was conducted according to these criteria

Experimental Approach

The solubilities of $^{237}NpO_2^+$, $^{239}Pu^{4+}$, and $^{241}Am^{3+}/Nd^{3+}$ were determined in J-13 groundwater from the Yucca Mountain region. To bracket a variety of possible pH and temperature conditions, solubility and speciation data were obtained for each radionuclide solution at three different pH values (pH 6, 7, and 8.5) and at three temperatures (25°, 60°, and 90°C). Further experimental details are described elsewhere [1, 2].

Neptunium

Results of the neptunium solubility experiments are shown in Figure 1. The steady-state solids in each experiment were sodium neptunium carbonate hydrates with different water content. The solid formed at 90°C and pH 7 was a mixture of sodium neptunium carbonate hydrate and neptunium pentoxide. The solubility decreased at each temperature with increasing pH; this is due to the increasing concentration of CO_3^{2-} with increasing pH, resulting in lower solubilities through the formation of more insoluble sodium neptunium carbonate hydrates. The supernatant solutions were analyzed by absorption spectrophotometry to determine the oxidation state and speciation. The solutions showed increased carbonate complexation with increasing pH for the 25° and 60°C series. The amount of carbonate complexing increased with increasing temperature for the pH 8.5 solutions. It decreased with increasing temperature for the pH 7 solutions. Very little carbonate complexation occurred for both pH 5.9

solutions. In the 90°C experiments only the pH 8.4 solution contained carbonate complexes.

Plutonium

Results of the tetravalent plutonium solubility study are shown in Figure 2. The solubility-controlling solids were mixtures containing mainly polymeric plutonium(IV) and smaller portions of plutonium carbonates. This explains the drastic decrease in plutonium solubility with increasing temperature. The plutonium(IV) polymer peptizes with increasing temperature and becomes more stable; over extremely long times it may possibly convert to PuO_2. This also explains why the solubilities did not vary significantly with different pH at each temperature. The solubility of Pu(IV) polymer remains rather unaffected by pH changes. Hydrous plutonium dioxide or plutonium(IV) polymer, however, is thermodynamically ill-defined, and the solubility product constant used in thermodynamic data bases may not be applicable to other polymeric plutonium(IV) precipitates. Such precipitates may differ in their amorphous composition, which may result in calculated solubilities. that are significantly higher or lower than the ones determined in experiments.

The plutonium supernatant solutions at steady state were analyzed for their oxidation state distributions. The speciation studies are made difficult by the low solubility of plutonium. The solutions' concentration levels lie below the sensitivity range of methods such as absorption spectrophotometry, which would allow the direct measurement of the species present. Therefore, we developed a method to determine the oxidation states indirectly. The method involves a combination of solvent extractions and coprecipitation. It was tested on solutions of known plutonium oxidation state mixtures with both high-level and trace-level concentrations [2]. Results of this study for 25°, 60°, and 90°C are given in Table I.

All solutions, except the 90°C solution at pH 7, contained predominantly Pu(V) and Pu(VI), whereas Pu(III), Pu(IV), and Pu(IV) polymer are present only in small or insignificant quantities. These observed valence distributions cannot be explained by disproportionation equilibria and complex stabilization [3]. It is possible that oxidation products formed by -radiolysis of the water may cause the predominance of high oxidation states in the plutonium solutions. It is noteworthy that the solutions were filtered through a 4.1-nm filter prior to the oxidation state determination because we wanted to determine only the true soluble plutonium fraction without any colloidal or polymeric plutonium being present. This treatment separates all Pu(IV) polymer larger than 4.1-nm from the solution. Therefore, we refer to Pu(IV) polymer in the context of this determination only to the fraction that is smaller than 4.1 nm.

At pH 7 and 90°C, Pu(V) is measured to be equal to the sum of Pu(III) and Pu(IV) polymer. We explain this measured decrease of Pu(V) and the increase of Pu(III + poly.) by leakage of the 4.1-nm Amicon filter used for phase separation. Such leakage would introduce more polymer and change the relative oxidation state distribution. This explanation is supported by comparison of the assay taken as a reference standard for the extraction at pH 7 and 90°C, with a parallel sampling for the solubility determination; the extraction sample contained 2.36 times more plutonium. Unfortunately, we could not repeat this experiment, because not enough supernatant was left for the test. From the other distribution results, we see no reason to doubt that this solution, too, contained probably mostly Pu(V) and Pu(VI).

Americium

Results of the americium solubility experiments are shown in Figure 3. No clear trend of the solubility was found with increasing temperature and increasing pH. Much higher solubilities were found for 60°C compared to 25°C and 90°C. All solids were $AmOHCO_3$, with orthorhombic structure for all temperatures at pH 7 and 8.5 and for 60°C at pH 6, and with hexagonal structure for 25°C and 90°C at pH 6. Orthorhombic $AmOHCO_3$ appears to have a much higher solubility at pH 6 and 60°C than the hexagonal form at the same pH and 25°C or 90°C. As could be expected for the experimental conditions, we found no higher americium oxidation states in the supernatant solutions. The trivalent americium did not change its oxidation state.

CONCLUSIONS AND RECOMMENDATIONS

This study, though limited in scope, shows that data for steady-state solids of some radionuclides are missing in the data base (e.g., $NaNpO_2CO_3 \cdot 2.5\ H_2O$, hexagonal $AmOHCO_3$, a range of amorphous plutonium(IV) hydrous oxide solubility products instead of one single value). Very limited data are available for higher temperatures.

Generally, solubility and complexation studies at higher temperatures, up to 150°C, are recommended in order to improve predictive modeling capabilities for scenarios that represent temperatures in the near field.

It is also of great interest to know how alpha self-irradiation effects the solubility of secondary solids. Is the solubility of short-lived ^{238}Pu significantly higher than that of ^{242}Pu with a 4483 times longer half-life?

Furthermore, model and data base validation should be extended through intermediate scale experiments and field tests. Kinetic limitations and heterogeneity of the geomedia should be incorporated in chemical/transport models. Solubility studies and subsequent comparison with results from modeling calculation should be extended to other important nuclear waste radionuclides, such as nickel, zirconium, cadmium, radium, and thorium.

In summary, we showed in this paper that experimental solubility and speciation studies are useful and very important in understanding radionuclide transport through the geosphere.

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APPENDIX

The data used to write this report are recorded in the following YMP Laboratory Record Books:

TWS-LBL-05-88-01, pp. 3299;
TWS-LBL-05-88-02, pp. 3251;
TWS-LBL-01-89-01, pp. 99293;
TWS-LBL-01-89-02, pp. 3251;
TWS-LBL-07-89-01, pp. 575;
TWS-LBL-02-90-03, pp. 3175;
TWS-LBL-02-90-04, pp. 63188;

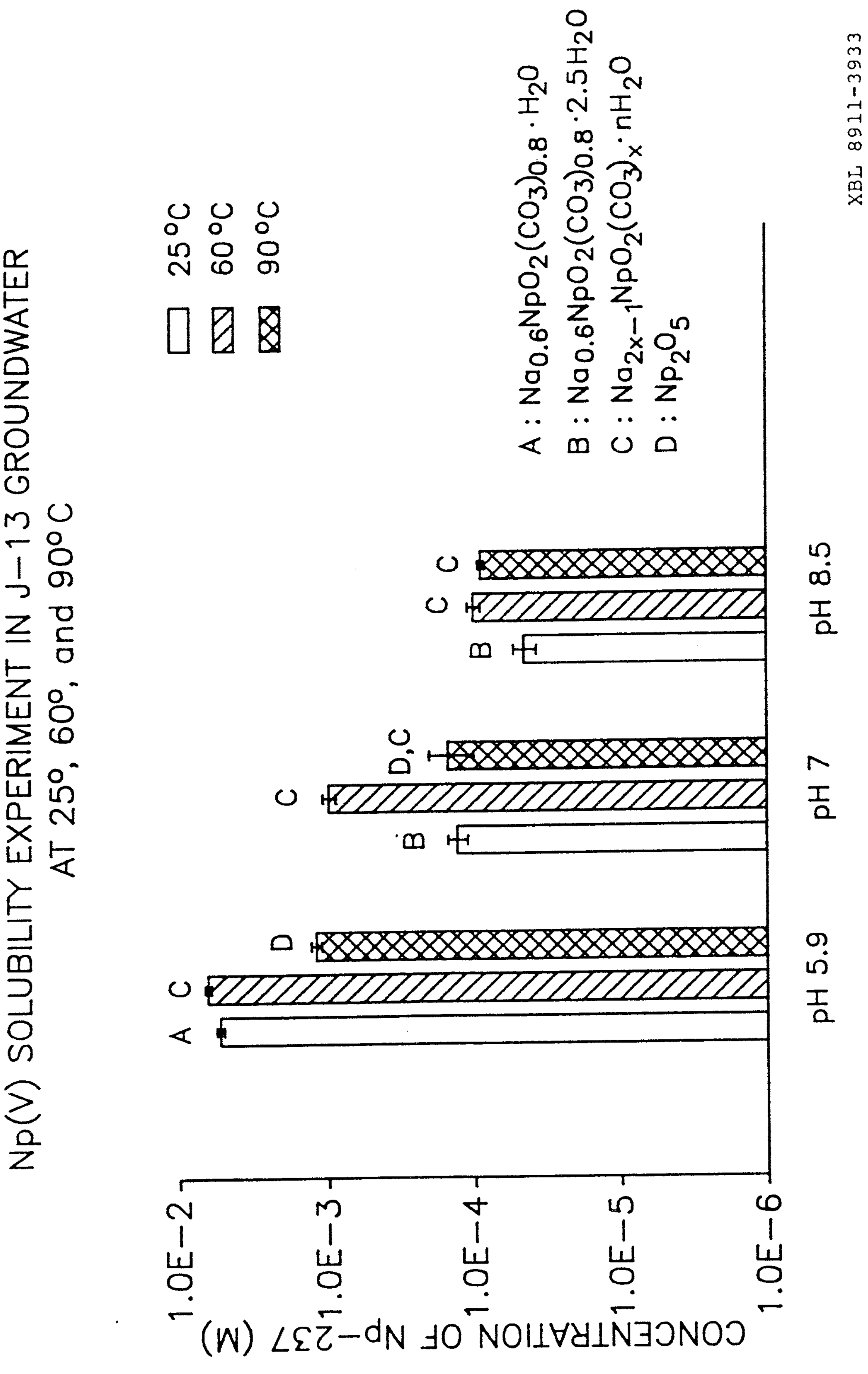

Figure 1. Results of Neptunium(V) Solubility Experiments in J-13 Groundwater as a Function of pH and Temperature.

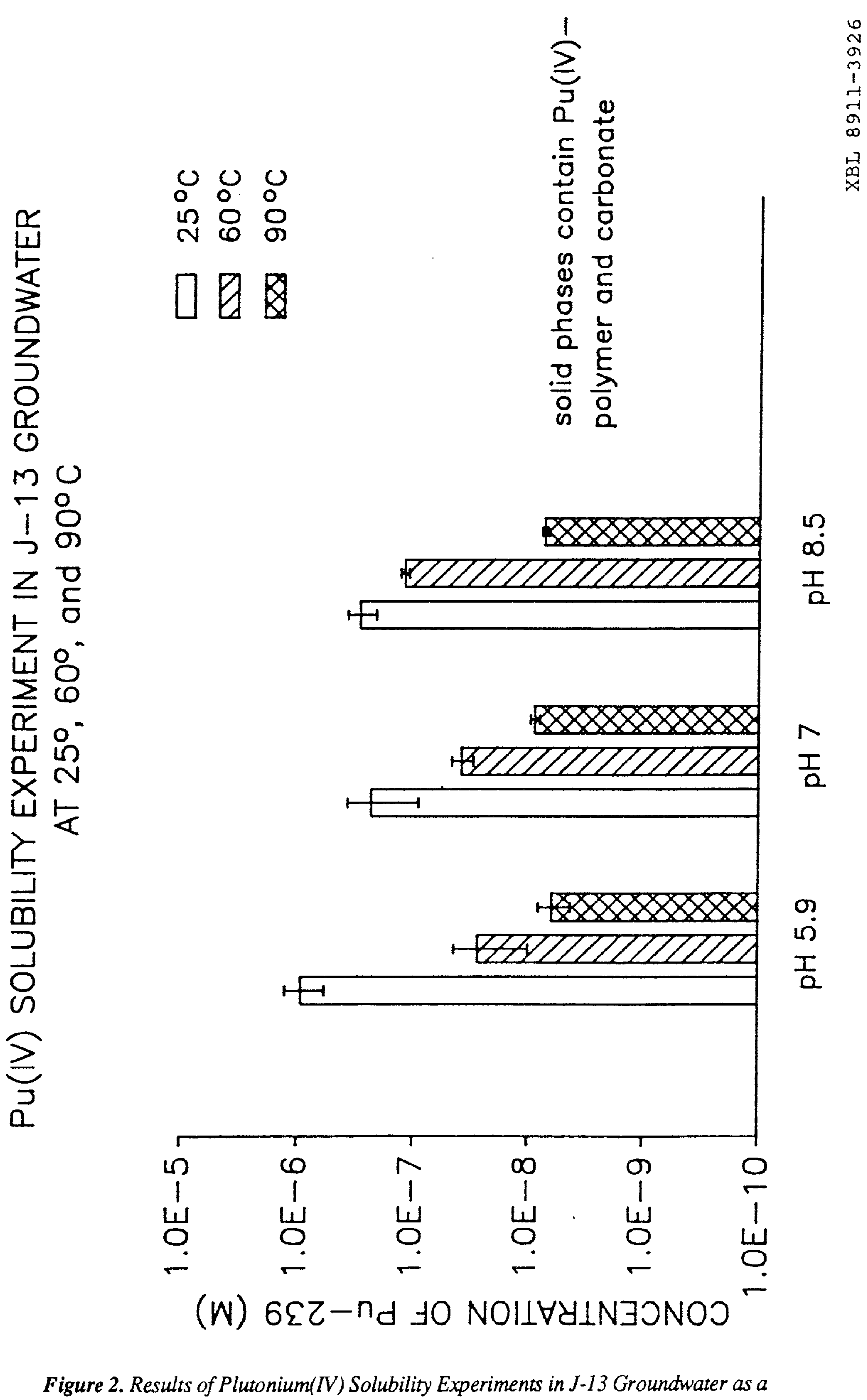

Figure 2. Results of Plutonium(IV) Solubility Experiments in J-13 Groundwater as a Function of pH and Temperature.

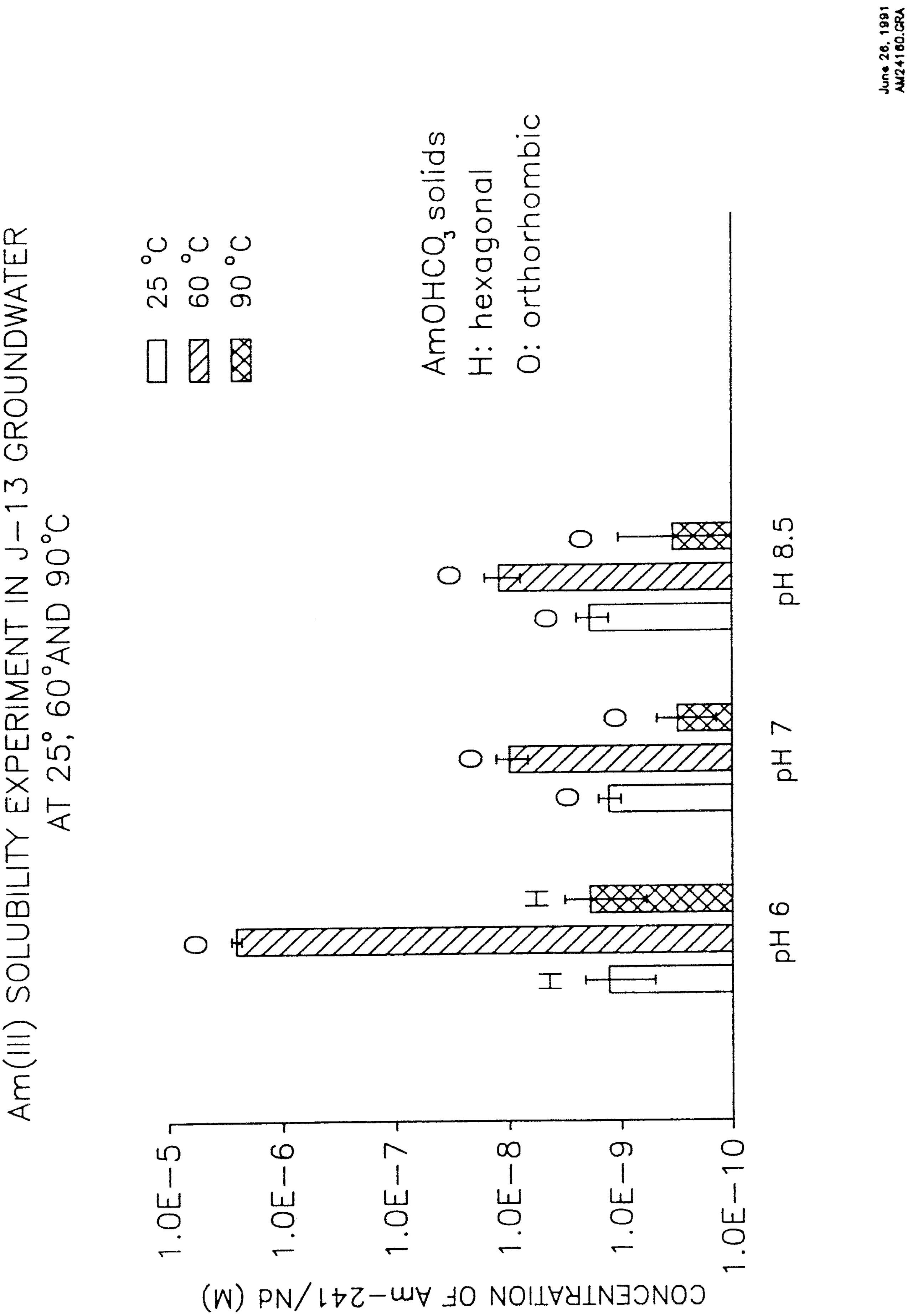

Figure 3. *Results of Americium(III) Solubility Experiments in J-13 Groundwater as a Function of pH and Temperature.*

THE USE OF RADIONUCLIDE SOLUBILITY IN A NEAR-FIELD PERFORMANCE ASSESSMENT

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Radionuclide solubilities are used in the performance assessment of the near-field to establish the upper limits of radionuclide release from the waste matrix through the canister (source term).

The applicability of the solubility assumption to long-term extrapolations is conceptually very straightforward because of the time-independence of the thermodynamic principles which it is based on.

However, the utilization of solubility models requires a knowledge on the solubility limiting phase for each radionuclide in the near-field and the corresponding thermodynamic properties.

Futhermore, both the experimental determination of radionuclide solubility and the application of these data to geochemical codes used in performance assessment are based on the assumption that the thermodynamic activity of the radionuclide solid phase is unity.

Normally, the thermodynamic properties of solid phases are determined for well characterized solid phases with a high degree of cristallinity. However, the less stable solid in morphologies (amorphous) are kinetically favoured to precipitate at low temperatures (Gay-Ostwald principle). These less-crystalline phases tend to become more stable upon aging. Although in the near-field the aging process is counterbalanced by radioactive effects.

Consequently, realistic solubility models should take into account all the processes that affect the thermodynamic activity of the solubility limiting solid phase. The solubility limiting solid phases should be identified under the conditions which will prevail in the near-field.

If the radionuclide solubility is limited by the precipitation of an individual solid phase the thermodynamic properties of the appropriate morphology of this solid phase should be used. The aging properties should be known. This is particulary critical for the transition:

$$Pu(OH)_4(s) \rightarrow PuO_2.xH_2O(s) \rightarrow PuO_2(c)$$

The radionuclide solubility may also be limited either by its dissolution from a solid solution form in the waste matrix or by co-precipitation with other major components of the waste and/or the intruding groundwater. In this case appropriate solid solution/co-precipitation models should be included in the geochemical codes. If individual solid phase solubilities are used in this case, the net result will be an overestimation of the source term for the corresponding radionuclide.

From all this it is very clear that the use of the solubility limiting assumption in the near-field requires the use of high quality thermodynamic data, which has been properly reviewed (NEA-TDB). It also requires the development of solid solution/co-precipitation models, which should by included in the geochemical codes to be used i PA exercises. There is currently a group working with these particular matters within the CHEMVAL2 project.

However, this model generation and development will be useless if the appropriate solubility data are not available. Consequently, there should be an international agreement towards obtaining these type of data.

As key areas for development in this matter the participants of this workshop have identified the following:

- Identification and quantification of the relevant solubility limiting phases for radionuclides in the near-field. Particulary for Tc, Np and Pu.

- Establishment of solid solution/co-precipitation models for radionuclide solubility in the near-field.

- The continuation of a large scale experimental effort in determining the solubilities of radionuclides in the near-field. These should cover critical gaps in the TDB compilations.

NEAR FIELD TRANSPORT PROCESSES

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ABSTRACT

In repositories for nuclear waste there are many processes which will be instrumental in corroding the canisters and releasing the nuclides. Based on experiences from studies on the performance of repositories and on an actual design the major mechanisms influencing the integrity and performance of a repository are described and discussed. The paper addresses only conditions in crystalline rock repositories. The low water flow rate in fractures and channels plays a dominant role in limiting the interaction between water and waste. Molecular diffusion in the backfill and rock matrix as well as in the mobile water is an important transport process but actually limits the exchange rate because diffusive transport is slow. Solubility limits of both waste matrix and of individual nuclides are also important. Complicating processes include gas generation by iron corrosion and alpha-radiolysis.

INTRODUCTION

The author has participated in the Swedish work on high level waste repository studies KBS-3 (1983) and earlier studies, The WP Cave design and the SFR repository for Low and Intermediate waste (Neretnieks 1989) as well as the Swiss Gewähr study (Nagra 1985), all in crystalline rock. The experience gathered is thus limited to crystalline rock repositories. Although many of the mechanisms which are active in this setting will be of importance in other repository designs and rock types such as clay and salt, this paper is limited to repositories in crystalline rocks.

OVERVIEW OF REPOSITORY TYPES

In high level waste and spent fuel repositories the radioactive waste will be emplaced in canisters. The canisters are deposited in holes or tunnels in crystalline rock at large depths, 500 m or more, and are surrounded by a backfill, often bentonite clay, with or without an admixture of sand or crushed rock to economize on the clay. Although the repository designs in Canada, Sweden (KBS-Type) and Switzerland differ in some important respects, the general long term performance and the mechanisms which are active are essentially the same. The Swedish alternative repository type, the WP-Cave concept, is based on a different idea. In the WP-Cave repository the fuels in their canisters is not individually imbedded in the clay but many hundred canisters are emplaced in tunnels in a large (hundreds of meters) egg shaped rock body. The whole rock body is surrounded by a thick (several meters) layer of bentonite-sand mixture. The individual canisters are surrounded by crushed rock. In this design a few mechanisms which are of no concern in the earlier repository types become important.

The low and intermediate level waste repository, SFR, at Forsmark started operating in 1988 and is also located in crystalline rock but at a depth between 50 and 100 m below the bottom of the Baltic. Many of the mechanisms of importance in the High Level Waste (HLW) repositories are active in this setting also. In addition some specific mechanisms related to the presence of concrete and large amounts of iron become important.

This paper first outlines some repository environments and materials and then proceeds to discuss the various transport and release mechanisms. Also some mechanisms of importance for the degradation of canisters are discussed. Some models and aspects of modelling the mechanisms are also discussed.

REPOSITORY DESIGNS AND ENVIRONMENT

Waste form

Spent fuel consists of about 95-98 % of crystalline uranium oxide. Other actinides and fission products are imbedded in the crystals with a few notable exceptions. Some nobel gases, Iodide and Cesium have migrated out from the crystals to some small but important extent and are found at crystal boundaries and outside the fuel pellets. These nuclides can escape more readily than those inside the crystals.

Vitrified waste consists essentially of a glass structure in which the nuclides have been incorporated. Release and transport processes from HLW and Vitrified waste are the same to a large extent although there are some important differences related among others to the redox chemical behaviour of uranium.

Canisters and canister matierals

Three types of canister materials will be treated. Copper is the candidate material in the KBS-3 concept. Copper will not corrode by reaction with water alone to any appreciable extent (KBS-3 1983). Corrosive agents dissolved in water must be present for corrosion to take place. Dissolved oxygen would corrode copper but at the depths considered for HLW repositories oxygen is not present. Any infiltrating oxygen with rainwater is consumed by reaction with reducing agents in the rock. Sulphide is another agent which can corrode copper. The corrosive agent must be transported to the surface of the canister. The corrosion rate will be limited by the transport rate of corrosive agents. The transport mechanisms are the same as those for transporting the dissolved constituents from the canister and HLW.

In contrast, iron canisters can corrode by reaction with water without the need to have other corrosive agents. The process is essentially governed by chemical reaction kinetics and will not be further treated here.

Concrete in concrete boxes or larger constructions containing and isolating the waste displays a very complex corrosion behaviour in comparison copper and iron. It may degrade by both dissolution of some readily soluble constituents such as sodium and potassium hydroxides, some less soluble compounds such as calcium hydroxide and silica but also by reactions with intruding species such as magnesium or sulphate which under some circumstances may form expanding precipitates which crack the concrete from within. Similar dissolution-precipitation processes in the concrete could possibly be active in the transport and retardation of escaping radionuclides.

Backfill

The backfill considered in all the mentioned repositories is bentonite clay. This clay is made up of very small particles with a very large specific surface, on the order of 1000 m^2/g. The surface is chemically active and will adsorb water molecules strongly which makes the bentonite swell very strongly. Compacted bentonite has very low hydraulic conductivity and water flow under normal repository gradients is practically negligible. Ions dissolved in water will, however, move in the voids between the clay particles by molecular diffusion. All cations will adsorb or ion exchange on the clay particle surfaces because these are negatively charged. Many neutral species will also sorb on the clay, whereas negatively charged species will be hindered from entering the smallest passages due to electric repulsive forces.

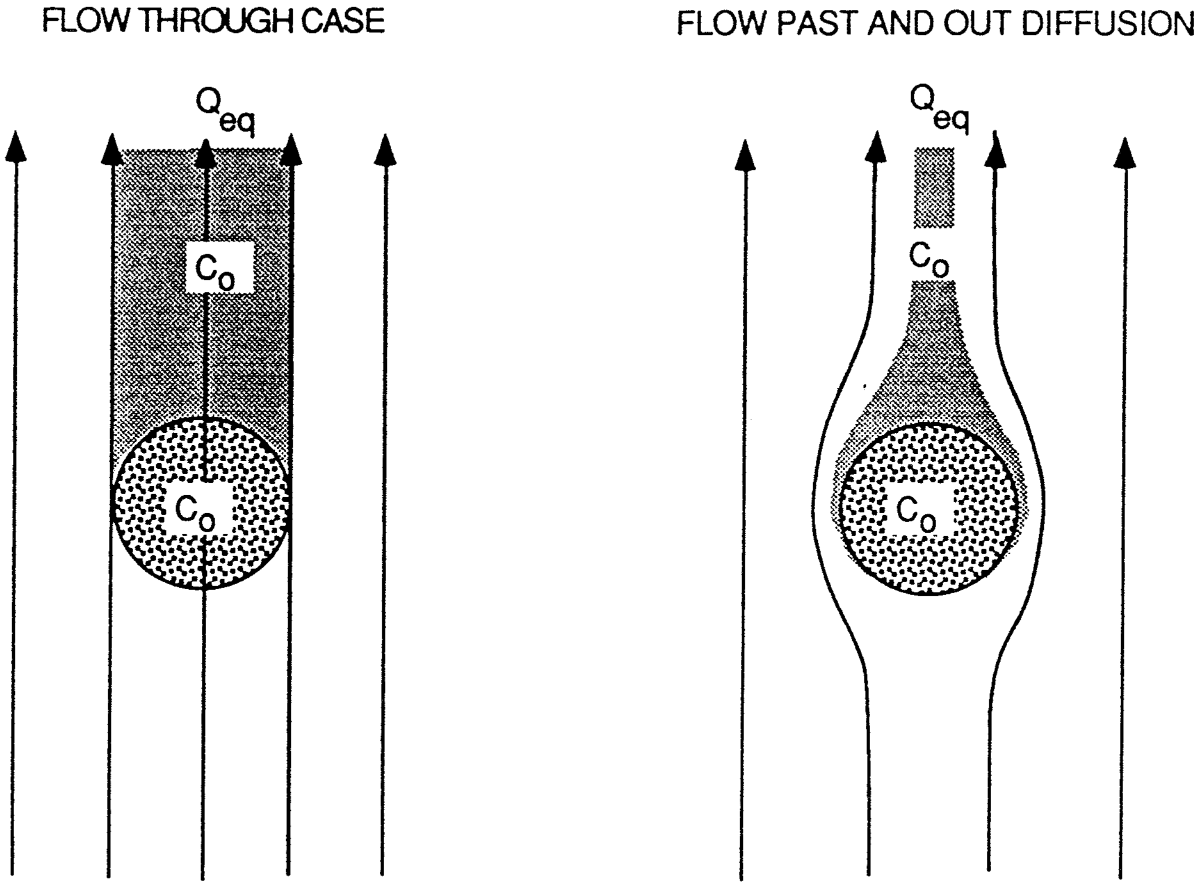

Figure 1. Contamination of water by advective transport (left) and diffusive transport (right)

Near-field rock

Crystalline rocks such as granites and gneisses are fractured and practically all the water flows in the fractures. The rock matrix is porous but the hydraulic conductivity is so low that practically no water flow takes place through the rock matrix. The porosity is connected over large distances (Skagius and Neretnieks, 1986, Birgersson and Neretnieks, 1990) and species of molecular size can move by molecular diffusion in the matrix. The frequency of conducting fractures is small and varies between 1 per a few meters and 1 per nearly 100 meters (Palmqvist 1987, Abelin et al., 1987, Neretnieks et al., 1987). Fractures are not open over their whole surface. Only small parts of a fracture conducts water in what is often called channels (Moreno et al., 1988, Abelin et al., 1990). The channel transmissivities vary within a wide range. This means that not all waste canisters need be located near a channel and only a few will have a channel with a high flowrate nearby.

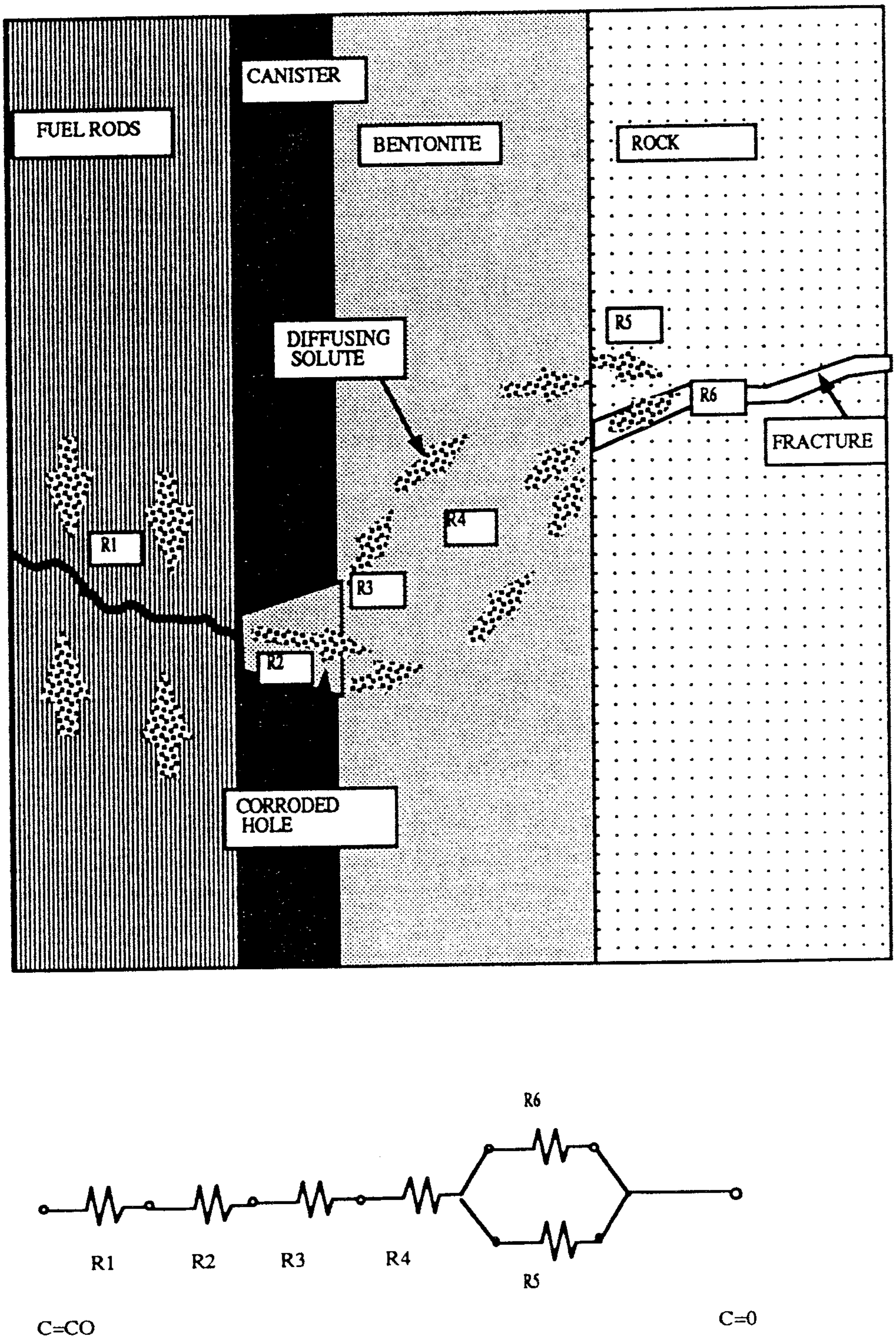

Figure 2. Nuclides from fuel rods in a degraded canister diffuse out to the water seeping in the fractures in the rock.

PROCESSES AND MODELLING

Generally speaking there are only a few basic processes which govern the release and transport of radionuclides in the near field. They are reaction rate, advection (flow) and molecular diffusion. In addition sorption processes may modify the rate of movement, radiolysis will change the chemical environment and may produce gas which will influence the transport processes. Chemical reactions such as precipitation will influence the release rate.

Some of the processes may dominate over others in one repository design whereas it may be different in other designs. In the following it will be attempted to illustrate both qualitatively and quantitatively some of the main mechanisms which have been addressed and modelled in the repositories discussed initially.

Some basic concepts

Corrosion of copper and concrete as well as the release and transport of the radionuclides strongly depends on the flowrate of water that carries the corrosive agents to the canister/waste and the dissolved nuclides from the fuel surface. In some cases when water actually can flow through a degraded canister and come in direct contact with the waste this flowrate will be the flowrate which contacts the waste and picks up the nuclide with its solubility concentration C_o. In most situations of interest, however, backfill, corrosion products or more or less stagnant water volumes will act as diffusion barriers decreasing the flowrate which actually comes in contact with the waste. The transport of corrosive agents into the system can be described in the same way. For the quantitative description of the transport processes it has been found convenient to introduce the concept of *Equivalent Flowrate* Q_{eq}. The rate of transport of a nuclide from, or a corrodant to the canister is the product of the concentration C_o and the equivalent flowrate Q_{eq}. Figure 1 below shows the concept.

In the advection case it is in principle straightforward to assess the flowrate which flows through a degraded canister. When there are diffusive barriers involved the process of diffusion and the geometry for diffusion must be accounted for. Figure 2 below illustrates a case where there are fuel rods within a corroded canister. The transport of dissolving nuclides will first be in the gaps between the fuel pellets and the tubes surrounding them (zircaloy in the Swedish case). The nuclides must find their way to the corroded hole in the canister, out through the backfill and to the water flowing in fractures in the rock. The figure illustrates the different paths the nuclides must take. Some paths have larger diffusion resistances than others because they may exhibit a smaller cross section for diffusion, a longer travel distance or a lower diffusivity. Conceptually it is illustrative to think of the various paths as having resistances which can be added like an electrical network. This is illustrated at the bottom of Figure 2. The over all resistance can be obtained from the individual resistances. The equivalent flowrate Q_{eq} is inversely proportional to the overall resistance.

In the KBS-3 (1983) and SFR Safety analysis it was found that one of the dominating resistances was that due to diffusion in the slowly seeping water in the fractures in the rock. The diffusion and uptake in the passing water in the fractures in the rock is essentially an unsteady state diffusion (Neretnieks, 1980, Pigford et al., 1990) in the sense that the water that approaches the canister is devoid of nuclide but as it passes the vicinity of the canister nuclides diffuse out into the water and contaminate it. The amount of nuclides which have passed to the water will depend on the residence time of the water, in a nonlinear fashion, as it passes the canister (or backfill outside). This transport process was found to make up the largest resistance by far in the central cases in the above studies both for the corrosion and for the contaminant release.

Corrosion

The corrosion of copper and of concrete will be governed by the rate of transport of corrosive agents. This is governed mainly by the diffusive processes discussed above. In the Swedish KBS-3 study (1983) it was found that the equivalent flowrate Q_{eq} which can carry corrosive agents to the copper was less than 1 liter per year for one canister. The main corrosive agent was found to be sulphide which is present in the deep groundwaters in concentrations less than 1 mg/l. This means that a canister would receive less than 1 mg of corrosive sulphide per year. It is evident that this corrosion would not have any serious impact on the integrity of a copper canister, weighing many tonnes, for many millions of years.

In the SFR repository for low and intermediate level waste (Neretnieks 1989), most of the intermediate level waste will be emplaced in a concrete silo surrounded by a bentonite and sand mixture. The silo is 50 m high, 30 m in diameter and has 0.8 m thick reinforced concrete walls. Also, in this case the diffusive resistance in the slowly seeping water in the rock will dominate over the diffusion resistance in the backfill and the concrete itself. The exchange of corrosive agents with the water in the rock will not be important in this case. There are other processes which will influence the integrity of the concrete and bentonite backfill which are more important than the exchange with the water into the rock. The bentonite acts as a source for sulphate and a sink for calcium and hydroxyl ions. Intruding sulphate from the bentonite will potentially form expanding solids, such as ettringite, and the depletion of calcium and hydroxyl ions will eventually weaken the concrete. The bentonite in turn will react with the hydroxyl ions and be degraded. In the time scale of a few thousand years these processes will at most have influenced a few tens of centimeters of the concrete and buffer.

Dissolution of waste and release of nuclides

Spent fuel and vitrified waste will dissolve and release its nuclides by several independent mechanisms. Dissolution of the matrix will take place when there is passing water which can pick up and carry away the dissolved matrix components such as uranium, in the case of spent fuel or silica, alumina, borates or other constituents of the glass matrix. The notion of the equivalent flowrate Q_{eq} can be used to conceptualize this process. In addition there will be diffusive processes which will allow readily mobile nuclides in the waste/fuel to move out independently of the dissolution of the matrix. The solubility of the matrix components C_o will together with the flowrate determine the rate at which the matrix dissolves.

The solubility of uranium in the spent fuel is strongly influenced by the redox conditions at the fuels surface. Mainly alpha-radiolysis will strongly influence the redox potential. The radiolysis splits water into a reducing fraction, mostly hydrogen, and an oxidizing fraction containing oxygen, hydrogen peroxide and other components. The hydrogen is a small readily mobile molecule which may diffuse out of the system before it has re-reacted. There will then locally develop an oxidizing environment in which the uranium has a solubility of the order of milligrams per liter instead of micrograms per liter or less under reducing conditions. The oxidizing species will oxidize the uranium from U(IV) to U(VI) which can dissolve at the higher solubility limit. There will then be a situation when either the rate of radiolysis limits the supply of U(VI) and it cannot be released to the passing at a larger rate, or if the rate radiolysis is large, the release is limited by the equivalent flowrate. In the KBS-3 study (1983) the maximum rate of radiolysis was estimated to be comparable to the maximum carrying capacity of the water. Even so, with an equivalent flowrate of less than a liter per canister per year and a solubility of a few milligrams per liter, the dissolution rate is extremely small.

When the rate of radiolysis and the resulting formation of U(VI) are larger than what can be carried away by the water, there will form new crystalline phases. The re-crystallized uranium will not necessarily re-incorporate the other radionuclides which originally were located inside the UO_2 matrix. The release rate of these will be determined by their own solubility and the equivalent flowrate. The latter is, with a good approximation, the same for all dissolved species with a small molecular weight. If the water flow rate does not have the capacity to carry away all of a dissolved nuclide, this will precipitate at the fuels surface as the surface dissolves away.

In recent work Neretnieks and Faghihi (1990) it has been found that the rate of radiolysis may be considerably lower than assumed in KBS-3 because the hydrogen gas and corrosion products formed during the radiolysis will strongly limit the amount of water which is present at the fuels surface.

Diffusion and sorption in backfill

The bentonite in the backfill has a low hydraulic conductivity but a high porosity even when compacted. Dissolved ions, such as radionuclides, migrate by diffusion through the water filled pores. Positively charged and many neutral species will sorb on the clay surfaces and accumulate there. Negatively charged species such as iodide may partly be excluded from the water by repulsive electric forces. Before the sites are saturated (equilibrated) with the sorbing species little of the substance will pass the empty sites. The sorbing nuclides will be retarded in relation to the non sorbing species. Many short lived nuclides with high sorption may be retarded to such an extent that they will decay to insignificant concentrations. Once the sites are saturated (equilibrated) the diffusion of the species will proceed without retardation with a rate similar to non sorbing species. A very simple criterion for when a nuclide would go through essentially without decay and when it would decay to insignificance in a backfill barrier. It can be expressed in the following way (Neretnieks 1985).

When the group of variables $H=Z_o(\lambda\ D_a)^{0.5}$ is less than 0.1 there is no significant decay in the buffer. For values of H larger than 30 the nuclide will have decayed to insignificance i.e. less than 10^{-10} of its original concentration. Z_o is the buffer thickness, λ is the decay constant and D_a is the apparent diffusivity which includes the retardation due to sorption.

Diffusion to and transport in the adjacent rock

It has been found that the rock matrices of crystalline rocks such as granites and gneisses have connected porosities in which small molecules move by molecular diffusion (Skagius and Neretnieks 1986, Birgersson and Nertenieks 1990). The hydraulic conductivity of the matrix is so low that water flow is extremely slow and over short distances, at least, the dissolved species will move faster by diffusion than by flow.

The dissolved species will thus have access to the interior of the the rock matrix, given time. Non sorbing species may reach very far into the rock matrix, 10's of meters, but strongly sorbing species will be retarded and reach only 10's of centimeters over periods of hundreds of thousands of years. The escape from the near field by molecular diffusion through the rock matrix is thus ruled out. Matrix diffusion may, however, play a very important role in the near field by allowing the oxidizing species generated by radiolysis to reach reducing iron minerals in the rock in contact with the backfill. Also sorbing nuclides will diffuse into the matrix, be sorbed and given more time to decay.

To a small extent, also, the diffusion in the matrix may form a transport path from the backfill to the flowing water in the fractures. This is illustrated by the path denoted R5 in Figure 2.

Fractures play a dominant role in transporting the nuclides from, and corrodants to, the canisters. Due to the low diffusivity of the matrix, only channels with flowing water which actually intersect the rock very near a canister will transport any nuclides. Channels which pass at more than a meter from the repository drift or hole will in practice be isolated from the dissolved species in the canister.

Gas evolution and transport

Corrosion of iron canisters or iron reinforcement in concrete constructions in the repository may generate considerable amounts of hydrogen gas. Alpha-radiolysis will also generate gas but to a smaller extent. The gas must escape by flow or diffusion. Otherwise overpressures may develop which may disrupt the rock. At the SFR repository the lid of the large silo will be designed with vents to let the gas escape from the silo to the surrounding backfill. Backfill with small pores, such as bentonite, exerts strong capillary pressures and an overpressure is needed in excess of the hydrostatic pressure to allow the gas to expel the water from the small pores in the buffer. For the sand-bentonite mixture used at SFR the over pressures needed are small, less than an atmosphere, but in the Swiss repository design with compacted bentonite surrounding the steel canisters, the opening pressure can reach many tens to hundreds of atmospheres (Nagra 1985). Once the pores have been freed from water, the gas permeability increases to high values and the gas escapes readily.

SUMMARY DISCUSSION AND CONCLUSIONS

The processes which govern the potential escape of nuclide from repositories in crystalline rock center around the transport capacity of the mobile water in the fractures in the rock. In repositories where a tight backfill such as bentonite is used water flow through the buffer will not act as an important transport process. Molecular diffusion will be faster. The rate of escape of the nuclides will depend on the diffusion paths and resistances. The diffusion in the mobile water in the very narrow channels in the rock often is the largest resistance. The low solubility of the waste matrix and of many nuclides will be an important limiting factor. Alpha-radiolysis may potentially increase the solubility of the spent fuel which consists of more than 95% uranium but there are several mechanisms which strongly counteract and limit radiolysis. A canister of a material such as copper will corrode only by reaction with corrosive agents transported by the water to the copper surface and because the equivalent (or effective) water flowrate is very small and because the water contains very low concentrations of the corrosive agents, the corrosion rate is extremely small. Gas which evolves due to corrosion of iron may build up considerable pressures before the capillary forces in the buffer let it escape.

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DISCUSSION ON NEAR-FIELD TRANSPORT PROCESSES

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The discussion and comments following prof. Neretnieks presentation indicated strong support for his concept of channel intersection, (which did not appear in the submitted paper). Channel intersection quantifies the steady-state capture cross-section of the canister for fracture flow, A, whose variations provide a more reasonable range for fracture/canister interactions that eliminates the unreal and misleading "conservative scenarios" that must be avoided for many parameters if Performance Assessment is to have any value.

Prof. Neretnieks pointed out that capillary suction in non-saturated bentonite backfill will, indeed, cause saturation of the backfill under saturated host-rock conditions.

Prof. Neretnieks also clarified that his diffusion resistor model, in which the equivalent flowrate in inversely proportional to the resistance to diffusion of each near-field component, does not include transient capacitance in the form of retardation and other chemical effects.

It was pointed out by Prof. Neretnieks that the corrosion hole in the resistor model is filled with a solid alteration product having a diffusion resistance greater than the backfill and that the overall diffusion resistance may be controlled by the host-rock or spent fuel flow paths.

COUPLED PROCESSES IN THE NEAR-FIELD

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INTRODUCTION

Underground radioactive waste disposal sites constitute systems of extreme complexity because they are the scene of a great number of physical and chemical phenomena, that have to be included in the safety assessment, and have numerous effects both on the solid confining media (natural and engineered barriers) and on the fluid phase as well as being mutually interactive. They are diffcult to quantify because of the lack of field and laboratory data.

Because these phenomena are so numerous and so complex, they have given rise to a considerable number of conceptual models of the near field whose common aim is to analyze quantitatively the transport of radioactive matter in the immediate vicinity of the disposal site. It seems to us that, paradoxically, these efforts do not lead to a clear understanding of the phenomenon as a whole, but rather add new questionmarks because they offer such a specialized and limited description of the physical characteristics of the system.

Although in recent years the tendency in model development has been to treat the phenomena conceptually rather than using the black box" approach, this has oriented the research more toward complicating the basic transport equations (advective-dispersive equation, Darcy's equation) than toward a comprehensive study which would lead to a complete, original and rigorous treatment of the problem as a whole. We are therefore, at present, very far from a unification of the tremendous amount of existing studies which, at the moment, is limited to simply collecting and combining them, more or less successfully (but, at any rate, very empirically).

In view of this situation, there is no way of avoiding a review listing the main research fields currently under investigation and the various models to which these investigations have given rise. However, and in the spirit of this workshop, whose aim is to collate these studies, which although they have a common objective are widely scattered, we will present the method which we think is best suited to a rational and exhaustive study of systems with multiple fields, potentials and flows, in particular the near field. In doing so, we are encouraged by the increasing number of studies in the same spirit and although this approach seems, at the moment, to belong to a more distant future in model development, we will give a specific example of a case where it can be used with success.

1. APPROACH TO COUPLED PHENOMENA THROUGH NONEQUILIBRIUM THERMODYNAMICS.

The most general way in which to approach coupled phenomena in a system which is undergoing an irreversible evolution is the one offered by Nonequilibrium Thermodynamics (De Groot et Mazur, 1961; Fer, 1971). In this field of thermodynamics one calculates the entropy production per unit volume caused by the transformation. This quantity is always positive whatever the transformation and strictly positive whenever the transformation includes an irreversibility (this is a consequence of the second principle of thermodynamic). In the case of a fluid system with n components, for an elementary volume domain of the system, it is written:

$$(1) \qquad \sigma = \vec{J_q} \cdot \nabla\left(\frac{1}{T}\right) + \sum_i \vec{J_i} \cdot \left(\frac{\vec{F_i}}{T} - \nabla\frac{\mu_i}{T}\right) + \sum_\alpha \frac{A_\alpha}{T}\, \chi_\alpha + \frac{V}{T}\, \nabla\, \vec{\omega}$$

with :

$\vec{J_q}$	heat flux
$\vec{J_q}$	diffusion flux of component i
$\vec{F_i}$	massic long-range external forces on component i
μ_i	massic chemical potential of component i
A_α	affinity of the α-th chemical reaction
χ_α	volumetric chemical reaction rate
V	viscosity tensor
$\vec{\omega}$	barycentric velocity of the elementary volume

The entropy generation appears as a sum of the monomial expressions obtained by the product of two quantities, one of which consists of a physical action and the other of the direct consequence of this action. These physical quantities can be classified into thermodynamic forces:

$\nabla(1/T)$, $\vec{F_i}/T$, $\nabla(\mu_i/T)$, A_α, $\nabla\vec{\omega}$ and related fluxes: $\vec{J_q}$, $\vec{J_i}$, χ_α, V.

Note that hidden under the convenient names "force" and "flux" we find terms of variable tensorial nature which can be ranked as suggested in Table 1.

tensorial rank	0 (scalar)	1 (vectors)	2 (tensors)
forces	A_α	$\nabla\left(\frac{1}{T}\right), \frac{\vec{F_i}}{T}, \nabla\left(\frac{\mu_i}{T}\right)$	$\nabla\,\vec{\omega}$
flux	χ_α	$\vec{J_q}, \vec{J_i}$	V

Table 1. Tensorial rank of the thermodynamic forces and fluxes appearing in the expression (1) of the entropy production.

The theory postulates that the fluxes entering into the entropy production are functions of all the thermodynamic forces and vanish with vanishing forces. Close to the stationary state one can use a linear expression of the following type:

(2) $$J_\alpha = \sum_\alpha L_{\alpha\beta} X_\beta$$

where the X_β's are the thermodynamic forces.

Equations such as (2) are called phenomenological equations and the $L_{\alpha\beta}$*'s* phenomenological coefficients. There are two possible simplifications of these equations: first of all, the so-called Onsager relations:

(3) $$L_{\alpha\beta} = L_{\beta\alpha}$$

secondly, the Curie Principle according to which a flux and the various forces that generate it are necessarily of the same tensorial parity.

Each term of equations (2) represents a coupling. The coupling is said to be *direct* when the force and its corresponding flux belong to the same monomial expression in the entropy production; they represent the first order and best-known phenomena (Ohm's law, Fourier's law, Fick's law, etc.). In the opposite case, the coupling is said to be *crossed* and the corresponding phenomena are called effects. These effects always appear in pairs in which each element is deduced from the other by transposing the force and the flux.

The extension of Irreversible Thermodynamics to porous media can be done in two ways. One of them consists in averaging the expressions of the laws (established in the pore water, where they are rigorously valid) on a representative volume of the porous medium. Two difficulties remain however: (i) the obtained formalism is very intricate (Hassanizadeh, 1986) and (ii) the interfacial phenomena are not taken into account. The latter point is an important restriction in the applicability of this theory to fine media.

In the second method, the starting point is to consider the porous media as a continuum (except, if necessary, for its mechanical properties). This method, although very crude, leads to more operational equations, and take the interfacial phenomena automatically into account. We have chosen this second method.

It can then be shown (Costesèque et al., 1990) that the phenomenological relations are still valid in porous media and that Darcy's law and the usual transport equations can be deduced from them (except for the phenomenon of hydrodynamic dispersion which falls outside the framework of this theory). In Table 11 we have shown a few examples of coupling which contribute to the flow of heat, fluid, solute or electric current in a fluid medium. The phenomena appearing on the bottom line are specifically due to the presence of a porous medium.

FLUX \ FORCE	$\overrightarrow{\mathrm{grad}}\, T$	$\overrightarrow{\mathrm{grad}}\, \mu$		E_0
		$\overrightarrow{\mathrm{grad}}\, p$	$\overrightarrow{\mathrm{grad}}\, C$	
$\vec{J_q}$	FOURIER's law	Thermal osmosis	Dufour Effect	Electrothermal effect
$\vec{J_i}$	Soret effect	Reverse osmosis	FICK's law	Electrophoresis
$\vec{j}$	Seebeck effect	Electrochemical effects		OHM's law
Percolation	Thermoosmosis	DARCY's law	Chemical osmosis	Electroosmosis

Tableau II. A few examples of possible couplings in a fluid medium (after de Marsily, 1986). $\vec{E_0}$ is an electric field and $\vec{j}$ the density of current.

In order to describe the global evolution of the system one has to add to the phenomenologic equations the n equations of continuity of the components, the equation of dynamics, the state equation and the heat transfer equation. Consequently, all the information concerning the coupled physical processes is contained in this set of equations, whether these processes are due to the gradients of the thermodynamic state variables or to their direct influence. However, the use of these processes in real contexts, in particular in the near field, poses two major problems, namely:

—the lack of experimental or field data which would make it possible to estimate the phenomenological coefficients $L\alpha\beta$;

—the difficulty of writing the equation of state in such a complex system.

In spite of these two obstacles, it is, however, true that nonequilibrium thermodynamics, because of its unified formalism, remains an outstanding tool for the study of the near field since, in order to be reliable, such a study cannot be allowed to take an incomplete view of the physical mechanisms that govern the transport of matter. However, one must not consider this theory as a panacea; it has obvious limitations of which the most serious one concerns the study of chemical reactions for which the linear formalism is far from being the ideal expression. Furthermore, it is incompatible with the hydrodynamic dispersion theory which, if merged with Irreversible Thermodynamics would make some phenomenological coefficients depend on the fluid velocity field (and not only on the state variables). This mechanism is unlikely to be important on the scale used to describe the near field, given the small magnitude of the fluid velocity.

2. COUPLED PROCESSES IN THE NEAR-FIELD

It is usual to distinguish between the processes that modify the local flow and those that have a direct impact on the transport mechanisms (Marsily,1987). In the approach suggested here, this division is artificial since a thermodynamic force cannot be assigned to one single flux. Furthermore, since the system is described as a whole, only classifications that help to describe it can be used. Unfortunately, this means that certain phenomena may appear simultaneously in several categories for various reasons.

In the first category we put the phenomena that are mainly the results of changes in the medium properties, in the wider sense, both in the solid and the fluid phase. This class includes both the effect corresponding to the changes in the dynamic viscosity of the fluid and that caused by the modification of the stress tensor in the solid matrix as well as local permeability changes due to mineral precipitation in the pores or fractures of the medium. These effects are all results of actions on the equation of dynamics or on the state equation of the system, either through the state variables themselves (i.e. volume, partial specific masses ρ_i specific mass ρ and temperature T), or through the other characteristic parameters (geometry, isotropy, etc.) of the medium.

In the second category we put the effects that appear in the phenomenological equations of the same type as those described in Table 11 and sometimes called *Onsager's coupled processes* (Carnahan, 1987). With the exception of the formalism which describes them and the reciprocity that links some of them to each other, most of these phenomena have few common features and are widely dissimilar. In the study of one particular system, efforts will therefore be made, above all, to single out the main effects that might appear and to eliminate all the other phenomena from the remainder of the study.

In practice and depending on the configuration that is being studied, the flow an transport models can borrow their formalism either entirely from one of the two categories (hydrodispersive or Thermal-hydro-Mechanical models) or from both of them; a good example of the latter is the solution of the thermoconvective problem.

2.1 Couplings resulting from changes in the properties of the solid or the fluid medium.

Mechanical "coupling"

It is linked to the release of stresses in the surrounding solid medium caused, for example, by the tunnelling and may affect an internal zone of the rock equivalent to several times the diameter of the gallery. In this way preferential flow paths may emerge and create hydraulic shortcuts in the medium. Moreover, the presence of the galleries and the new backfill material create a weakness in the local tectonic equilibrium which may, in the long tem, lead to the formation of extensive faults.

Thermomechanical "coupling"

In this case, it is the thermal stress imposed on the host rock by the heat flux from the disposed waste that causes changes in the hydrodynamic properties along the edges of the excavation. In fractured media (granite) certain fractures with low conductivity can thus be opened up and allow fluids to pass through. In clays, the thermal expansion of the material can cause significant movement of the interstitial water. Conceptual models are now being developed, mainly in fractured media (e.g. Bruel, 1989).

Thermal coupling

Historically, this was one of the first mechanisms to be studied within the framework of waste disposal (se e.g. Cordier and Goblet,1987). It has its origin in the differences in density and viscosity in the fluid phase due to the temperature field. This mechanism has been well described for a continuous porous medium (Combarnous and Bories, 1975; Coudrain-Ribstein, 1983). In discrete fractured media the models are still being developed.

Geochemical coupling

This aspect of the problem is currently the subject of a great many studies such as the development of models coupling geochemistry and transport now in the process of being verified and validated. This type of model takes into account, in particular, the phenomena of complexation in the aqueous phase, the redox equilibria or disequilibria and the exchanges of matter between the fluid and the solid phases (through precipitation, dissolution, ion exchange). The driving forces of the chemical reactions in the near field are mainly the temperature heterogeneities, the mineralogic differences between the artificial barriers, the waste and the host rock, the mixing of water from inside and outside the disposal site and the redox disequilibrium caused by the excavation. A phenomenon which has been particularly well investigated is the alteration of the properties of the artificial barrier (e.g. the bentonite) through the replacement of alkaline or alkaline-earth ions in the exchangeable sites of the clay (e.g. Jamet, 1989). The study of natural analogues (e.g. Jamet et al., 1990) also provides interesting cases for both the validation of the coupled geochemistry-transport models and the study of reactive processes in the near field.

Chemical-mechanical "coupling"

This coupling is the result of the precipitation or dissolution of solid matter which may block the system or increase its hydraulic conductivity. This type of phenomenon is often found in hydrothermal systems in nature and can occur as well in the immediate vicinity of the disposal site as long as the temperature field prevailing there constitutes a driving force for

—chemical reactions. It concerns both the host rock and the engineered barriers. The following are a few examples of such effects:

—increase in the hydraulic conductivity of the bentonite engineered barrier by Na-Ca substitution or the transformation of the bentonite into illite. This kind of transformation can be found in nature;

—total obstruction of part of the system which may cause interstitial fluid pressure to rise and create natural hydraulic fracturing;

—partial obstruction of the conducting channels inside which the fluid velocity increases preventing the dissolved matter from being adsorbed to any greater extent. The result is a swifter outward migration of the dissolved matter.

2.2 Onsager's coupled processes

Because these processes are so numerous and the form in which they appear so heavily influenced by the boundary conditions of the system, we shall only mention those that probably have a nonnegligible effect on the transport of solutes in a near field consisting of weakly permeable material. The main thermodynamic forces active here are the gradients of temperature, fluid pressure and chemical potential and the main effects influencing the solute transport seem to be thermodiffusion (Soret effect), chemical osmosis and thermal osmosis (which appear at the same time as their mirror effects, respectively, the Dufour effect, reverse osmosis thermal filtration).

Chemical osmosis and reverse osmosis

These two phenomena represent respectively the fluid flux due to the gradient of chemical potential (which, to simplify, roughly corresponds to the concentration gradient) and the solute flux due to the pressure gradient. The latter phenomenon which plays an important role in semi-permeable media, such as membranes, is put to use e.g. for the desalinisation of seawater. It requires large overpressures in order to be significant and is not likely to greatly influence the flux of matter in the near field. Carnahan (1984) has shown that this term is, at the most, of the same order of magnitude as the flux caused by convection (very weak in clays).

Chemical osmosis can, however, cause a significant flux of water, up to 3 or 4 orders of magnitude greater than Darcy's flux, from less concentrated to mor concentrated zones (Carnahan,1984). Depending on the values of the corresponding phenomenological coefficients for the various dissolved elements, this flow can be oriented into or out of the disposal site. Unfortunately, the lack of numerical values makes it impossible to say more for the time being.

Thermoosmosis thermal filtration

Thermoosmosis appears as a flux of water through a porous medium subjected to a heterogeneous temperature field. It is a well-known phenomenon in earth sciences to which clays seem susceptible. Srivastava and Avasthi (1975) have demonstrated that the flux of water moved by this effect can reach 10^{-8}m.s.$^{-1}$ (0.5 m.yr.$^{-1}$) in compacted kaolinite and for a temperature gradient on the order of 20 K.m^{-1}, i.e. much larger than Darcy's flux in this type of medium. This result s confirmed by Carnahan (1984) who estimates the ratio between the two fluxes at around 3 orders of magnitude. This flow is always oriented out of the disposal site since it runs counter to the temperature gradient.

The mirror phenomenon of the thermoosmosis corresponds to a heat flow and is called thermal filtration. One can show that, on the whole, the cross effects capable of creating a heat flow are negligible compared to transport by conduction (Fourier's law).

Soret and Dufour effects

The Soret effect which corresponds to a solute flux in a medium (porous or not), where there is a prevailing heterogeneous temperature field, becomes an important phenomenon whenever the temperature differences are large. For instance, in a geothermal setting, this effect may result in the formation of ore deposits (Costesèque, 198, Fargue et al., 1990). In a system with closed boundaries, stable concentration differences are thus obtained under which the Soret flux is balanced by the molecular diffusion flux (Fick's law). These differences can vary from a few percent to one order of magnitude depending on the temperature difference and the sensitivity to the Soret effect of the dissolved element. This sensitivity is measured by the Soret coefficient S_T:

$$(4) \qquad S_T = \frac{D'}{D} = \frac{1}{c(1-c)} \frac{\nabla c}{\nabla T}$$

where D and D' are respectively the molecular diffusion coefficient and the thermo-diffusion coefficient which enter into the expression of the solute flux and c is the solute mass fraction. S_T is generally positive, i.e. the Soret flux is opposed to the temperature gradient. Among the most sensitive chemical compounds, note the presence of the aqueous complexes of the uranyl ion (UO_2^{+2}). No S_T values are reported for actinides.

In the near-field context the situation is slightly different because the boundaries of the system (e.g. the artificial barrier) are not no-flow but rather constant-concentration boundaries. One must therefore think in terms of fluxes rather than in terms of concentration. Figure 1 shows that the contribution by the Soret effect to the transport through this barrier increases with the temperature difference. Here, in addition to the Soreteffect, we have only taken the molecular diffusion into account; these two fluxes are oriented in the same direction because the radionuclides escape into the geosphere where the external boundary condition on the concentration is close to $C = 0$.

Thornton and Seyfried (1985) have investigated the importance of these phenomena in connection with waste disposal in the pelagic silts (SEABED programme). Marsily et al.(1987) have calculated interesting orders of magnitude on the consequences of the Soret effect on the safety of a waste disposal during its thermally active phase.

The symmetric effect (Dufour effect) is, like thermal filtration, negligible compared to the Fourier heat flux.

Thermogravitational effect (TGE)

This is a very important effect which is the result of the coupling of the Soret effect and thermally-driven water convection (see above Thermal Coupling") and which appears mainly when the temperature gradient is horizontal; then, the transport mechanisms are no longer governed entirely by diffusion since the temperature differences give rise to a vertical water flow, upwards in the hot zones and downwards in the cool ones. The Soret effect moves the solutes along a horizontal path, from the hot toward the cold zones, where they are caught up by the downward water flow. The end result is that there is a large increase in the concentration of dissolved element in the lower regions of the system and by the same token, a depletion of the upper regions until a stationary state is reached, when the molecular diffusion flux exactly compensates the vertical convection flux. For a given temperature gradient the concentration gradient obtained in the stationary state through the thermogravitational effect may be much larger than the one obtained through the Soret effect alone.
Consequently, the TGE acts as an amplifier of the Soret effect, which transform; a weak horizontal flow of matter into a stronger vertical flow whose stationary state is characterized, subject to certain conditions, by a very large difference between the concentrations t either end of a closed system.

The magnitude of the Soret flux depends only on the physical and chemical characteristics of the elements and the prevailing difference in temperature, whereas the convection velocity depends on the geometric features of the

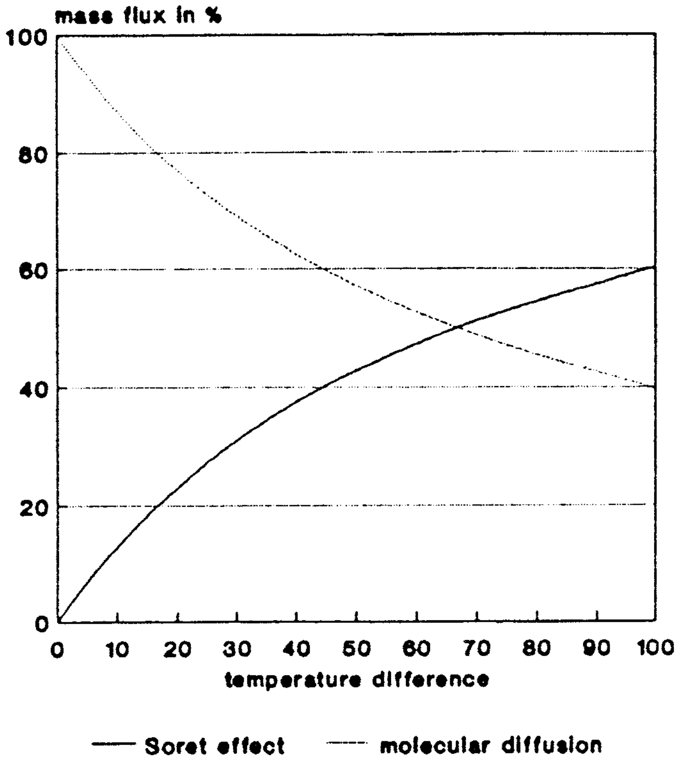

Figure 1. Illustration of the relative contributions by molecular diffusion and Soret effect in the mass transport through a system with constant concentration boundaries.

system as well. This velocity can be adjusted so as to produce the best possible coupling. In fact, if it is too low, the horizontal concentration gradient is not disturbed and the steady state reached by the system is, taken as a whole, a horizontal concentration field obtained by pure thermodiffusion. If the velocity is too high, the fluid becomes homogenized more rapidly than it separates and the concentration differences, that could established are nullified. Between these two extreme cases lies a domain where the coupling is optimum and a maximum separation effect can be achieved. Therefore, there is a permeability for which the coupling is optimal when the effect occurs in a porous medium.

The near field conditions can be favourable to the TGE if the temperature gradients are large enough and the fractured host rock contains zones where stable thermal convective cells can subsist. In order to illustrate the importance of this phenomenon in a near-field setting, we will present an imaginary case which is not necessarily unrealistic considering that natural media have a tendency to create unfortunate coincidences.

A not very extensive subvertical fracture (length L and aperture a) has opened up in the vicinity of a recent waste disposal site. We assume that zone I, of width A, surrounding the fracture has a porosity accessible to diffusion ε and that it has no flow whatsoever. The fracture (zone II) if filled with rock material with an intrinsic permeability k and porosity ε'. The lower end of this fracture links up with another fault where the fluid velocity is constant and oriented upward (zone IV) through a very weakly permeable plug where the solutions can only diffuse (zone III). This "natural" configuration is shown in figure 2.

Since the action of the fracture has torn open the end of the disposal installation, the broken canisters are leaking radionuclides of constant mass fraction c_0.

The migration processes of the radioactive solute are the following:

—*Zone I*: molecular diffusion and Soret effect.
—*Zone II*: thermogravitational effect in the fracture.
—*Zone III*: molecular diffusion only.
—*Zone IV*: advective transport.

We shall now examine, one by one, the points where the thermodiffusive phenomena significantly influence the evolution of the system:

Mass transfer in zone 1

The transport equation contains an additional term (Soret effect) which acts in a constant temperature gradient (whereas the migration by molecular diffusion vanishes with the concentration gradient). Since the transport of elements is thus increased, the same concentration is obtained more rapidly at a given pnt if the two effects are combined.

The relative contribution by the Soret effect to the total transport of matter can be estimated as follows. If we write:

$$c \approx \frac{c^0}{a} \quad \text{et} \quad T \approx \frac{\tau}{a}$$

τ is the temperature variation across zone 1. Then, the solute flux in zone 1 is written:

$$(5) \qquad \vec{J} = -\frac{\varepsilon\rho Dc}{a}(S_T\tau + 1)$$

and the relative contribution by the Soret effect to the total transport is:

$$(6) \qquad J^s = \frac{S_T\tau}{S_T\tau + 1}$$

Figure 1 represents J_s for $S_T = 1.5\ 10^{-2}K^{-1}$.

Asymptotic concentrations in zone I

One must take into account the decrease with time of the temperature difference which makes it possible to describe the progressive cooling of the waste. This decrease is expressed by a law of the type:

$$(7) \qquad \tau(t) = \tau(0)e^{-\lambda t}$$

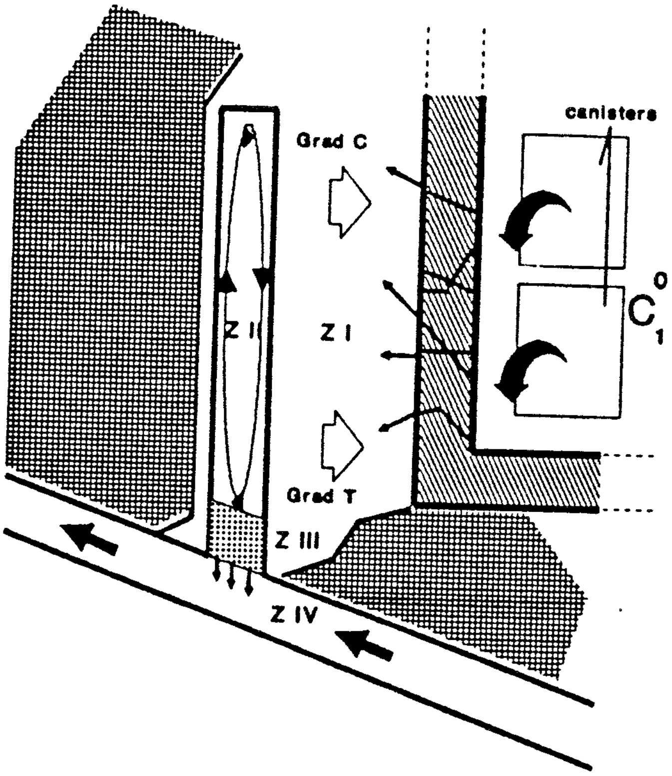

Figure 2. Thermodiffusion-thermogravitational scenario in the vicinity of an underground radioactive waste disposal site (from Fargue et al., 1990).

we have taken $\lambda = -0.6\ 10^{-2}yr^{-1}$, $\tau(0) = 60$ K, $C(0) = 10^{-2}mol.1^{-1}$, $A = 2m$. In these conditions we notice (figure 3) that the concentration difference versus the simple molecular diffusion is large enough not to be disregarded. Moreover, the overconcentration step ($C > 1.2\ 10^{-2}mol.1^{-1}$) lasts for quite a long time.

Concentration through h T E in zone 11

If the thermogravitational effect operates in this zone, one must expect an additional overconcentration in the lower part of the fracture ($S_T > 0$). The concentration in the fracture varies continually depending on the transport across zone 1. Therefore, it is not possible to use the analytical solution of the thermogravitation as such. It is possible, however, to estimate the concentration obtained at time t at the bottom of the fracture using Debye's formula:

$$(8) \qquad (c^{bot} - c^{top})\,(t) = (c^{bot} - c^{top})_{stat}(1 - \frac{8}{\pi^2}e^{-t/\theta})$$

The relaxation time θ near optimum is given by:

$$(9) \qquad \theta = \frac{L^2}{2\pi^2 D}$$

L represents the length of the fracture.

For $L = 10$ m we have $\theta \approx 400$ years. The optimum permeability and the corresponding concentration factor $q^{opt} = c^{bot}/c^{top}$ are given by the Lorenz and Emery equations (1958).

$$(10) \qquad k_{opt} = \frac{\varepsilon D \eta \sqrt{120}}{g \tau a \rho \beta} \qquad q_{opt} = \frac{S_T \tau L \sqrt{120}}{24a} \qquad \text{where} \quad \beta = -\frac{1}{\rho}\frac{\partial \rho}{\partial T}$$

As τ decreases fairly slowly, one can consider k^{opt} to be almost constant and choose directly the case of optimum permeability. With the following data:

$$\varepsilon' = 0.4 \quad \eta = \ 1\text{cp} \quad \tau = 15\text{K}$$
$$a = 0.5\text{m} \quad \beta = 410^{-4}\text{K}^{-1} \quad \rho = 10^3\text{kg.m}^{-3}$$

one finds $k_{opt} = 210^{-15}\text{m}^2$.

Provided the permeability of the rock material has this value, one can evaluate the concentration factor at steady state and for the temperature difference at time t. We can then calculate the mass fraction c at the bottom of the fracture as a function of time. Figure 3 shows that the thermogravitational effect can lead to enrichments of more than 3.

Leakage by diffusion cross zone III

This transport process also occurs without thermodiffusion, but the concentrations prescribed at time t on the upper face of zone III are then much lower (lower curve in Figure 3).

If the fluid velocity in the fault (zone IV) is large compared to the diffusion velocity of the solute, one can assume that the lower face of zone III remains at zero concentration. Under these circumstances, one can calculate the mass flux crossing zone III since the concentration prescribed on the upper face is the already calculated function $c^{bot}(t)$.

The mass flux is given by the formula:

$$(11) \qquad \phi(t, z) = \rho \varepsilon D \frac{\partial c}{\partial z} \approx \varepsilon D \frac{\partial C}{\partial z}$$

where z is the ordinate on the vertical axis crossing zone III which will be taken to be of length $l = 20$ cm. Figure 4 shows the function $\phi(t)$ for the case with only molecular diffusion and for the one where the Soret effect and the TGE add themselves to the former.

When we include both the Soret and the thermogravitational effect, we observe, for instance, that the disposed waste would release about three times as much matter should an accident happen during the first 200 years of its existence. Although this calculation does not raise any doubts about the technological orders of magnitude used in designing the artificial barriers, it demonstrates, all the same, that in this context the consequences of the Soret effect are not necessarily negligible.

A computer code has been developed at the Paris School of Mines on behalf of the CEA/IPSN. It integrates into the transport equations the thermoosmotic effect and the Soret effect. At the same time, a considerable amount of theoretical work has been one in order to ascertain that the classical equations

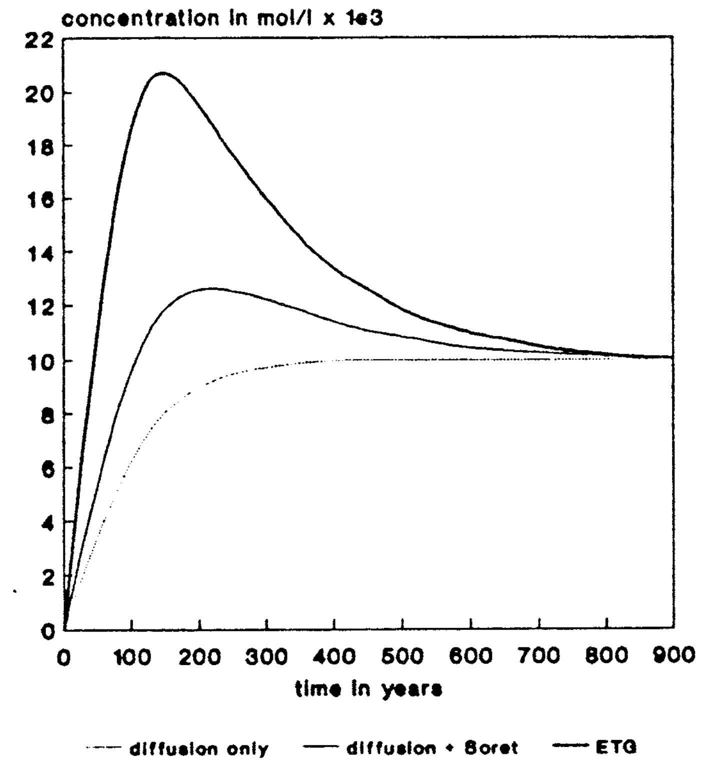

Figure 3. Concentrations reached at the bottom of the fracture for the three transport scenarios.

(Darcy, dispersion) are compatible with those of nonequilibrium thermodynamics. Moreover, an experimental program has been initiated in order to validate this numerical model (Costesèque et al., 1990).

Electroosmosis and electrokinetic effect

This is the phenomenon responsible for fluid movement in porous media under the influence of an electric field. It is used geotechnically for consolidating loose backfilling or unconsolidated clays.

Srivastava and Jain (1975) made a series of experiments in the laboratory using various clays. Their results show, for example, that bentonite has an electroosmotic conductivity three times higher than kaolinite (whereas the hydraulic conductivity ratio is on the order of 15). Although bentonite is less permeable than kaolinite, according to Darcy's law, fluids would be able to travel through the former, if it were subjected to a difference of electric potential.

The difference of electric potential in question could arise from natural phenomena (telluric current) or from other crossed effects such as the electrokinetic effect (MacInnes, 1961), the Seebeck effect or even redox effects of great amplitude if the disposal site is in the vicinity of a large ore body (Sato and Mooney, 1960).

CONCLUSIONS

In modelling transfer of fluid, matter or heat in the near field, it is not enough to take only a partial view of the physical mechanisms and concentrate on a particular one. A

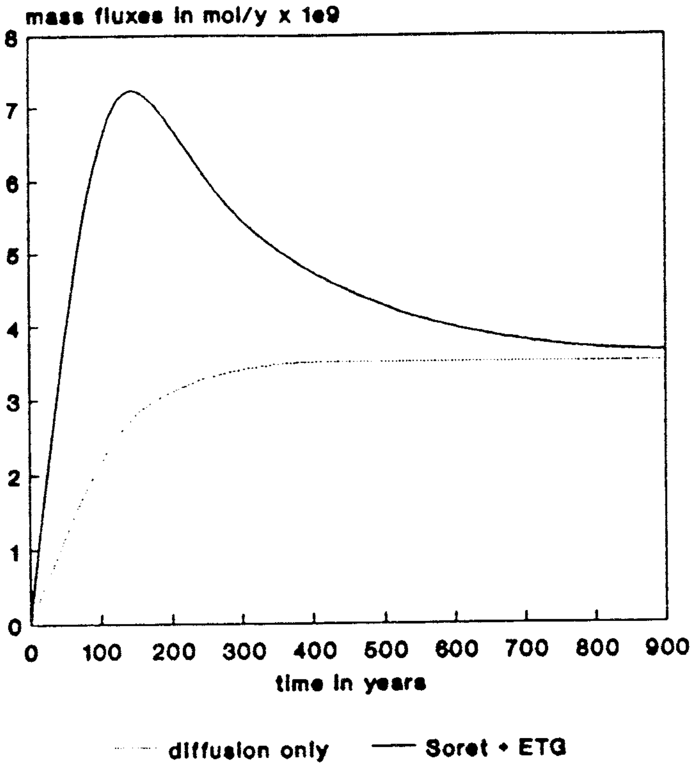

Figure 4. Function of flux exiting from zone IV.

global view of the problem could prove more efficient in the long run since it is the only one that will make it possible to determine the identity of the main mechanisms, bearing in mind the special conditions of each problem.

To this end, and in spite of the large gaps in our knowledge when it comes to the quantitative phase of evaluation, nonequilibrium thermodynamics seems to be the best available tool except in the case of chemical mechanisms to which the only realistic approach still remains that of the conceptual models currently being developed.

The complete coupling (i.e. including thermoconvection) between the temperature field and the concentration field can easily be represented in transport models: Work is continuing on this subject and it is probable that it will be possible, in the not too distant future, to introduce thermomechanical equations. One still uninvestigated area is that of crossed phenomena involving electric fields.

The task of experimentally acquiring the phenomenological coefficients needed to quantify the phenomena is enormous and complicated because of the great number of effects and their weak amplitude. However, it is possible to imagine experimental devices which would make it possible to study each of the crossed phenomena separately.

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DISCUSSION ON COUPLED PROCESSES

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Processes acting on a nuclear waste repository can be largely divided into four categories, i.e., hydrological, chemical, thermal, and mechanical. these processes are generally interrelated to each other and changes in one affect the others in varying degrees, i.e. "coupled". Understanding the effects of these processes on the release of radionuclides from waste canisters and their transport to the geosphere requires decoupling of the complex process into individual processes conceptual and numerical. As the processes are better understood, the individual models are recoupled to evaluate the effect from their interactions. By necessity, the coupled models include only the major processes that have most influence on the repository performance, and often the submodels representing each individual process are simplified representation of the more detailed process model. It is plausible, however, to assume that the effects from weakly coupled processes are not negligible in an environment where the gradients are relatively high, such in the near field around waste canisters during the early years after waste emplacement. Dr. Jamet's paper discusses the effect of one such coupled process in the near field, more specifically, the effect of thermal gradient on fluid flow, commonly known as the Soret effect.

The following summary of the discussion session on "coupled processes" covers subject that address directly Dr. Jamet's presentation as well as subjects on coupled processes in general, although the majority is on the former. No attempt has been made to discuss the individual comments made in the workshop, rather similar comments have been addressed as a whole in an attempt to bring out the key points and counterpoints.

1. SORET EFFECT

Dr Jamet's analysis was based on the use of irreversible thermodynamics and Onsager's reciprocity relation. A question was raised whether such an approach would be valid when many geochemical systems in nature are not in equilibrium and the fluxes may not be linear to gradient.

Many geological system are in transient states and they are not in equilibrium on a geological timescale. However Onsager's reciprocity relation assumes only a microscopic reversibility, which does exist in many geological systems, and in addition the phenomenological coefficients are measured in such systems on a time scale far less than the geological time scale

Many commenters questioned the need to consider such a secondary effect from weakly coupled processes in view of the fact that a relatively high temperature gradient may exist only for a short term after the emplacement and may also be limited to the immediate vicinity of the waste canisters. Under and early accident scenario and unanticipated conditions, however, the effect can be very significant, although in such a disturbed case the effects from primary coupled processes may dominate the repository performance. In addition, with a high temperature gradient, there also is a counter balancing effect from chemical osmosis. There are several other questions we have to answer before we consider the effects from weakly coupled processes.

— Considering the uncertainties in the system, how well do we understand the coupling of these processes?

— Are the data to analyze the system available? Are the values measured ore assumed? And, are the results from analysis consistent with our current scientific understanding and observations?

— Is the quantitative effect significant enough to make it worthwhile to take them into account?

Dr Jamet's paper answers some of these questions. He showed that the enhanced flow due to Soret effect could be as high as 1000 to 10,000 times of the Darcy flux in a bentonite backfill under the assumed conditions. There also are measurements made on the phenomenological coefficients for some media such as bentonite. Question still remains whether we can make reliable quantitative assessment for a system which has a large overall uncertainties. It should also be noted that the enhanced flow is locally limited and the water does not flow through the backfill. Then is the net effect significant enough? On the other hand, it is also conceivable that a relatively high temperature gradient may persist a long time, e.g. a few thousands of years, at a specific site with a specific repository design and the secondary effects may become significant.

2. COUPLED PROCESSES IN THE NEAR-FIELD

Most system level performance assessment models are probabilistic in nature in order to accommodate uncertainties in the future state of the system and the parameters representing it. Simplification of process models are often required. Performance assessment scientists are already facing computational limitations running Monte Carlo type of simulation with only the major processes coupled. The problem compounds when 2-D and 3-D analyses are required. a specific question was asked how we can couple geochemistry with transport and whether we can do it. Suggestions were made to use two-level models, in which we use a simple model to assess the system performance and a more detailed model to understand the scientific principles involved.

One significant manifestation of hydraulic-mechanical coupling is change of fracture flow under mechanical stress, generally resulting in an uneven fracture flow. Chemical-hydraulic and mechanical-chemical-hydraulic coupling also affect the fracture flow. We use conventional tool to measure parameters that characterize fractures. Often the measurements obtained with different methods vary by several orders of magnitude even for seemingly simple systems. Predicting performance of future states will be almost impossible without understanding the effect of coupled processes. Unfortunately, however, our understanding of some coupled processes is not mature enough to model them. In such cases, we are forced to ignore them or accommodate them with models that inadequately describe the system. We may also have to use average values that do not take individual differences into account.

It was also pointed out that in the thermo-mechanical coupling, which has a great significance for backfill material near waste canisters, we do not have detailed knowledge

In practice, however, performance assessment scientists use basic independent process model in the form of flow + transport and the geochemical interaction of the radionuclides with the rock is lumped as a single parameter known as retardation factors. Although it was also pointed out that the retardation factors are not important in the near field, geochemistry plays a significant role in the near field such as by precipitating secondary minerals, thus affecting the solubility limit of radionuclides. Generally, scientists from process side favored to pursue the coupling effect one step further in complexity than the use of simple retardation factors, while total system performance assessment scientists argues against such an approach citing the robustness of the design and the environment based on some prototype field tests.

INTEGRATED NEAR-FIELD ASSESSMENT

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ABSTRACT

In an effort to ensure conservatism, performance assessment models generally treat the near field in a rather simplistic manner – often ignoring the reactions between various barriers and, indeed, the existence of particular barriers entirely. This paper presents an alternative approach in which the near field is evaluated in an integrated manner which is intended to be as realistic as possible. Such an approach, when applied to the current Swiss HLW near-field design, predicts that no significant releases will occur and that, as performance is provided predominantly by massive geochemical buffers, the analysis is very robust.

1 INTRODUCTION

Even within the nuclear industry, the disposal of high-level radioactive waste (HLW) is often reported as a key problem – which, among opposition groups has been translated into the "ultimate unsolvable" problem and a major reason for abandoning nuclear power. Many analyses of repository performance appear to support these suppositions as they attempt to quantify the sequential degradation of safety barriers, with great emphasis on the uncertainties involved. Such analyses are useful when seen in context, but are oversimplified to the extent that they do not give any information about how the disposal system is really expected to behave. This paper contrasts such a reductionist approach with an alternative holistic treatment – which could be considered as a geochemical prognosis of expected behaviour, unconstrained by any consideration of demonstrable conservatism.

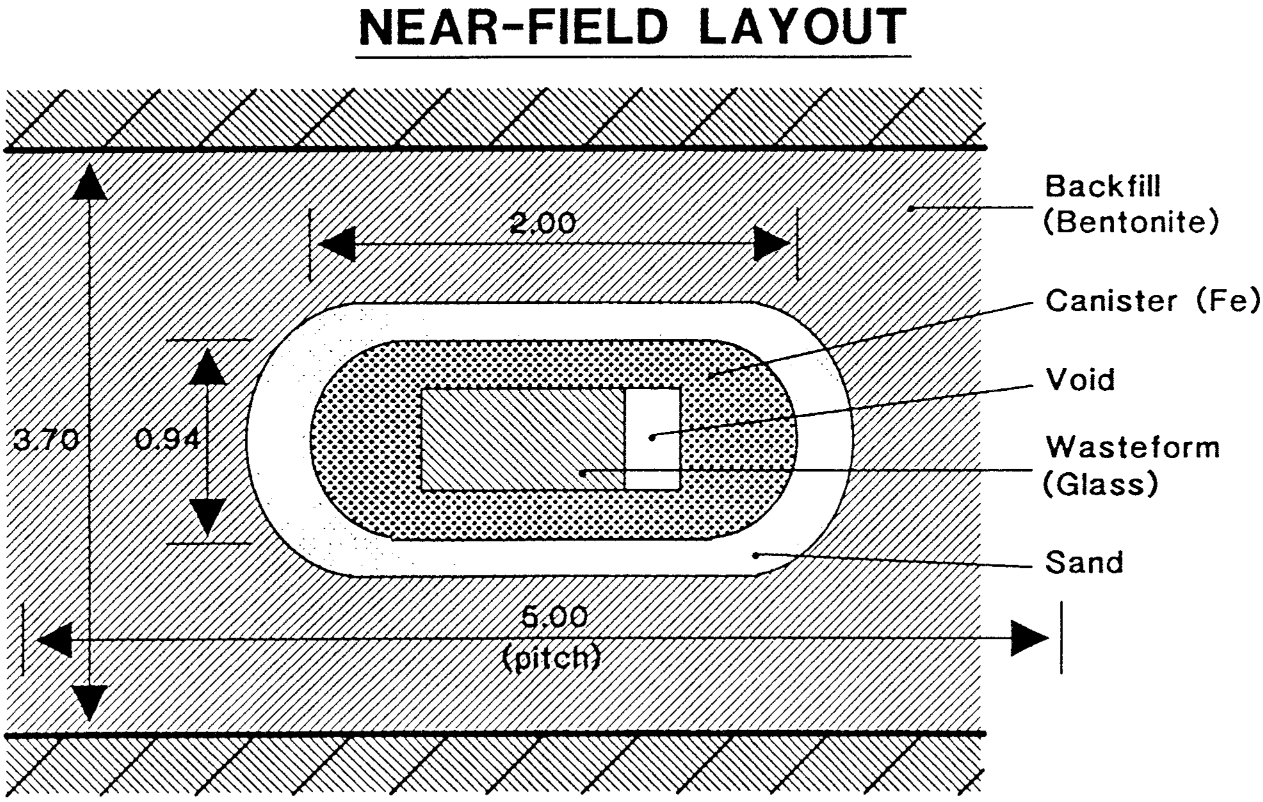


Figure 1: Diagrammatic representation of the HLW near-field

As far as the near field is concerned, simple models have been successfully utilised to demonstrate the basic feasibility of disposal concepts (e.g. KBS, 1983; NAGRA, 1985). More realistic models should, however, be used for evaluating specific sites and are essential for sensitivity analyses aimed at either design optimisation or identifying research programme priorities. An integrated, realistic analysis should also be used as the basis for any planned model comparison or benchmarking exercise.

The integrated approach is illustrated by considering a Swiss disposal concept. This analysis shows that the near field can provide much more performance than is generally accepted and, with rather small demands on the far field, can assure negligible releases for all reasonably modelled periods of time ($\approx 10^6$ years).

1.1 Reference near-field layout

In our discussions, we will concentrate on the Swiss reference HLW disposal concept for a crystalline host-rock (NAGRA, 1985) as illustrated in Figure 1. Here, vitrified reprocessing waste in a thin steel fabrication container is sealed in a massive cast steel canister (or overpack) and emplaced horizontally into tunnels which are backfilled with compacted bentonite. A thin layer of quartz sand or fine-pored sandstone may be emplaced between the canister and the bentonite. The quantities of materials in each waste "package" are summarised in Table 1. The Swiss concept involves very deep disposal in a purpose-built mine – at a depth of ≈1200-1300 m below surface in the crystalline case considered. At such depths, the overall conductivity of the host-rock is rather low, as are the hydraulic gradients. The advective water flow which does occur is localised in distinct features – e.g. shear-zones or fractures associated with various intrusive features.

The geologic environment of the repository is characterised by a low water flux - ≈litres/year or less if averaged over all canisters – and chemically reducing conditions. The very thick bentonite annulus ensures that solute transfer through the backfill occurs predominantly by molecular diffusion – placing considerable constraints on the rates at which solute exchange between the waste and advecting groundwater can occur.

Table 1: Material inventory in the near-field (per canister)

Material	Volume (m^3)	Mass (kg)
Borosilicate glass	0.15	405
Steel fabrication container	0.01	75
Fabrication void	0.03	-
Canister (cast steel)	0.9	6.5×10^3
Backfill	52.8	-
a) Quartz sand (dry)	0.7	1.4×10^3
b) Bentonite (dry)	32.0	8.6×10^4
c) Pore space	20.1	-

1.2 The Project Gewähr near-field analysis

Project Gewähr 1985 (PG'85) was a major study to demonstrate the feasibility of nuclear waste disposal in Switzerland (NAGRA, 1985). As the aim of this study was simply to demonstrate the concept, there was no attempt to optimise either the engineered barrier design or the safety analysis procedure. The very thick backfill (and large pitch between canisters) was selected to ensure that temperatures at the rock wall remained below 100°C, even for fairly pessimistic resaturation scenarios. Similarly, the massive canister was selected on the basis of a 20 cm thickness for mechanical strength (ensuring the ability to withstand the maximum bentonite swelling pressure of 300 bars with safety margins above those required by ASME) and 5 cm corrosion resistence (which includes a safety margin of $\approx 70\%$ over the maximum penetration expected in 10^3 years).

The release of radionuclides from the near-field was based on the following assumptions (c.f. McKINLEY, 1985):

1) All waste packages behave identically
2) The bentonite acts as a chemical buffer and colloid filter for periods $>10^6$ years
3) The canisters fail mechanically after 10^3 years, but continue to act as redox buffers for $>10^6$ years
4) The glass block is initially fractured, increasing its surface area by a factor of 12.5, and corrodes at a constant rate of 10^{-6} kg m^{-2} day^{-1}
5) Radionuclide transport through the bentonite only accounts for those nuclides which can be shown to decay to insignificant levels during such migration. For all other nuclides, release to the far field is taken directly from their release rates from the glass matrix, constrained only by elemental solubility limits in the average advective groundwater flux (0.7 litres $canister^{-1}$ $year^{-1}$).

This analysis was considered to be conservative and, when coupled to realistic models of the far-field and biosphere, result in neglibly low doses (over 8 orders of magnitude below official limits, at times $>10^6$ years after repository closure). By selection of more conservative far-field and biosphere models, however, the calculated doses would be considerably increased (even though staying below regulatory guidelines).

2 BACKGROUND FOR REALISTIC MODELLING OF THE NEAR-FIELD

2.1 Boundary conditions

The first point to establish when discussing realistic modelling is the timescale involved. Reported model predictions in the nuclear waste field almost invariable use logarithmic time axes and commonly extend to periods $>10^9$ years. Such timescales are not only nonsensical in their extrapolation of constant behaviour but also consider periods when the potential radiological hazard of the waste is less than that of the host-rock excavated to construct the repository (NAGRA, 1985). We will consider a cut-off for quantitative considerations at 10^6 years (at which point the toxicity of the waste is roughly comparible to the original uranium ore). The justification of extrapolating models over this period is discussed in section 6.

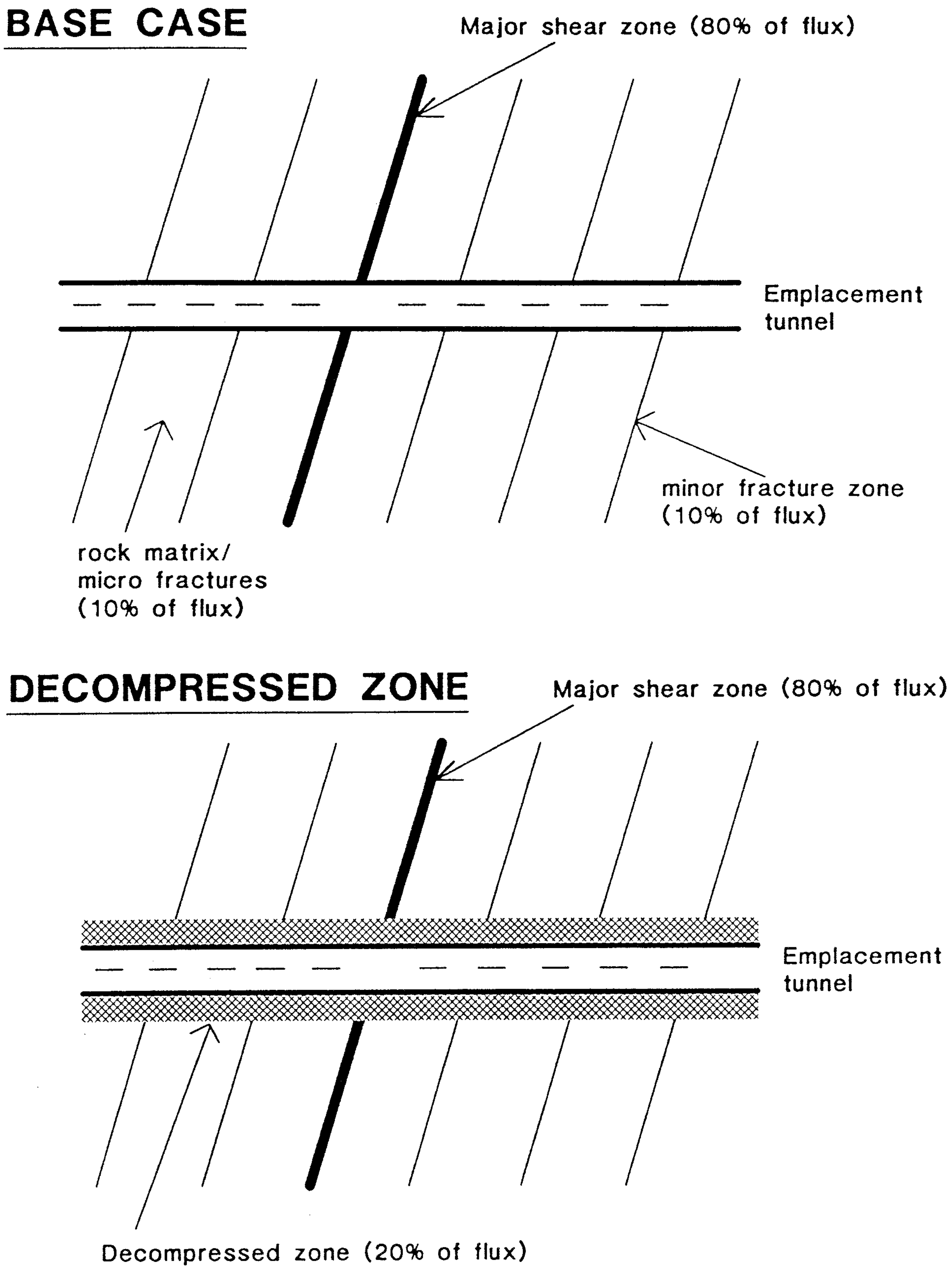


Figure 2: Water flow in the near-field

A second key point to establish is the hydrology of the area surrounding the near-field. In the crystalline host-rock case, advective flow occurs predominantly in massive shear-zones which are relatively easy to identify and are separated by distances on the scale of ≈100 m. Any waste emplacement tunnel would be expected to intersect several such zones, but waste packages would not be emplaced in their immediate vicinity. A second flow system would consist of smaller fractures, which may be associated with intrusive features such as aplitic and pegmatitic dykes. Advective water flow through the bulk rock is neglegible and, if any connected porosity exists in such rock, transport would be dominated by diffusion.

In the area of northern Switzerland considered, a reasonable estimate of the total water flux through the area of a repository is ≈4 m^3/year. In PG'85, it was assumed that this entire flux could exchange solute with the waste packages, and was averaged to ≈0.7 litres per year for each canister. Given a realistic consideration of the distribution of water flux (Figure 2), this is clearly overly pessimistic. Even if the existence of preferential flow paths in the mechanically disturbed zone surrounding the emplacement tunnels is assumed, the true geometry of the flow system must be taken into account.

2.2 Thermal pulse, resaturation

After waste package emplacement, the near-field environment will evolve relatively rapidly as oxygen in trapped air is consumed by canister corrosion, saturation of the bentonite occurs and the radiogenic temperature increases occur. Resaturation was not considered directly in PG'85 – it was assumed to be negligibly slow in thermal calculations (thus maximising near-field temperatures) but effectively instantaneous for corrosion calculations (maximising the transport rate of corrodants through the backfill). Fully coupled analysis of heat and water flow in the near-field is very complex and particularly dependant on the outer boundary condition assumed for water supply to the bentonite. For the greatly simplified case of a fully saturated, homogeneous host-rock, no thermal impulse and "non-swelling bentonite", resaturation times are expected to be $>10^2$ years and possibly $>10^3$ years (Andrews et al., 1986). The effect of coupled processes such as chemical or thermal osmosis is difficult to evaluate but could dominate purely hydraulic effects (c.f. paper by Jamet, these proceedings). Nevertheless, the very large pore volume present, the low availability and dispersed sources of water in the host rock and the relatively macroporous sand in contact with the canister would limit the rate of saturation.

On the timescale of the main thermal pulse (≈50-100 years), it is probably reasonable to neglect resaturation except in the outermost few centimetres of the bentonite. The PG'85 base-case temperature calculations assume maximum expected thermal output and a homogeneous backfill with pessimistic values for the bentonite thermal conductivity/ heat capacity. As the bentonite does not resaturate during this period, air gaps between the compacted blocks used will exist and, especially if more realistic parameter values are used, it can be shown that maximum temperatures within the outer half of the bentonite annulus remain <100°C although the temperature at the canister surface may be reasonably high (≈160°C).

In the zone with temperatures >100°C, which may persist for ≈50 years closest to the canister, two important chemical processes will be the corrosion of the canister and the alteration of the bentonite. Canister corrosion will initially occur in the presence of oxygen from trapped air and might initially be quite fast, but would slow down as protective layers build-up. The maximum extent of corrosion from this source would correspond to <0,7mm, out of the total corrosion allowance of 5 cm

(NWGCT, 1984). After consumption of oxygen by trapped air, anoxic corrosion by reaction with water vapour may occur, but this would be relatively slow. By the time that the bentonite in contact with the canister is saturated, temperatures there will be insignificantly different from repository ambient (≈55°C).

The mineralogical alteration of bentonite is very slow at the temperatures involved and, additionally, is constrained by the supply rate of K^+. The maximum extent of alteration over 10^6 years would not extend beyond the outermost few tens of centimetres (McKINLEY, 1985). At temperatures <100°C, in the presence of a water vapour phase, irreversible loss of bentonite swelling pressure due to cementing of bentonite platelets by amorphous silica has been reported (Couture, 1985). This process seems, however, to be much less significant for highly compacted bentonite (discussion of the paper by Murphy, this workshop). In the worst case, however, the inner annulus of bentonite would only become somewhat more rigid.

2.3 Canister corrosion

Canister corrosion in the anoxic phase will occur in unsaturated conditions for ≈500 years due to the slow rate of water transport through the bentonite. Over this period, corrosion may continue either by reaction with water vapour or with liquid water drawn by capillary suction through the finest pores of the bentonite. As discussed in PG'85, the latter process might be minimised by including a thin layer (≈10 cm, say) of fine-grained quartz sand (or sandstone) around the canister and this is assumed in this analysis. The corrosion which occurs, nevertheless, results in the production of hydrogen, e.g.

$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2$

or

$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$

Anoxic corrosion rates at temperatures ≈100°C in the presence of liquid water are reported to be ≈1-6 µm/a (MARSH and TAYLOR, 1988) which are consistent with sensitive H_2 production measurements (<2.5µ m/a in crystalline groundwater – SCHENK, 1988). For the canister surface area of 6 m^2, a value of 5 µm/a corresponds to a gas production rate of ≈4 moles /year. The quartz sand layer would have a pore volume of ≈0.3 m^3 (50% porosity) which gives rise to a pressure build-up rate of ≈0.3 bar/year. Assuming no hydrogen losses, the time required to build-up a gas pressure equal to the swelling pressure in bentonite would be ≈10^3 years. As has been clearly shown by WALTON and SAGAR (1988), however, the corrosion rate decreases with build-up of hydrogen pressure and a pessimistic maximum rate of 1 µm/year is presented for 100 bar H_2 overpressure (pH = 8.5). As the H_2 "bubble" in the quartz sand will also exclude water, actual corrosion rates may be much lower. With a pressure of 100 bars, the rate of loss of H_2 by diffusion in solution would be ≈0.3 moles/year – a factor of 2-3 less than the possible production rate above. At such a pressure, however, advective gas flow can occur (PUSCH and FORSBERG, 1983) which, for a constant pressure of 100 bars, could remove >20 moles H_2/ year. Gas flow will thus be the main factor limiting the internal H_2 pressure reached.

Although several competing processes occur, it seems reasonable to assume that a H_2 bubble with pressures in the range of 50-100 bars will build-up around the canister and, during this period, corrosion rates will be ≈5 µm/a or less. The 5 cm corrosion allowance should thus last for at least 10^4 years.

Even after the canister fails mechanically, ≈20 cm of unreacted Fe will remain around the waste. Even a point failure would be quite sufficient to equalise pressures inside the canister and there is no reason to expect that such failure would be more than a single crack. If the failure of the outer canister did not mechanically destroy the inner steel fabrication container this, being more noble, would not corrode significantly until the mass of iron was corroded – requiring ≈5×10^4 - 10^5 years. During this period, in any case, the canister would be expected to be in a hydrogen gas envelope. Even if the fabrication canister was destroyed, therefore, there is no reason to expect significant loss from the glass matrix of any but gaseous/volatile nuclides would occur (which have, in any case, neglegible concentrations in vitrified waste).

Eventually, however, H_2 production rates will drop to the point that diffusive transport in solution will prevent build-up of a hydrogen gas phase and the canister corrosion products will saturate. As the products of oxidation have a significantly lower density than the original Fe, these oxides/oxyhydroxides would be expected to swell against the sand/bentonite and also seal any fractures/holes caused by the mechanical failure of the canister.

2.4 Waste leaching

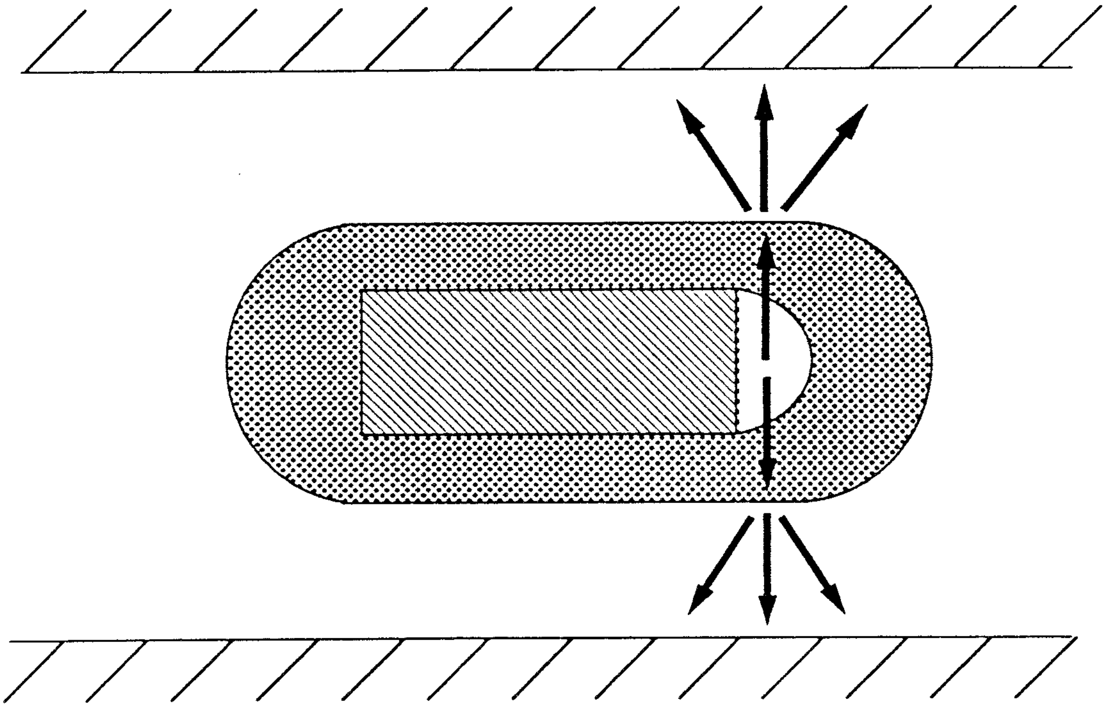
The thin walled fabrication canister may fail mechanically at the same time as the overpack (≈10^4 years) or, by corrosion, after the canister corrosion is effectively complete (≈5×10^4 years, say). In either case, leaching of the glass matrix would only occur when liquid water builds up within the canister (5×10^4 years). At this time, the fractured glass block will be surrounded by a 25 cm thick mass of compacted iron corrosion products. When water contacts the overpack surface, some loss of Fe could occur by diffusion but, even neglecting the fact that such water would probably be already iron saturated, it can readily be shown that, under the mildly alkaline conditions expected (c.f. section 3), Fe removal will be negligible over ≈10^6 years (McKINLEY, 1985).

Waste leaching experiments are inevitably carried out over short periods of time and at high water to glass ratios and often high temperatures. Within the failed canister, water will be present only in fine pores and fractures, which may be partially filled by iron corrosion products, and at repository ambient temperature.

Even though glass is thermodynamically unstable, leaching studies show that corrosion rates are dependant on the concentration of dissolved silica in solution and are minimised at a hypothetical "saturation" concentration (e.g. GRAUER, 1983, 1985). Depending on the extent to which bentonite may penetrate the failed canister, the silica concentration in the overpack "void" space might be set by amorphous silica saturation, quartz saturation or saturation by Fe silicate phases. Although such levels may encourage corrosion at any "exposed" glass surfaces – these would be expected to be limited and, in most of the glass block, silica levels would be set by the rate of diffusive solute transport. In the absence of a sink for Si (e.g. Fe Silicate formed from in-diffusing Fe (II)), "saturation" levels would be quickly reached. If in-diffusion of Fe did occur, a short-term increase in leach rates would probably be compensated by long-term decrease in leaching due to Fe silicate precipitation blocking connected pores.

The overall picture is thus that, at "free-surfaces", the glass corrosion rate may be enhanced by low silica concentrations but the mass of the block mass would sit in a stagnant system in which corrosion rates would be minimal. Even though derived from relatively short-term studies, the PG'85 corrosion rate of 10^{-6} kg m^{-2} day^{-1}

POINT FAILURE OF A CANISTER



GENERAL FAILURE OF A CANISTER

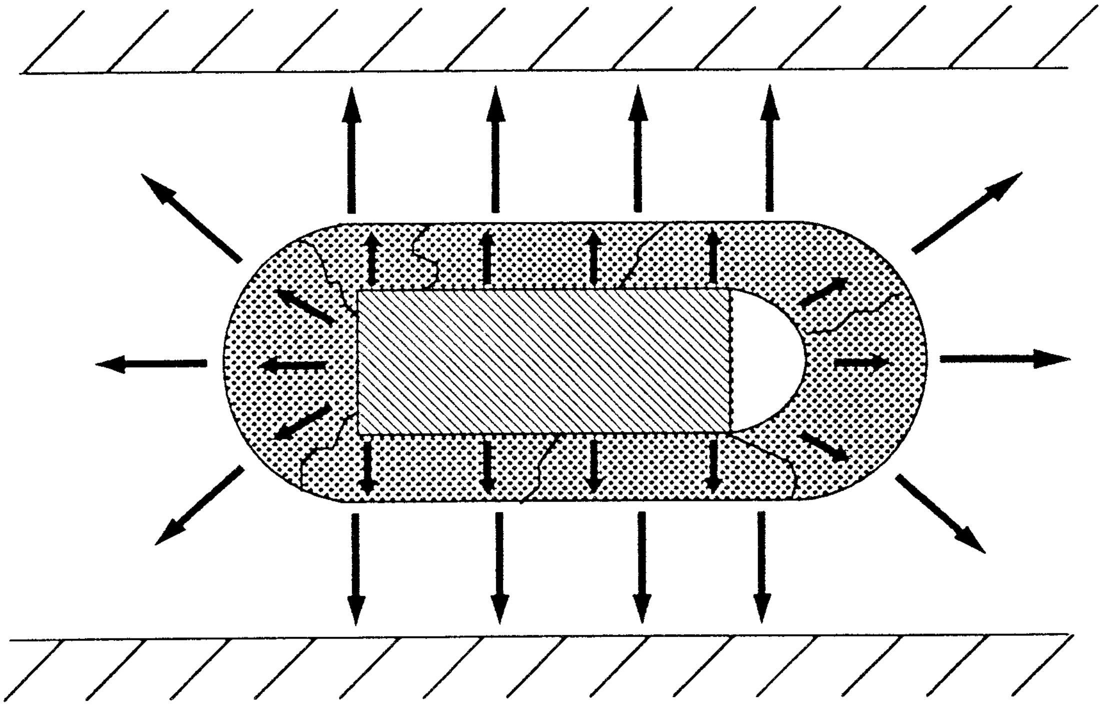


Figure 3: Canister failure scenarios

might be reasonable at exposed surfaces, but an average of 10^{-7} kg m^{-1} or less might be more reasonable for the block as a whole.

The corrosion rate is simply a measure of the rate at which the glass matrix degrades, the extent to which nuclides contained in the glass are free to migrate is very dependant on the extent to which they are incorporated into new phases (or, indeed, are released in a particulate or colloidal phase).

In the PG'85 base case, this constraint was addressed by considering limiting solubilities in "undisturbed" groundwater. Even then, the solubilities were evaluated by use of a very limited thermodynamic database – in most cases considering only oxides and hydroxides of the nuclides as potential limiting solids.

Glass leaching experiments under static conditions have shown the formation of secondary products on corroding surfaces and, at higher temperatures, some pure minerals have been identified (e.g. LUTZE, 1988). At the expected temperatures, the rate of formation of pure minerals may be very slow but amorphous or cryptocrystalline phases would be expected. In such a case, solubilities would not be set by pure oxides/ hydroxides but rather by solid solutions in/co-precipitates with fairly amorphous oxyhydroxides (probably Fe rich) and silicates. This would result in lower (and possibly much lower) solution phase concentrations.

2.5 Radionuclide release and transport

Radionuclide release is very dependent on the results of the mechanical failure of the overpack and its physical evolution thereafter. Two extreme cases could be a) dramatic failure at a single site, b) general failure throughout. These are illustrated diagramatically in Figure 3.

In the former case, the geometry of the diffusive path greatly limits release while the extent of interaction with the corroded canister is minimised. The latter has, vice versa, more extensive diffusion but more interaction with corrosion products (see the paper by Neretnieks, these proceedings, for more discussion of transport limitations).

Once the release from the canister has been specified, diffusion through the bentonite can be readily evaluated when the internal and external boundary conditions have been specified.

Diffusion through both the canister corrosion products and the compacted bentonite will be retarded by sorption processes. The microporous structure of the bentonite will also ensure that no significant colloidal transport occurs (McKINLEY, 1985). Fe oxyhydroxides are very efficient scavengers of trace elements by both sorption and uptake into the mineral latice (co-precipitation or solid solution). The description of sorption in a microporous medium like bentonite is somewhat controversial but, in any case the transport of most species is observed to be strongly retarded in this medium (McKINLEY and HADERMANN, 1984). The rate of transport through the thick bentonite annulus is so slow that many nuclides will decay into insignificance during this period.

3 CHEMICAL EVOLUTION OF PORE WATER IN THE NEAR-FIELD

3.1 Groundwater chemistry and advective fluxes

The pore water chemistry in the near-field is influenced by two main external boundary conditions – the groundwater chemistry in the surrounding rock and the groundwater flow system around the emplacement tunnels. The regional groundwater flow and water chemistry is the result of a major hydraulic system stretching from the Alps to the Rhine. The isolation provided by the great depth of emplacement ensures that the water flux and chemistry currently measured should be stable for periods $\approx 10^6$ years or more. The detailed flow distribution in the near-field will depend on the damage caused by excavation and the extent to which such damage "heals" with time. Two extreme cases which could be considered are the excavation causing an increase in hydraulic conductivity by 2 orders of magnitude (i.e. to 10^{-10} m s^{-1}) in a zone extending 1 tunnel radius into the host-rock and an alternative in which no significant excavation damage occurs (Figure 2).

The water chemistry in the undisturbed host-rock is given in Table 2. It is assumed that any chemical disturbance caused by excavation will be minor – during the repository operational phase the open tunnels will tend to drain the surrounding rock and hence, with a net flow towards the tunnels, chemical contamination by the penetration of air, drilling fluids etc. into the rock are expected to be minimal.

Table 2: Crystalline reference groundwater (derived from NAGRA, 1985)

Temperature (°C)	55
pH	6.8
pe	-2.5 (±1.5)
Major dissolved species (M)	
Na	1.8×10^{-1}
K	1.2×10^{-3}
Mg	1.1×10^{-4}
Ca	2.2×10^{-2}
Sr	2.4×10^{-4}
Cl	1.9×10^{-1}
SO_4	1.6×10^{-2}
[Fe]	8.0×10^{-6}
[C*]	2.0×10^{-6}
[Si]	2.7×10^{-4}

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* total carbonate system

During resaturation there is a net flow of groundwater into the bentonite. Thereafter, solute transport is predominantly by diffusion although, during the period of canister corrosion, a small net inflow will occur to balance water consumed in corrosion reactions – a maximum of 0.07 l/year. When averaged over the bentonite around a canister, such a flux would correspond to an inflowing water velocity of $\approx 3\times10^{-6}$ m/year at the tunnel wall – a velocity which is low when compared to rates of solute transport molecular diffusion.

3.2 Interaction of groundwater with bentonite

Two main types of interaction between inflowing groundwater and the compacted bentonite can be identified. The first set of fast processes involve $Ca^{2}+$ for Na^{+} ion-exchange with associated calcite dissolution. The major net consequence of this interaction is to increase the pH, values up to ≈10 being possible (c.f. WANNER, 1986). On a somewhat longer timescale, mineralogical alteration of the bentonite will occur. This will tend to buffer the pH, empirical values of pH in the "mildly alkaline" (i.e. pH ≈9; JOHNSTON and MILLER, 1984) range are commonly reported for waters equilibrated with bentonite.

Rigorous chemical thermodynamic modelling of bentonite/water interaction is limited both by the very slow kinetics of reaction at temperatures <100°C, the difficulties in defining the activity of water in such a microporous environment and the lack of data for mixed layer clays/solid solutions which may be important solid phases in this system. Nevertheless, pore waters with mildly alkaline pH and an ionic strength similar to the original groundwater may be expected.

3.3 Interaction of bentonite pore water with the canister

The main effect of the corroding canister will be to buffer the redox conditions in this system. The presence of such a vast quantity of steel will initially ensure very reducing conditions – characterised by the presence of hydrogen gas. After all accessible Fe (0) has been oxidised, Fe (II) minerals will continue to act as redox buffers. In the presence of water vapour in the hydrogen gas envelope, the main Fe minerals formed will be oxyhydroxides but, when liquid water is present, silicates and carbonates may also form. All such minerals will have a lower density than the original steel canister, and hence there will be a tendency to swell and fill any available void space.

The solubility of Fe is relatively low under alkaline conditions (10^{-5} - 10^{-6} M at pH 9-10) but some diffusion into the bentonite would be expected with associated formation of Fe rich clays. Both the formation of iron rich clays and buffering by ferrous oxyhydroxides will tend to slightly reduce pH - values in the range 8.5 - 9.5 being reasonable for this region.

Fe minerals in general, and amorphous oxyhydroxides in particular, tend to be efficient scavangers of many trace elements which will considerably reduce their concentrations in the vicinity of the corroding canister (c.f. further discussion in the following sections).

3.4 Pore water chemistry within the canister

Although initially, a void space of ≈30 litres will exist within the canister, this will tend to decrease with time due to mechanical compaction and filling with lower density products of both canister and glass corrosion. The chemistry of water in this region will be similar to that in contact with the outside of the canister modified by the products of glass leaching. Corrosion of borosilicate glasses tends to buffer pH in the range of 9-10 (LUTZE, 1988) and leads to relatively high concentrations of Si and Na (≈10^{-2} - 10^{-1} g/l) within short periods of time (JSS, 1986). Unfortunately, very few data are available for relevant temperatures and timescales (>1 year). In long-term experiments, especially at higher temperatures (>100°C), the formation of secondary minerals on the corroding glass surface is evident with associated lowering of solution phase concentrations. In shorter term experiments, significant colloid formation may be observed (e.g. LEE and CLARK, 1986).

In determining the chemistry around the corroding glass, one further process which has to be taken into account is radiolysis. Due to shielding by the canister (and the absence of liquid water during the period of greatest activity), only α-radiolysis within the canister needs to be taken into account (McKINLEY, 1985). Radiolysis of water can, pessimistically, be assumed to produce an active oxidant (represented as H_2O_2) and an equivalent amount of inert reductant (H_2). It can readily be shown that the redox buffer capacity of the canister corrosion products is quite sufficient to compensate for any oxidant produced but, due to the relatively low solubility of Fe (II), considerable redox gradients may exist in the pore water within the leaching glass – internal zones being fairly oxidising while reducing conditions are maintained at the internal canister surface.

Currently, it is not possible to rigorously model the pore water composition within the glass block but alkaline conditions, redox gradients (most oxidising in the centre, fairly reducing at the canister) and silica saturation (limited by amorphous silica, Fe silicates or secondary aluminosilicate phases) can be expected.

4 QUANTIFICATION OF RELEASE AND TRANSPORT

4.1 The source term for the glass

The most important characteristics of the near-field constraining the corrosion rate of the borosilicate glass matrix are the very low water content and the limitations of transport of solute reactants/products. Even if the matrix degrades at a rate of 10^{-7} kg m^{-2} day^{-1}, the release rate of contained radionuclides will be limited by their transport through the material of the corroding glass block with associated sorption and incorporation into secondary phases. This latter process is particularly important as it may result in effective immobilisation of the elements involved. A conservative approach is to consider only the solubility of pure solid phases (i.e. not considering solid solutions/co-precipitates) but sharing elemental solubilities between all isotopes present. Even then, there are only 3 radionuclides which could be released from the glass at rates >10 Bq/a - Se-79, Tc-99 and Cs-135 (c.f. Table 3). All other radionuclides would be released at rates <10 Bq/a.

Table 3: Maximum release rates from the glass

Rate (Bq/a)	Solubility limited	Matrix release limited
1-10	Np-237, Pu-242	I-129
$10-10^2$	Se-79	-
10^2-10^3	Tc-99	-
10^3-10^4	-	Cs-135

4.2 Transport through the near field

Solute transport through the near field will occur predominantly by diffusion which will further limit the releases of radionuclides. The distance between the glass surface and the nearest advecting groundwater will vary with canister location relative to major shear zones and the near-field hydrology (Figure 2) and canister failure mechanisms (Figure 3). In any case, there will be a minimum of a 1 m annulus of compacted bentonite which, for strongly interacting nuclides (e.g. actinides such as Pu-242) will ensure that concentrations are reduced to negligible levels due to radioactive decay during transit. If the full three-dimensional geometry of the disposal system is taken into account, significant decay of even very long lived nuclides (e.g. Np-237, Tc-99, Cs-135) would occur during transit from all but the containers nearest to the major shear zones (≈5 % of all containers).

In the case of point failure of the canister (Figure 3a), releases would be further constrained by the geometry of the system. For general failure, the sorption by the canister corrosion products could be taken into account. The latter is particularly important as iron oxyhydroxides scavenge many trace elements with very high efficiency and uptake is often effectively irreversible. To put the situation in context: the total release of radionuclides from the glass corresponds to only $\approx 10^{-4}$ moles/year of trace elements which can be compared with $>10^{5}$ moles of canister corrosion products.

4.3 The significance of releases

In the base case considered, no releases from the canister occur for $\approx 5 \times 10^{4}$ years and, thereafter, only a few nuclides could be released from the glass in significant quantities.

The first important nuclide to break through to the advective flow in the far field will be Se-79 which, as an anion, will exhibit minimum retardation during transport. The transit time involved $<\approx 10^{4}$years is short relative to the half-life of this nuclide and hence the far-field releases could approach those set by the solubility limit (≈40 Bq/canister/year). The releases would, however, decrease with the half-life of Se-79 (in line with its decreasing contribution to the total elemental Se pool) and thus would be <10 Bq/canister/year after $\approx 2 \times 10^{5}$ years.

The release of Cs-135 would be delayed by its greater retention although this would be offset, to some extent, by the large concentration gradients possible as its near-field solubility is predicted to be rather high (n.b. Cs-bearing secondary minerals are not taken into account). Depending on the geometry of the transport path considered, the time taken for steady state releases to increase to the level of the releases from the glass matrix would be $\approx 10^{5}$-10^{6} years. At such a time, the release rate would be $\approx 10^{4}$ Bq/canister/year. The breakthrough time for Tc-99 would be of a similar order of magnitude but, as Tc is solubility limited with a shorter half-life, the release rate of this element will not exceed ≈100 Bq/year. The releases of all other radionuclides will be trivial by comparison.

The releases are thus dominated by Cs-135 and could give rise to a maximum concentration of $\approx 5 \times 10^{4}$ Bq/l in the water of the near field. The total flux of contaminated water is, however, only ≈1 m^{3} $year^{-1}$. Input of this water to even a minor aquifer would cause dilution by a factor of $\approx 10^{5}$ and, for the case of outflow into a major surface water body, a total dilution by a factor of $\approx 10^{9}$ would be expected. The concentration in accessible water is thus <≈Bq/l (possibly <1 mBq/l) and is thus comparable or less than with the concentration of natural radionuclides. In fact, Cs sorbs relatively strongly on most rocks and further decreases in concentration due to the processes of decay and temporal dilution are to be expected. Calculated breakthrough times for a 500 m flow path through crystalline rock are generally $\approx 10^{7}$ years with resultant decreases in peak concentration of >≈4 orders of magnitude depending on the assumptions involved (Jakob et al., 1990). Further, Cs-135 (as with Tc-99 and

Se-79) is a weak ß-emitter which has a very low radiotoxicity in comparison with natural radionuclides such as Ra-226 (about 3 orders of magnitude lower dose conversion factor).

5 POSSIBLE PERTURBATIONS OF THE BASE CASE

In the base case scenario previously described, no significant releases occur to the far-field within the first 10^6 years. A number of possible perturbations of the base case scenario could, however, potentially decrease performance. In a rather crude manner, these can be classified as physical or chemical perturbations.

5.1 Physical perturbations

The most dramatic physical perturbations conceivable would involve catastrophic geological events (e.g. massive earthquakes, vulcanism, meteorite impact etc.). Site selection insures that these are unlikely and it can readily be shown that the non-radiological consequences of vulcanism or meteorite impact scenarios would render any effects of nuclide releases negligible by comparison.

Although earthquakes would be expected to have minimal direct input on a backfilled repository, movement along fracture zones could cause direct physical damage to the engineered barriers and large water flow patterns. A crystalline host-rock has the great advantage that major shear zones are easily identified and would be avoided during emplacement. Major movements (>1 m, say) would be expected to occur in such zones as they are, inherently, much weaker then the surrounding rock. Smaller movements (<1 m) could occur at smaller fracture zones but their direct effects would be minimised by the presence of the plastic clay backfill. In any case, even if the physical barriers were somewhat disrupted, the geochemical barriers limiting nuclide release would remain.

Altered groundwater flow patterns may also occur as the result of such movements. The overall flux through the repository would not, however, be expected to change much as it is defined by larger scale rock properties. In general, radionuclide releases are fairly insensitive to the flow outside the bentonite and, even if there was a slight increase at one location, it will probably be balanced by a reduction elsewhere thus ensuring little change in the total releases from the repository.

A further physical perturbation would be caused by canister sinking. Calculated sinking rates are very low ($\approx$mm/10^6 years: PUSCH, 1983) and, even if rates a couple of order of magnitude higher occured, the effect on releases would be minimal the sinking rate being not much faster than the rate of nuclide migration.

5.2 Chemical perturbations

The previous analysis assumes that the groundwater chemistry remains constant and tacitly assumes that the effects of "complicating factors" such as colloids, organic compounds and microbes can be ignored.

The near-field chemistry is so strongly buffered by the engineered barriers that small changes in groundwater composition have no effect on releases. Major changes in water chemistry are precluded by the buffering effect of the host-rock.

The effect of colloids formed within the near field can only improve performance as long as transport through the bentonite backfill is negligible. Evidence for this comes both from experimental measurements and theoretical studies of bentonite pore structure (McKINLEY, 1990). The concentrations of low molecular weight (MW) organics in crystalline groundwaters is negligible – higher MW organics may be present but, as colloids, would not be mobile in the bentonite. Although the near-field cannot be assured to be sterile, microbial activity is limited to negligibly low levels by constraints set by available energy and nutrient sources (McKINLEY et al. 1985).

6 JUSTIFICATION OF EXTRAPOLATIONS

The preceeding sections predict high performance of the near-field over very long periods of time. Given that the experimental database is limited to periods of a few years, at most, and the mechanistic models have inherent uncertainties, how can such predictions be justified? The evidence here comes predominantly from the study of natural analogues.

The use of natural analogues to justify particular models of material properties has been discussed in detail elsewhere (McKINLEY, 1989; PETIT, 1990). This section, however, considers the overall performance of the near-field in a more holistic manner.

Basically, the near-field as specified consists of a high trace-element anomaly within an iron oxyhydroxide zone which is enclosed in a low permeability, plastic clay. The entire system lies in a low flow environment. Similar geochemical conditions exist in a number of locations. On the large scale, the uranium ore body at Cigar Lake (CRAMER et al., 1987) has some similarity to this near-field and represents a case where releases have been very low (or negligible) over a period of very many millions of years. It may also be noted that the Cigar Lake ore body contains relatively high concentrations of dissolved organics, colloids and microbes and, as predicted in section 5, these do not appear to cause any enhanced release of trace elements.

Although on a much smaller scale, the redox haloes found in Swiss Permian sediments also have some characteristics reminiscent of the near-field (HOFMANN, 1990). A central reducing core causes the build-up of a sheath of reduced iron minerals which are associated with very high concentrations of a range of relevant trace elements (U, Th, Pb, Pd, Sn, etc.). Here, the reducing conditions (which may be maintained by microbial activity) and the Fe minerals present actually scavenge trace elements from the surrounding environment. Such a process also occurs at redox front ore deposits. Extensive work in Poços de Caldas project has shown very effective scavanging of a wide range of trace elements by both reduced and oxidised Fe minerals (MacKENZIE et al., 1990; BRUNO et al., 1980). Trace element modelling has shown that, for many cases, such co-precipitates (or solid solutions) greatly reduce trace element concentrations in solution. This study has also shown that, although a range of natural colloids may greatly concentrate particular trace elements, they are not mobile and hence improve overall performance.

In general, therefore, the evidence from natural systems is not only that the predicted performance of the near-field is reasonable but also that, in real life, such an environment may act as a trace element trap
– actually reducing the concentration of radioelements naturally present in the groundwater!

7 CONCLUSIONS

Even the "realistic" base case scenarios used to define the source term for repository performance assessment tend to be very conservative in terms of both parameter choice and ignoring processes which would have only positive effects. Using the particular example of a Swiss HLW disposal concept, it is demonstrated that no significant releases of radionuclides are to be expected over a period $>10^6$ years (the limit at which quantitative analyses have any kind of meaning). As performance is ensured predominantly by the geochemical buffering by massive engineered barriers and the well-established hydraulic properties of the thick bentonite backfill, it is relatively insensitive to changes in the surrounding geological environment.

The analysis above was intended only to demonstrate how a realistic, integral treatment can be used to illustrate the great degree of conservatism introduced into the current generation of near-field performance assessment models. This could be formalised as a more rigorous mathematical model which could be used for sensitivity analysis – determining the realistically expected impact of alteration of the performance (or design) of one or more barriers. Such a model would also provide an essential reference point for any future intercomparison or benchmarking of near-field codes.

In order to demonstrate the multi-barrier concept for nuclear waste disposal, it is important to illustrate how retardation, dilution, dispersion and decay in the geosphere and biosphere could function in the event that any near-field releases occurred. The source terms used for such analysis should, however, be carefully distinguished from expected releases – which are too low for any further calculation to be meaningful.

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DISCUSSION ON INTEGRATED NEAR-FIELD ASSESSMENT

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The discussion about Dr McKinleys presentation on "integrated nearfield assessment" focused on three different areas:

1. "Technical" observations about the presented evaluations of the nearfield corresponding to the crystalline host rock for a repository studied in Switzerland.
2. Interest in using a 3D nearfield modelling instead, for instance, of the 1D "electric analog" presented just before by Prof. Neretnieks. Such a 3D modelling fits better the reality and in that satisfies the main preoccupation of Dr McKinley : to describe what will be and not what happens in our mind. However, according in particulary to computer time consumption, one must restrict, in the realization of the model, to what is really necessary just for representing the mainpoints in order to reach a satisfactory order of magnitude of the results. Presence, among the radionuclides giving way to relatively consequent release, of I-129: is due to the quantity of this radionuclide present in the waste inventory taken from COGEMA used by NAGRA: the amount of I-129 indicated in the inventory might be overestimated.
3. Observations about the role in a global safety assessment of the presented evaluation: Some additional arguments seem to be needed for being really convinced that the kind of hypothesis made for claiming that no significant release should occur from the nearfield (and that, in consequence even with a "not too excellent"geosphere the risk should be limited) should be valid during the huge period of time ($>10^6$ y) taken into account. For instance, in France, in addition of what is done for the nearfield, a very strong effort is realized for being able to select a really good geosphere, where properties may be easier (according to what has been done in the field of natural analogues) to guarantee for a so long period of time.
   On the other hand, presented nearfield performance assessment could also play an important role in a global safety assessment: not only for the normal evolution scenario consequence assessment, but also for the treatment of altered scenarios (geosphere faults, human intrusion...); in these cases, the presented evaluation could have a quite efficient "protective" function.

For what regards the possibility of using this kind of evaluations for the case of non-crystalline host rocks, we may consider that such an approach seems possible for clay and even for tuff formations, but seems rather difficult for salt formations, according in particular to the absence radiological consequenses corresponding, in the that case, to the normal evolution scenario: the nearfield could be quite "altered" in almost each scenario studied in the salt case.

The two preceding items led us to more "philosophic" comments about the intent of the modelling approach for a really convincing safety demonstration.We must keep in mind that the pressure (safety authorities,political decision makers) is quite high and has led to regulatory requirements which are quite beyond what is asked for other non-nuclear industries.

For fitting these requirements, a really rigorous safety approach has to be followed and we have to be sure that:

* On one hand, we are not going to complicate the assessment by considering points which are not really of importance.

* On the other hand, what is really important for us has been effectively taken into account

Our task should now be taking into account these two considerations in performing the coming nearfield assessments as a part of the global performance (safety) assessment. According to the evident difficulty of convincing people by considerations concerning so huge periods of time (10^6years), only a strong methodological framework (taking into account the time cutoff problem) may be able to provide us with a satisfactory convincing power.

SENSITIVITY ANALYSIS AND VALIDATION

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ABSTRACT

In the field of performance assessment modelling for high-level radioactive waste disposal in geologic repositories, evaluating model uncertainties is a key factor in estimating of radionuclide transport rate and extrapolating thousands of years into the future. Sensitivity and uncertainty analysis is performed to determine the relationships among the input and output variables of a mathematical model through numerical methods. Because post-closure performance assessment relies heavily on models, sensitivity and uncertainty analyses will become an integral part of the model evaluation and validation process.

Model validation is also needed to establish the credibility of predictions to the technical community, and to achieve greater public confidence in the long-term safety of a geologic repository. In this paper, the role of sensitivity analysis as a part of near-field performance assessment will be discussed in terms of model validation. A description of the ENTRY (the Engineered Scale Test and Research Facility) project for validation study will also be presented.

1. INTRODUCTION

Safety assessment is performed through the analysis of future behaviour of the overall waste disposal system and of its potential impacts on humans and the environment, followed by comparison of the results with appropriate safety standards. Because such analysis should be carried out for over timescales far beyond the normal horizon of social and technical planning, it is clearly understood that safety assessment require effective use of predictive modelling methods and a wide range of scientific information that describes the disposal system and its possible evolution. Therefore, building confidence in the results predicted by the models applied for safety assessment is a critical issue.

Uncertainty and sensitivity analyses, and validation, which are elements in the general approach to safety assessment, are conducted to build confidence.

Uncertainties are always associated with assessment results and never eliminated because of spacial variability in natural system and time scale in the assessment, even though they could be partly reduced by further model development and data acquisition. Uncertainties associated with assessment results can be treated quantitatively through uncertainty analysis and then reliability of the results is clarified.

Confidence is also built through validation process of predictive models used in the assessments. Validation process requires a systematic evaluation of modelling results against data from experiments in laboratories and in the field, as well as against data from studies of representative natural analogues.

Prior to uncertainty analysis and validation, sensitivity analysis is done in order to identify phenomena which are important to model prediction. Uncertainty analysis and validation study could be conducted in more effective and systematic way by using the information derived from sensitivity analysis.

Model validation should be performed under the close linkage between model development and well defined experiments, otherwise the issues to be validated are not defined clearly. In order to realise such appropriate condition for effective validation, development of the computer-oriented system for managing model hierarchy on the whole will be needed in which all of processes relevant to performance assessment could be considered. Sensitivity analysis will be done through developmental phases of the system integration model based on the model hierarchy.

A comprehensive plan for experimental study will also need to be introduced to carry out validation corresponding to the issues which are identified through sensitivity analysis. ENTRY project is being carried out by Power Reactor and Nuclear Fuel Development Corporation (PNC) for the purpose of such experimental study.

Both development of the computer-oriented system and ENTRY project are the central part in the multi-year program of PNC, which is designed to integrate the research and development activities with generic performance assessment studies.

2. MODEL HIERARCHY FOR PERFORMANCE ASSESSMENT

2.1 Model Hierarchy

The necessity of using predictive models to assess potential radiological consequences in safety assessments is well recognised, and the general procedures for development of models are well accepted (McCombie et al. 1989). There are models available, at different levels of detail and realism, to evaluate and quantify the effects of the key processes determining the performance of radioactive waste disposal systems and these models tend to be of two complementary types: detailed research models and simplified system models.

The detailed research models and their results are needed to assure that we can appropriately model the reality of actual system, and are used to provide a defensible basis for excluding processes not important to safety in the simplified modelling. These models generally contain detailed models of selected physico-chemical processes and retain a high degree of geometric detail. They are useful for detailed studies of the response of repository components and subsystems, such as the waste package; however, they cannot simulate the response of the total repository system because disparate size scales and the number and complexity of physical processes results in impractical long computational time, even for the fastest computer.

On the other hand, the simplified system models which are used for safety assessment are needed to assure that the assessment is comprehensive for future behaviour of disposal system. The total system models, approximate the response of major repository subsystems. These models achieve practical computational times by sacrificing detailed geometric and process modelling. Accurate system-level modelling must therefore depend upon reliable approximations for repository components and subsystems. These approximations will be based on a large base of information from performance assessment calculations, laboratory experiments, and in-situ experiments. In the bounding approach using simplified system model, scenarios, models, and parameter values are chosen conservatively as usual way in compensation for loss of reality.

Detailed research model and simplified system model become an element of model hierarchy for performance assessment as shown in Figure 1.

Confidence in the performance assessment of the repository system is totally reliant on the confidence in the calculational tools. Because of the time and space scale of the system it is not possible to perform real-time and real-scale proof tests. The confidence in the calculations is then completely dependent on the demonstrated integrity and control of the calculational methods. The system integration model (a calculational system) must be developed with such integrity and control in order to manage hierarchy of models on the whole. Both verification and validation are designed to build confidence in the course of development of the system integration model.

Verification is usually a straightforward process, while validation is very difficult because of the long time scales and because of the complexity of the geologic environment.

2.2 The System Integration Model

Currently, large improvements toward more realism and detail have been made and further development is still needed in some areas because better modelling could clarify or reduce uncertainties associated with assessment results. In recent years, special attention has been paid to the interdependence between model development and corresponding data gathering efforts. In addition, a main area of ongoing work is the coupling of models for specific processes into larger integrated models and the simplifications needed to make them practical tools for safety assessments.

This circumstance requires development of integrated computer programs (also called codes), but it is difficult because of the large number of complex physico-chemical processes that may be important in a geologic disposal system. In addition, accurate prediction of repository response over very long periods of time and in the inhomogeneous geologic environment is a very challenging task, requiring extensive verification and validation of the computer programs.

Conceptual Approach to Development of the System Integration Model

From a geometric point of view, it is very difficult to simulate the fine details of a waste package, with a size scale of 1 meter, in a regional model with a size scale of 100 km. In fact, the computational cell in the regional model usually spans hundreds of waste packages in order to be practical and efficient. It is therefore necessary to use separate models, each of which can capture the appropriate level of geometric detail for the specific analysis and size scale of interest.

A conceptual approach to integrate large research codes into useful computational tools is structured, around size scales: for example, regional, repository, mined facility, and waste package. The different size scale are useful because they allow a very large and complex computational problem to be broken into simpler pieces. These simplification occur on several levels: geometric, process, coupling, and computational sequence.

A similar simplification is also possible for processes. For example. processes that are important at the waste package scale may be unimportant for the mined facility, repository, or regional scale, and so on. In addition, gradients and coupling are strongest near the waste package, and decrease as the size scale of the model increases. These facts mean that the model for each size scale is generally simpler than a model used to simulate the total system simultaneously. The size scales are therefore used as a framework to identify and list the important phenomena for the repository. These processes can be classified into several types, thermal, mechanical, hydrological, geochemical, and so on.

Coupling is also simplified by the size scales because process coupling can usually be described within a given size scale, rather than across size scale. Again, the size scales and the process hierarchy serve as a framework for describing coupled phenomena.

Finally, from the point of view of computational sequence, the size scale streamline the performance assessment for the total repository system because the various size scale couple primarily through boundary conditions.

Developmental phases of the System Integration Model

The implementation of the system integration approach must deal with all the process as they exist in the schematic hierarchy, coupling of these processes, and means to maintain the quality and integrity of the system models including code configuration control, preservation and documentation of parametric calculations, and verification and validation.

The integrated systems approach includes iterative process of simplified modelling, detail modelling, and system integration modelling.

The primary focus of simplified modelling will be the development of conceptual models. The effort will focus on learning the relative importance of the principal processes and comparing different methods of representing and coupling them. The verification efforts will begin to build up a background of confidence with these simpler combinations of models. Such simple models can be used for better understanding of the general behaviour of disposal system under a variety of scenarios.

The more prominent coupled processes are modeled in many existing codes. For example, thermal-mechanical rock response, flow and equilibrium physical adsorption, and thermal-chemical interaction for elementary relationship such as solubility of single species are simulated by several state-of-the-art computer codes. Coupling within a particular scale (such as the waste package) is done in existing codes such as Analytical Repository Source-Term code, PNC version (AREST-PNC) (Liebetrau et al. 1989).

As more is learned from laboratory and field investigations and more experience is gained with the simpler calculations, then more second order types of processes and process couplings will be studied in order to provide complete understanding of the role of all possible processes in the total system performance. The main objective of this phase will be to obtain sufficient understanding and data to be able to reduce the total system response to a more simplified model which reflects the important processes and their function. This provides the basis for system integration model development.

Each of the large codes used during the research period will need to be independently verified through the use of expert review, comparison to analytical solutions and code to code comparison (benchmarking). In addition, the research codes must be validated (i.e. compared to measurements in the laboratory, large scale tests or in-situ tests). Many codes currently in use have some degree of verification and a few have been partially validated. This is useful but it must be recognised that modifications to such codes require a certain degree of revalidation and reverification. It is also true that the current state of verification and validation of existing codes is usually not complete enough for confidence in performance assessment calculations.

The final stage of model development is the system integration model. The degree of complexity of this model becomes very small compared to the large engineering codes. This does not mean that the code is simple in the sense that it does not simulate all the necessary processes and couplings. Rather the code is less complex because it only simulates what is essential for representation of the system. This simplification results from what has been learned during the studies with the large research codes. There are several approaches that might be used to develop the final system integration model. These include:

- Simplification of models through sensitivity analysis - Development of response surfaces (data correlation)
- Use of simplifying assumptions("conservative")
- Simplification of models through uncertainty analysis

The experience of all these studies will help to guide which of these techniques will be used to develop the system integration model.

As the system integration model is developed, verification and validation problem is somewhat simplified and changed. If the system integration model consists mainly of response surfaces, the main task will be verification. This approach is valid because if response surfaces are constructed from data generated by validated research codes, it can then be assumed that the response surfaces will be validated if it can be shown that they are faithful representations of the results from the research codes and that any other codes used to fit or manipulate the data are correct. Therefore, what is mainly needed here is data base and code verification to produce an system integration model with full verification and validation.

2.3 Integration for Near-Field Phenomena

Engineered barrier system components in the near-field can be controlled through the design process, while natural components cannot be controlled except through the site selection process. The engineered barrier system, therefore, has some advantages in achieving acceptable confidence and reliability in isolation of radioactive waste (Apted 1989). In terms of model validation, processes expected to occur in the near-field can be more easily characterized than those in the far-field, and the validation process would be done in a more systematic way. This is also important in development of the system integration model. In the R & D program of PNC, emphasis of developing integrated model is mainly placed on near-field phenomena reflecting these features of near-field (Masuda et al. 1990). The AREST-PNC model are under developing for the purpose of integration model in near-field.

The AREST-PNC is a performance assessment model that was developed to assess the overall performance of the Engineered Barrier Subsystem (EBS) within a geologic repository; therefore, concerted efforts were made to incorporate submodels of all the physico-chemical processes that are important to EBS performance. In addition to calculating waste package release, the AREST-PNC code also estimates the time to container failure and integrates release from many containers to estimate the repository source term. The code was also designed with sufficient flexibility to allow incorporation of new process models as they are developed.

The AREST-PNC is based on analytical solutions to the mass transfer of radionuclides within the near-field environment. For system-level analyses, analytical solutions have several advantages, including ease and speed of computation, and provide direct insight into the sensitivity of radionuclide release on key performance parameters. Although these analytical solutions may not always apply to the full range of input data, these limitations may be better understood and more easily avoided than the convergence considerations that must be dealt with in numerical models.

When analytical models are not available for some processes, calculations are performed by using numerical models and the results are provided as input to AREST-PNC. Waste package thermal histories, for example, are computed externally by thermal support codes and the results are input to AREST-PNC in tabular form. Thus, AREST-PNC can be computationally efficient without sacrificing accuracy.

Numerical models designed to solve similar transport problems also have been devised. These models have several advantages which include the treatment of complex geometries, spatial heterogeneities in material properties, a wide array of boundary conditions, coupled processes, and the graphical portrayal of results over time and space. Because of these offsetting (and complementary) advantages, it is important to compare and contrast predictions from the analytical release models in the AREST-

PNC code with calculations from numerical models of mass transport in the near-field.

The advantages of analytical and numerical models for near-field analysis are different yet complementary. Each modelling approach has specific capabilities that are suitable for its intended application. The analytical models provide a computationally efficient method of combining the effects of multiple parameter distributions. Simplified process models also provide a basis for quantifying both the conservative performance of the near-field and the relative uncertainty in that estimate. Numerical models provide a detailed mechanistic understanding of the processes affecting near-field performance, as well as their relative performance (sensitivity). Such detailed solutions can provide much insight into the effects of different materials, different engineered barrier system designs, and various unexpected conditions on the release of contaminants.

Thus, analytical and numerical codes and models must be viewed as part of a spectrum of assessment tools that will form the model hierarchy. The comparison and benchmarking of these codes, is an explicit technique for confirming that these two different yet complementary approaches provide a similar description of near-field release performance.

3. SENSITIVITY ANALYSIS

3.1 The Role of Sensitivity Analysis

In performance assessment, it is important to evaluate uncertainties associated with performance estimates and rank parameters in terms of their effect on the performance measure of interest. As part of integrated safety assessments, sensitivity studies provide guidance on which areas uncertainties most need to be reduced.

Uncertainties arise from the selection and specification of scenarios, the formulation and actual computation of the conceptual and mathematical models, and the quality and appropriateness of input parameters (NEA 1987). The sensitivity of performance to uncertainties in a parameter depends upon the performance measure, the site, the design of the waste package and the repository, and the performance model. Sensitivity and uncertainty analyses are conducted to quantify the relative influence of these parametric uncertainties on the selected system performance measures. Uncertainty analysis refers to the estimation or quantification of the uncertainties in the input variables and propagating these uncertainties through the model to determine the corresponding output distribution together with some assessment of model uncertainty. Sensitivity analysis. on the other hand, refers to the examination of the effects of a change or perturbation in one or more input variables on the output or predicted performance. Sensitivity analyses are traditionally used to identify factors that have a significant effect on performance assessment results, and to guide uncertainty calculations.

However, the main use of sensitivity analysis is to direct research and on the collection of data to those areas that have the most effect on performance(NEA 1987). It is possible to use sensitivity analysis not only to reduce the number of parameters to be considered but also to assess the importance of individual process models to performance. When insensitive parameters are identified, portions of the model using these parameters can be simplified (Umeki et al. 1988).

Because the number of process models involved in near-field performance assessment is large, it may be advantageous to exploit hierarchical structures that exists when performing sensitivity and uncertainty analyses. The AREST-PNC code, for example. is composed of a number of component models involving a number of process models. A strategy was proposed for sensitivity analysis of this complex model using multipletiered modelling hierarchies. This approach requires that significant interactions among the models at any given level are carried on to the next higher level (Liebetrau et al. 1990) .

This proposed analytical strategy is illustrated in Figure 1. At the highest level, sensitivity analysis is concerned with the effect of model output to known changes in inputs from the component models and data at lower levels. At lower levels, the concern is with the effect of variations in the input variables on the process model output variables. In uncertainty analysis, on the other hand, the consequences of measurement errors and unresolved questions about model structure are evaluated in terms of system response.

There are two types of sensitivity analyses; differential and statistical. The features of these sensitivity analysis methods and their application are reviewed elsewhere (Iman et al. 1988, Ross et al. 1989). A number of studies has been done on sensitivity analysis from a methodological point of view. Further experiences with sensitivity analysis are needed for performance assessment in term of its purpose, scope and adaptability. In the following section, some examples are given for illustration of the role of sensitivity analysis in near-field performance assessment.

3.2 Illustrated Examples of Sensitivity Analysis

The sensitivity to variations in input parameters was assessed in terms of release and transport modelling by a sensitivity analysis based on the KBS-3 case (Neretnieks 1989). Firstly, the release of 5 important nuclides, U-238, Tc-99, Np-237, I-129 and Cs-135 was calculated for the central case of safety analysis in KBS-3. Then systematically one parameter at a time was then increased by a factor of 2 and subsequent release from the near-field and from the far-field was calculated. Sensitivity of release was expressed as the ratio of the maximum release for the varied case to the base case as illustrated in Figure 2. It should be noted that fracture spacing is inversely proportional to the flow wetted surface and that the fracture aperture is proportional to the porosity. It is clearly seen that the water flow rate, the transport distance, fracture spacing (wetted surface), effective diffusivity in the rock matrix and the dispersion have large effects on release, where as the fracture aperture in the far-field (water velocity) has no impact. This example well illustrates the utility of sensitivity analysis.

Another example is the preliminary sensitivity analysis performed using the AREST-PNC code (Liebetrau et al. 1990). In this analysis, screening calculations were performed for a limited number of input parameters that were judged to be important for repository performance. For this series of calculations, the selected parameters were varied one at a time from their Base Case values to determine Alternative Bounding Cases, which are obtained by multiplying by an arbitrary factor and by assigning conservative values, respectively. The Alternative and Bounding Cases were then compared with those for the Base Case.

Cumulative releases of radionuclides were calculated over time following containment failure for Tc-99, Np-237, U-238, Pu-239 Am-241, and Am-243. A containment time of 1,000 years following emplacement was assumed. Comparative results are presented for cumulate releases at 10,000 years after initiation of release. The parameters varied in the sensitivity analysis included the solubility of the radionuclide, sorption coefficient of the radionuclide on the backfill and host rock, radius of the waste form thickness of the backfill, precipitation distance (from waste form), tortuosity of the backfill, porosity of the backfill and porosity of the host rock.

The ratios (R) of the 10,000-year cumulative releases for the Bounding Case with those for Base Case releases are shown in Figures 3 and 4. Over the range of bounding values of physical parameters selected for this study, it is shown that radionuclide releases are extremely sensitive to the porosity of the host rock. Release was also shown to be essentially proportional to the change in radionuclide solubility values. This result provides further confirmation of the central role that solubilities play in the assessment of near-field performance.

Release were found to be less sensitive to variations in, backfill thickness and tortuosity. The conclusions of this preliminary sensitivity analyses are 1). the relative sensitivities of these parameters must be examined over a wider range of possible values in order to fully understand their impact on release, 2). it is critical that the selected values for parameters be based on laboratory or field data or, as a last resort derived from a true bounding-value assessment, and 3). it is crucial that the values of key parameters be varied jointly so that the combined effect of these parameters on release can be evaluated.

4. VALIDATION PLAN IN ENTRY PROJECT

With the broad view of model validation, there have been a number of definitions of model validation in the literature. For Example, model validation is defined as the process of assuring that the models used adequately represent the real system behaviour through comparison of the model prediction with independent field observations and experimental measurements (IAEA 1988), and efforts have been done during recent years in this area. Validation of long-term predictions must focus on the adequacy of specific aspects of the modelling may be supported through a variety of laboratory, field, and natural analogue studies. Several international co-operative projects have been established to investigate the possibilities for validation of the models used within safety assessments (Grundfelt 1989; Andersson 1989; Broyd 1989).

Validation issues associated with each step of the modelling process was discussed for both conceptual models and computer codes (Tsang 1989). Tsang concluded that a model should be validated with respect to individual processes and a model or group of models should be validated with respect to a given site. Thus, validation of performance assessment models for a given site involves evaluation of both engineered components and the geologic setting.

ENTRY project aims to systematically conduct those experiments which are closely associated with development of the system integration model from the broad view of validation.

4.1 Overview of ENTRY project

The ENTRY project aims mainly to validate individual process models with well--controlled large-scale tests and to integrate various studies which are part of performance assessment. The study plan of ENTRY is developed as a synthesis of numerical simulation and experiments. It covers broad scope such as;

—development, evaluation of performance assessment models
—collection of non-radiogenic laboratory data

—development of database for performance assessment.

Experiments in ENTRY project provide complementary data to small scale laboratory tests for individual process and in-situ tests by means of observation of interaction between processes and step-wise validation of assumptions which are used to interpret the complex structure of geological environment.

An unique feature of the ENTRY project is to include large-scale and flexible test configuration that enable experiments on coupled processes to be performed. Large-scale testing permit data collection on an integrated system of barrier material components in their proper geometrical arrangement that cannot be achieved in small-scale tests. Furthermore, it can demonstrate complex or unexpected changes of chemical and physical processes affecting the performance of geologic repository between small and large scale. Some stochastic processes, such as localised corrosion of metal, and coupled process in mass transport induced by gradients in temperature, hydraulic head, and concentration could cause these complexities. Therefore, large-scale testing is considered to be a necessary component in overall research and development program for assessing the feasibility of geologic disposal. In ENTRY study plan, several experimental tests will be conducted from small- to large-scale in systematic way.

Those processes that will focused on in the ENTRY project are as follows;

—chemical processes such as speciation, dissolution/precipitation and sorption
—mass transport of species in groundwater
—interactions of these processes

Experiments with respect to these processes will be conducted in order to examine competing chemical reactions and mass transport mechanisms and to develop models for coupled chemical reaction and mass transport. Model development for processes related to some perturbations, such as bentonite erosion, will be also considered as well as those processes related to normal groundwater scenario.

The ENTRY project has been divided into several tasks corresponding to processes focused on in order to cover a scope of performance assessment issues on both near- and far-field as follows;

—Exploratory Data Acquisition System(EDAS)
—Integrated Simulation of Mass Transfer and Geochemistry(IMAGE)
—Coupled hydro-thermo-mechanical processes in near-field
—Bentonite extrusion and erosion
—Hydrogen gas generation and migration
—Laboratory tests of mass transport in heterogeneous rock media - Laboratory tests with fractured rock and geotextiles.

In this paper, the first two tasks. EDAS and IMAGE, are briefly described as examples of validation study for near-field modelling.

4.2 Validation Study for Near-Field Modelling in ENTRY Project

(1) EDAS

EDAS program is a systematic experimental investigation of the closed-system chemical interactions of groundwater with the natural and engineered barrier materials of the near-field. The objectives of EDAS are to identify and characterize the geochemical processes and physical parameters that affect the performance of near-field barrier materials. Geochemical models will be used to design and evaluate EDAS experiments. and the results will be used to derive new information on kinetics and thermodynamics that will be able to be incorporated into such models. EDAS test equipment is designed to conduct an integrated test under anaerobic condition through the series of experimental procedures from the stage of sample preparation to analysis of experimental results.

The issues considered in EDAS are divided into following three test categories:

(a) **Chemical reaction tests.** These tests will be conducted to identify major chemical reactions between groundwater and components of EBS under reducing conditions, which are important to describe mass transport and chemical conditions in the near-field. Thermodynamic data in terms of these chemical reactions will be obtained as chemical equilibrium constant, standard formation energy, mineral dissolution equilibrium constant and ion exchange equilibrium constant in order to further develop reliable database.

(b)Long-term reaction rate tests. These tests aim to measure reaction rates of rather slow processes which could be observed in the interactions between groundwater and components of the EBS. Information from IMAGE-GEOCHEM study (see below) which will investigate the opensystem chemical interactions and mass transport will be useful to focus the processes to be studied in EDAS test.

(c)Basic study on colloid formation. In this study, mechanism of colloid formation will be pursued through identification of type and properties of colloids and measurement of formation constants under reducing conditions. These informations will be used in colloid transport experiments to be carried out in IMAGE-GEOCHEM study.

Tests in EDAS will be performed for both equilibrium and kinetic models. Analytical results of geochemical codes such as PHREEQE and EQ3/6, which calculate speciation and precipitation, will be compared with experimental results so that unknown reactions or errors in modelling of the chemical systems can be identified. Test equipment that has precise atmospheric control capacity will be utilized for this purpose.

First priority will be given to model development for processes which determine pH, Eh and activities of ligands in the vicinity of waste in order to quantify maximum concentration of radioactive elements. Initial tests will consist of mixtures of iron minerals (i.e. corrosion products) and clay minerals that are chemically active and located adjacent to the waste.

Tests of kinetic models will be performed in the same way as described above. However, rate determining processes have to be identified and modelled for this purpose. Accordingly, in-situ measurements or flow through tests should be carried out, while batch type tests are will be used for development of equilibrium models.

Evaluation of colloid formation and transport are included in the future program plans to develop conceptual models for these processes. Numerical codes and/or data bases will also be modified as the program proceeds.

(2) IMAGE

The IMAGE study will be conducted to validate mass transport models and coupled mass transport and geochemical models. Key technical issues in mass transport are mechanistic linkage of diffusion theory and advection/dispersion theory for the boundary between permeable and less permeable regions in heterogeneous systems (IMAGE-MASTRA study). Tests for development of integrated models of chemical and mass transport i the near-field will be included in the future scope of this study.

Flow cell type experiments with reacting solute (IMAGE-GEOCHEM) will be utilized as comprehensive experiments to identify important minerals that determine groundwater characteristics and to test assumption and predictions from appropriate computer codes. Availability of the minerals to moving groundwater and reaction-rate versus flow-velocity relationships will be investigated. A geo-hydro-chemical code which treats mass transport and chemical reaction will be developed, and this code will be validated through comparison to the test results.

IMAGE-MASTRA

The purpose of IMAGE-MASTRA is to study mass transport phenomena in the nearfield which contains EBS of PNC's reference design. These tests will establish the range of conditions over which currently available mass transport models are valid, as well as identify the needs for further development of model.

The IMAGE-MASTRA experiments are designed to evaluate the effects of spatially varying hydraulic conductivity on the mass transfer rate at the interface of bentonite and surrounding host rock. This experiment will be useful for mass transport theory and is also logical extension of experiments (McGrail et al. 1985; Geldart et al. 1988) which were carried out for validation of key aspects of the analytical solutions developed by Pigford and his colleagues. A conceptual view of this experiment is shown in Figure 5. In order to carry out the experiment as extension of the previous study, near-field is simulated by three components, i.e. source term, low-permeability porous medium and highpermeability porous media. Source term and simulated buffer material (low-permeability medium) are set up so that the direction of mass transport in simulated buffer material is perpendicular to the streamline in the simulated host rock (highpermeability medium).

IMAGE-GEOCHEM

IMAGE-GEOCHEM is a task which is similar to EDAS in its emphasis on geochemical environment in near-field. The experiments and numerical simulations performed within IMAGE-GEOCHEM study will focus on developing a better understanding of key processes affecting geochemical evolution of groundwater in the near-field. The initial emphasis of the study is placed on investigation of water-rock interactions in the opensystem, particularly the relation between groundwater flow rates and rates of mineral-fluid reactions. Subsequent studies will be done in order to clarify the effects of heterogeneities in the geologic environment on groundwater compositions. The effects caused by the interactions between groundwater and components of EBS will be also investigated.

IMAGE-GEOCHEM will develop conceptual models of major processes which control coupled fluid transport and rock-water interactions using laboratory experiments and numerical simulations. This work will provide general understanding of rock-water interactions in the open-system which can become a basis for predicting evolution of groundwater compositions.

5. CONCLUSION

The role of sensitivity analysis in performance assessment modelling was reviewed through some examples. Even though these examples are preliminary, the results confirmed intuitive expectations of parametric sensitivities and also identified further modelling efforts needed.

In order to proceed with validation of near-field assessment models in a systematic way, the link between sensitivity analysis and comprehensive validation tests needs to be further developed. The ENTRY project is one example to establish these linkages.

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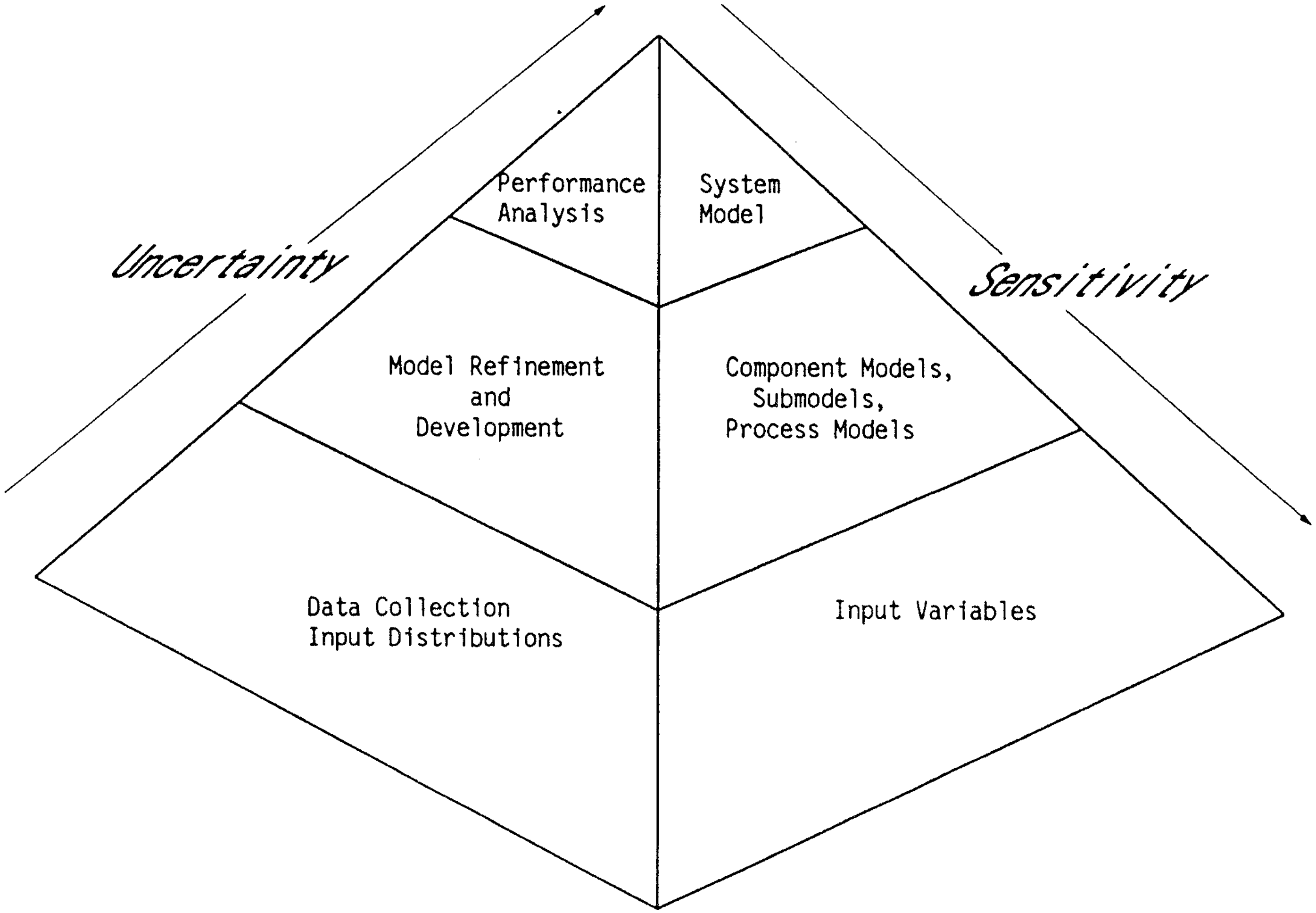
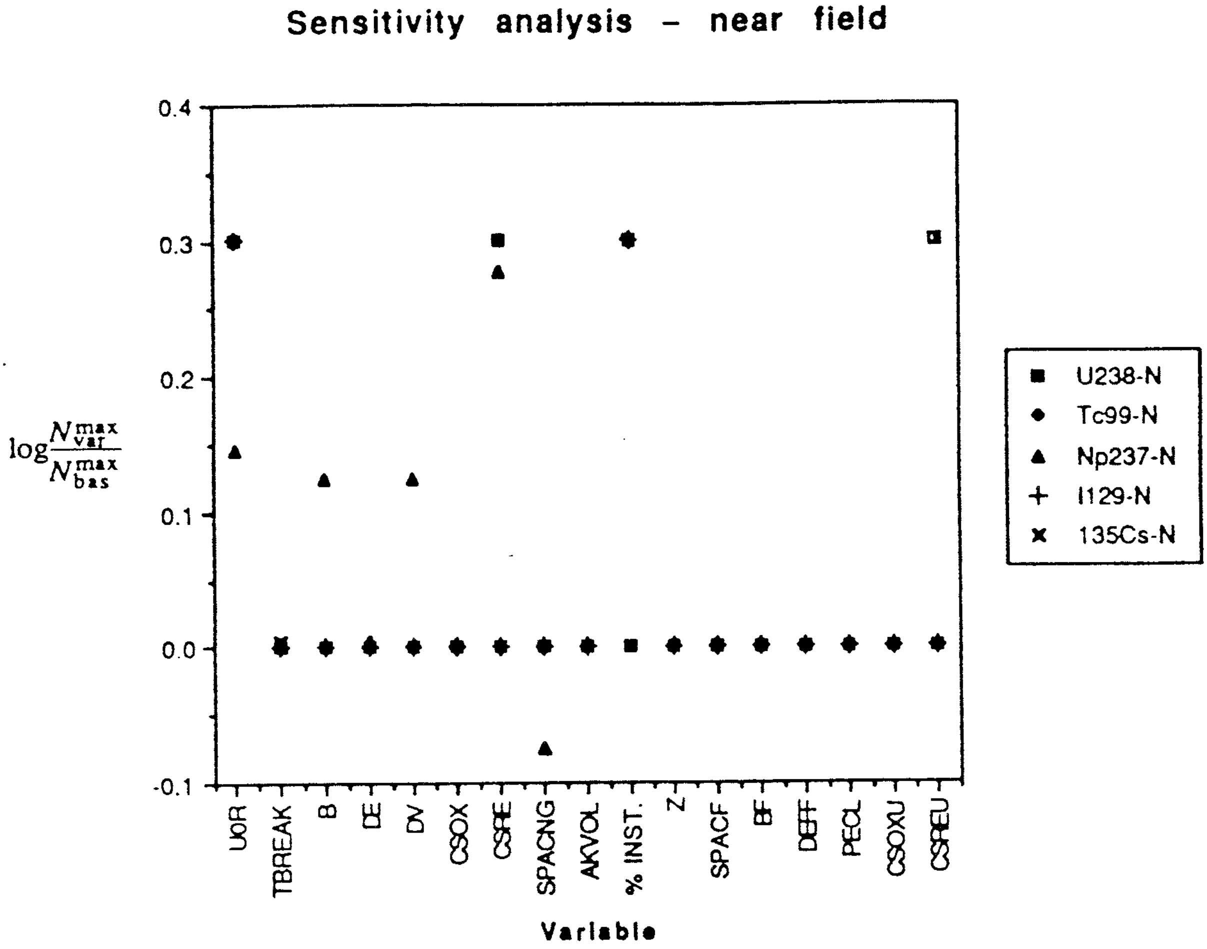


Figure 1. Elements of Performance Assessment.



Notation

UoR	Water flow rate
TBREAK	Canister life
B	Fracture aperture in near field
DE	Diffusivity in backfill
DV	Diffusivity in water
CSOX	Solubility in oxidized water
CSRE	Solubility in reducing water
SPACNG	Fracture spacing near field
AKVOL	Sorption coefficient
% INST	Fraction of Cs, I immediately soluble
Z	Path length in far field
SPACF	Fracture spacing in far field
BF	Fracture aperture in far field
DEFF	Effective diffusivity in rock matrix
PECL	Peclet number
CSOXU	Solubility of uranium oxidizing cond.
CSREU	Solubility of uranium reducing cond.

Figure 2. *The ratio of the nuclide release from the near field in the varied case to that in the base case.*

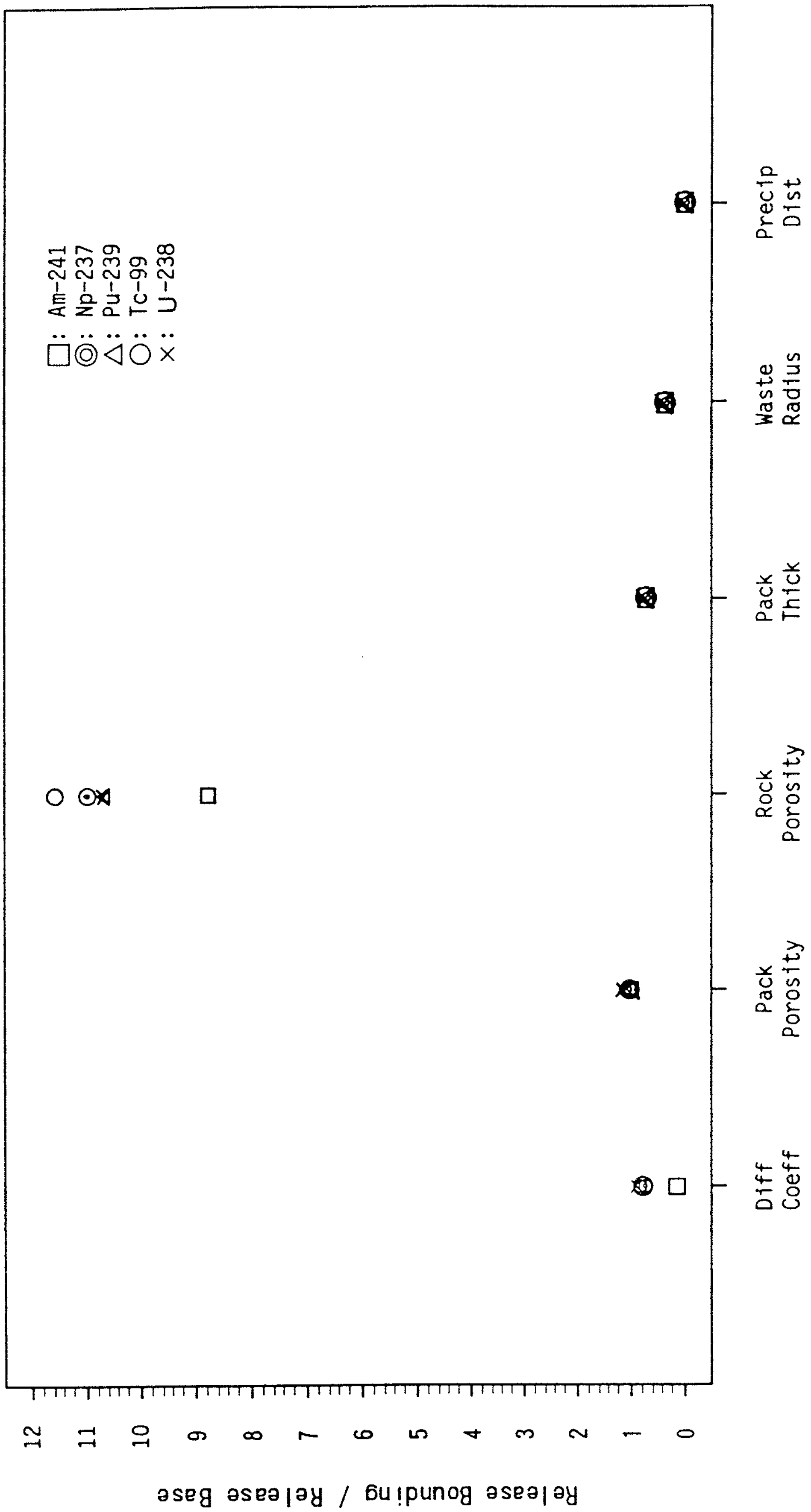


Figure 3. Cumulative Release from Solubility-Limited Release Model: 10.000-Year Bounding Case Release Normalized by 10.000-Year Base Case Release - Physical Parameters.

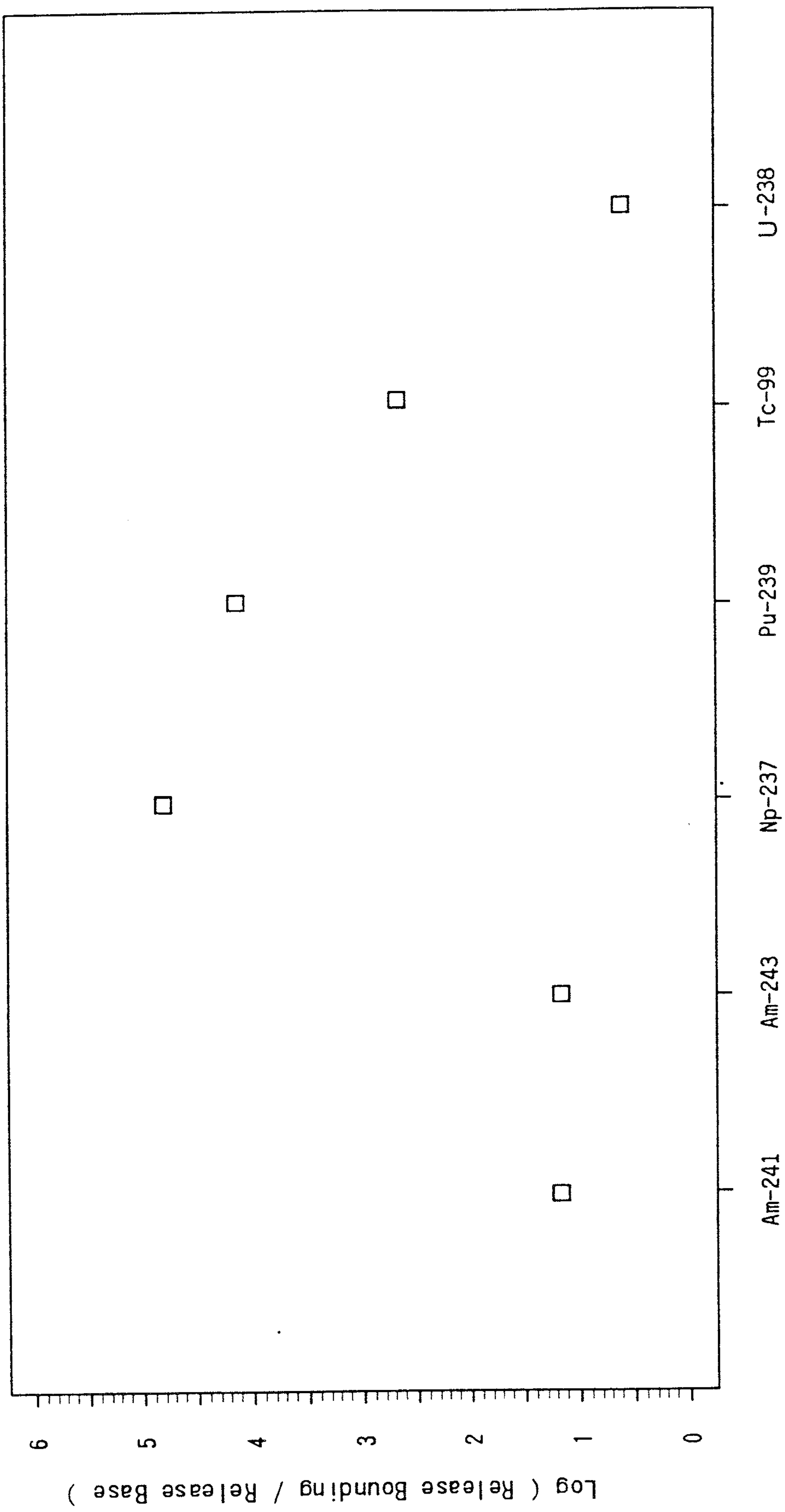


Figure 4. Cumulative Release from Solubility-Limited Release Model: 10.000-Year Bounding Case Release Normalized by 10.000-Year Base Case Release - Chemical Parameters.

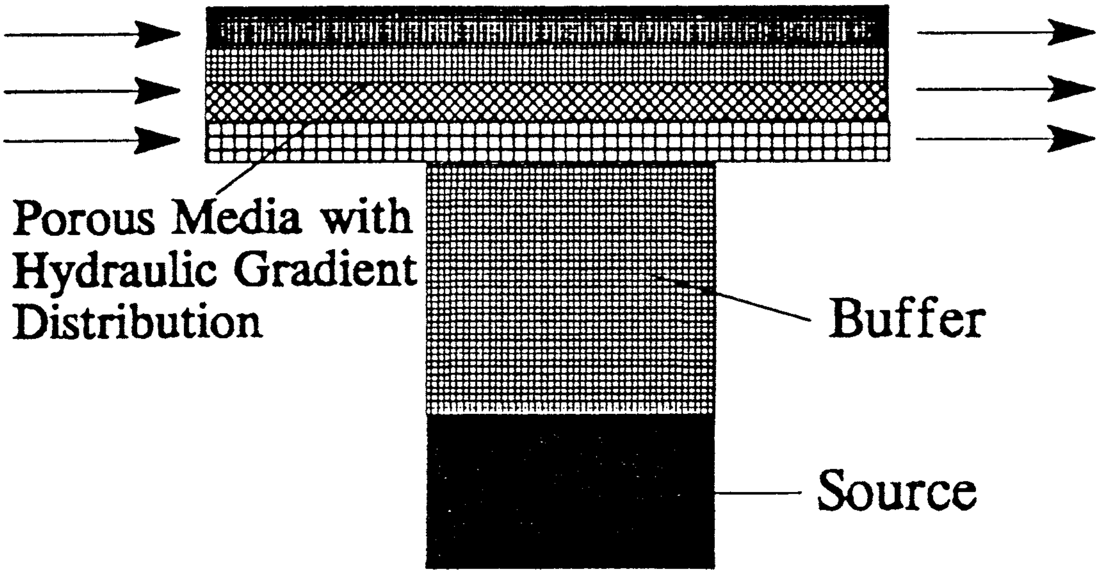


Figure 5. Schematic of IMAGE/MASTRA Experiment to Investigate Effects of Flow Velocity Distribution on Mass-Transfer Rate.

DISCUSSION ON "SENSITIVITY ANALYSIS AND VALIDATION"

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INTRODUCTION

There was a general agreement regarding the definition and role of sensitivity analysis and validation as presented in this paper. Further clarifying remarks were offered regarding the associate roles of verification and benchmarking of codes; it was felt a clear distinction should be made between verifying the mathematical correctness of a code and the process of validating the conceptual model on which a code is founded. Specific programs on sensitivity and validation studies being conducted in Switzerland and Sweden were described by representatives from those countries.

SENSITIVITY AND UNCERTAINTY ANALYSES

The overall principles and work-to-date reviewed in this presentation were accepted. Discussions regarding the difference between sensitivity analysis and uncertainty analysis seemed predicated on semantical or cultural biases. One suggestion to distinguish these terms was to use the hierarchial structure of performance assessment (PA) described in this paper. "Sensitivity analysis" would, in this context, be those studies in which the results of higher-level PA models were passed "downwards" to guide the activities of lower-level PA models or data collection; for example, using system-level codes to indicate the relative importance (sensitivity) of hydrological versus geochemical factors affecting containment, or use of a detailed mass-transfer model to identify the relative sensitivity of several parameters affecting transport of radionuclides. "Uncertainty analysis", in contrast, would be reserved for activities in which basic uncertainties in parameter values (or correctness of conceptual models) were passed "upwards" to higher levels of performance assessment. This proposition was debated but not fully endorsed.

Discussion shifted to limitations to such studies and how sensitivity/uncertainty analyses should be expanded in the future. One area that was stressed by several participants was the need for a system-level "model" for describing the time-dependent variation in the near-field environment, especially the potential complex variation in groundwater chemistry across barrier materials that are compositionally dissimilar. A second area was the need to develop a systematic method to quantify uncertainties arising from expert judgement and other subjective inferences/assumptions. Such subjective information, that may be included in total system performance assessments, defies conventional statistical treatment. The use of fuzzy-set theory was briefly mentioned as a possible approach that is under investigation.

VALIDATION

The oral presentation and published paper by the authors focused on laboratory validation, specifically the new PNC ENTRY program on large-scale, non-radiogenic testing. Several participants noted that natural analogue studies also have a prime role in achieving model validation. Comparative advantages and disadvantages of the analogue versus laboratory studies were discussed. The firm consensus of the group was that both approaches are needed, in part because they present complementary advantages regarding measurement/control of conditions (laboratory studies) and time/ scale realistic samples (analogue studies). A CEC conference on natural analogues, held at Pitlochry, Scotland in June 1991, was noted as an excellent forum showing the potential for model validation using natural analogues.

The purpose and scope of the ENTRY program received general support from the participants. It appears that certain ENTRY test are aimed at rigorous validation of performance assessment models, other tests are intended to collect key data for performance assessment models, while other tests are designed to provide qualitative guidance on the performance of near-field components. In all cases the importance of communicating these results to the scientific and public communities is stressed.

One important recommendation was that each ENTRY test should be designed on the basis of a specific conceptual/mathematical model, and that this model (or hypothesis) should be used to predict expected results prior to conducting the test. If possible, the ENTRY tests should be designed in such way that the results can be used to distinguish between the predictions of alternate, competing hypotheses. Detailed questions regarding the design and intended results could not be answered, however, because of the preliminary status of the ENTRY program.

TESTING NEAR-FIELD MODELS FOR DEEP DISPOSAL

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ABSTRACT

The near field of a deep radioactive waste repository is a complex environment whose spatial and temporal evolution is determined by many different physical and chemical processes. For near-field performance assessment modelling, this system has to be simplified whilst ensuring that the key processes determining radionuclide release and transport are accounted for.

This paper discusses the various types of near-field models developed and the strategies that can be employed to test them. Model testing within an international framework is seen as an important step towards establishing the credibility of current near-field performance assessment codes. The considerable benefits to be gained from organising such an exercise are highlighted drawing upon experience from similar activities in other fields.

1. INTRODUCTION

Nuclear waste disposal in a deep geologic repository is currently based upon a multiple barrier strategy, which is conceived to contain and isolate the waste from the surface environment until it no longer presents an unacceptable risk to man and his surroundings. The three primary components to the performance assessment of such a repository are the engineered barriers of the waste package and surrounding backfill, the intervening natural barriers of the geosphere, and the biologic pathways of radionuclide transfer within the surface environment. These are conveniently referred to as the near field, far field or geosphere and biosphere, respectively.

Within each of these component performance assessment models, there is a hierarchy of processes and parameters that must be considered. At the top of the hierarchy are system-level models that integrate a series of phenomenological process models. These process models, in turn, are based on environmental models that define the temporal and spatial variation in environmental parameters.

Data collection is driven by consideration of all three levels of models. Uncertainties in data measurements and conceptualisation of processes must be passed upwards through the hierarchy of models. Conversely, the relative importance of different processes and parameters must be established through a "top-down" approach to sensitivity analysis. Sensible guidance to various field and laboratory data collection programs can only be achieved from a system-level assessment that permits relative sensitivities to be established among different process submodules.

This paper considers the role of the near field in the safety of deep geologic disposal systems and discusses the types of model developed for performance assessment. The need to test such models is discussed along with a hierarchy of possible testing strategies. The considerable benefits to be gained through organising such an exercise on an international basis are highlighted, drawing upon experience from similar exercises in other fields.

2. IMPORTANCE OF THE NEAR FIELD

The near field is defined as encompassing both the engineered barriers of the waste package and the surrounding backfill as well as that portion of the host rock directly affected by the repository. Included in near-field performance assessment are both the effect of waste package emplacement on the local properties of the host rock and the subsequent containment and release ("source-term") of radionuclides from the engineered barriers to the host rock.

The near field is well characterised, being constructed from engineered materials whose properties can be tested over a wide range of conditions. Consequently near-field performance can potentially be predicted with a high degree of confidence ("robustness"). In practice this confidence may be reduced by the uncertainties in the net effect of the very many phenomena acting simultaneously within this environment. These include both the effect of waste emplacement on the properties of the surrounding host rock and the influence of the host rock on the engineered materials.

In contrast, the geosphere is more difficult to characterise, owing to the inherent heterogeneity of the flow systems on both large and small scales in the host formations. Efforts to characterise the rock by drilling a large number of boreholes only tend to highlight the very complexity of such systems. Despite this, considerable effort has been expended at an international level to improve both the understanding and confidence in models developed to predict groundwater flow and radionuclide transport in the geosphere. Indeed, the progress which this has stimulated in this area has been very significant.

3. BACKGROUND

Considerable previous benchmarking exercises have been conducted on far-field assessment codes (eg. HYDROCOIN [1], INTRACOIN [2]) and on biologic pathway models (eg. BIOMOVS [3]). Unfortunately, very little benchmark testing, or even comparison of conceptual models, has been performed for near-field performance assessment.

Despite this, there has been considerable study of near-field processes and associated data collection. For example, the annual Materials Research Society (MRS) symposium contains many experimental and theoretical studies on the properties of engineered barrier materials and the behaviour of radionuclides under simulated near-field conditions. One is struck, however, by the general disconnection between many of these material studies and the identified data needs from system-level performance assessments such as KBS-3 [4] and Project Gewähr [5]. This misplaced emphasis arises from a focus on intermediate process models rather than the integration of such models within a system-level model. This approach can, and has, led to over-emphasis on certain near-field processes (such as leaching over short timescales) and general misapprehension of the parameters needed for a technically definable assessment of the engineered barrier system.

The NEA/OECD has previously conducted a Workshop on source-term modelling of the near field (Muller and Hunter, 1985 [6]). The proceedings of this workshop contained a good introduction to the subject, but lacked any critical analysis of models or intercomparison of approaches to near-field assessment.

Since this workshop, the only joint work on intercomparison of near-field system-level models has been a study conducted by the Atomic Energy of Canada Limited and the U.S. Department of Energy on their respective SYVAC-Vault model (SVM) and AREST Code [7].

In view of the importance of the near field to the safety of the entire disposal system, a full-scale international comparison study would provide considerable support to the safety case of any proposed repository. The reason that near-field modelling has not been the subject of an international study is not clear. Until recently, the number of near-field performance assessment codes available for comparison was limited. Also, there may be a false perception that the differences in waste forms, near-field design, or host rock properties preclude intercomparison. A more formidable problem is the differences in the number and detail of sub-processes included in different system-level models. As described below, however, none of these issues are insurmountable obstacles to organising a worthwhile and technically credible benchmark comparison of near-field assessment models. A step-wise approach towards establishing this goal is recommended.

4. TYPES OF NEAR FIELD MODEL

Analysis of the near field involves evaluation of a complex spatial and temporal evolution of the environment in which many different chemical and physical processes occur simultaneously.The relative magnitude of these processes will change with the temporal and spatial conditions of the near field and hence so will their significance with regard to the release of radionuclides to the far field. Three main categories of near-field models can be identified. For convenience, these are described as environmental models, process models, and system models.

4.1 Environmental Models

The most fundamental models required for near-field performance assessment are those that describe the spatial and temporal evolution of physiochemical parameters of the near-field environment. The basic categories include thermal, chemical, mechanical, and hydrological models. Radiological models may represent a fifth type of model, although possible radiolytic effects on groundwater chemistry would seem to be best integrated with existing chemical models. These parameters only indirectly affect system performance of the near-field through their effects on process submodules (see next section). Nevertheless, temperature and groundwater chemistry are perhaps the two most important parameters that affect a wide range of processes.

The environmental models provide the link between the radionuclide transport calculations of the system level models and scenario analysis as they allow the conditions within the near-field environment to be defined. They are used to establish the boundary and initial conditions for system-level models. For example, the near field includes that part of the host rock which immediately surrounds the waste package and engineered barriers. The flux of radionuclides from the waste package will be affected by the porosity and fracture characteristics of the host rock, the dominant transport mechanisms in the host rock (diffusion, advection, fracture flow, matrix diffusion), on its sorption properties and the prevailing chemical conditions, such as the redox potential.

Considerable benchmark testing of codes has been conducted for many of these separate categories. For example, there have been benchmark calculations among various geochemical codes (Nordstrom et al., [8]; Pearson and Norohama [9]; CHEMVAL [10]) as well as mechanical codes (CEC COMPAS project [11]).

So-called "coupled models" that evaluate thermal effects on mechanical properties, thermal effects on flow, mechanical effects on flow, etc have also been developed (eg. see Tsang 1988 [12] for excellent overviews of such work). In some cases, their coupling is the basis for evaluating processes such as resaturation of the near-field or mechanical stability of the host rock adjacent to the emplacement hole of the waste package. It is planned to consider this topic in more detail in the DECOVALEX study [13].

4.2 Process Models

Process level or research models examine in isolation phenomena directly affecting the system with regard to radionuclide behaviour within the near field, paying particular attention to the chemistry of the system. They are often based on empirical relations derived by the analysis of results from laboratory or field experiments. Prior to container failure, these processes include transport of corrodants in the groundwater, corrosion of the container, and migration of mobile corrosion products. Subsequent to containment failure, many complex processes occur with respect to the nuclear waste form itself. Dissolution of the waste form matrix and subsequent formation of more stable, radionuclide-containing alteration solids are two of the most important processes that constrain overall release from the waste package system. The release of radionuclides from the waste form will be different for spent fuel or vitrified waste. The processes studied for spent fuel will include immediate release from cracks and fuel/cladding gaps, release from grain boundaries, dissolution of the $U0_2$ matrix or radioelement solubilities. For vitrified waste, release may involve congruent and incongruent matrix dissolution, or radio element solubilities. These processes will be influenced by the chemistry of the groundwater, and geochemical conditions of the near field which are defined by the environmental models.

Another set of processes is concerned with the performance of the buffer and backfill layers surrounding the waste canisters. These include diffusion, sorption and precipitation. These processes will determine the mass transfer characteristics of the buffer and corroded canisters.

4.3 System-Level Models

System-level or integrated models consider the behaviour of the near field as a whole rather than considering the effects of individual processes in isolation. They provide the source term for the subsequent geosphere transport modelling for performance assessment. These models attempt to account for the most important phenomena occurring in the near field by coupling together a number of processes which influence the release of radionuclides. In general, due to analytical constraints, the sub-models are simplifications of the process models considered above. System models aim to evaluate the impact of process coupling and reactions at interfaces, and to indicate which are the dominant processes in the containment and eventual release of radionuclides to the far field. The current generation of system level models vary with regard to the number and types of processes they consider, depending on the underlying conceptual model. For example, the CALIBRE code [14] developed for the Swedish Nuclear Power Inspectorate (SKI) explicitly accounts for the migration of a redox front.

Of necessity, system-level models include only a limited number of process models which may contain differing levels of detail. The basis for the selection of the processes is not always clear, in the absence of an international consensus of opinion. It would be one of the tasks of an intercomparison study to address this aspect of near-field models, so that important processes are not omitted through lack of information or understanding.

5. MODEL TESTING APPROACHES

Models are simplifications of reality and by their very nature may have associated errors or uncertainty, independent of model type. Possible errors include incorrect formulation of the conceptual basis of the model, mistakes in the mathematical description of the phenomena or boundary conditions, and inadequate or inappropriate databases.

The models used must therefore be evaluated with regard to their validity, both in terms of their accuracy in calculating the model equations and their adequacy in representing the real system.

5.1 Verification

The first stage in the evaluation of a mathematical model is to check that the conceptual model of the real system is adequately represented by the numerical solution algorithms – commonly termed verification [12].

It should also ensure that the model is fully operational, in the sense that all possible pathways through the code have been exercised, using the complete range of input parameters for which it was designed.

Depending on the complexity of the model, verification will usually be conducted at the modular level, where the computed output from individual subroutines or procedures is compared with the results obtained from hand calculations of analytical solutions to subsets of the model equations. At a system level checks can be made on the conservation properties embodied in a model, such as mass and energy balance.

5.2 Benchmark Comparison of System-Level Codes

A second stage to model testing involves comparing the results obtained by different codes for a specified hypothetical system. Although absolute answers are generally unavailable for these problems, they enable comparison not only of the algorithms employed to solve a given set of equations, but also the relative importance of the various processes included in the models. Thus, not only are the conceptual models compared but also the different submodels used to account for the various processes. This approach to the design of benchmark problems for system-level models has been used successfully in other areas of repository safety assessment, for example in hydrology [1], the geosphere [2] and the biosphere [3].

Problems based on hypothetical systems are designed to fully exercise all facets of the models. Although exact solutions may not exist the results from different models can be compared, and their agreement towards a consensus solution can be discerned. Discretisations in space and time can also be refined to check for convergence of solutions, although this does not automatically ensure their correctness.

Specification of benchmarking problems will include a statement of the problem in terms of the processes involved and their governing equations; the problem solution or physical description of the system; any assumptions made; and specification of input data parameters, initial and boundary conditions. The ranges of the input parameters and choice of output should be chosen so that, as far as possible, any weakness in the models is clearly demonstrated, and the extent of their applicability is established. As problems may arise during this phase, an iterative procedure is suggested. This may be achieved by first establishing a smaller task group who carefully check the problems (using several codes) to ensure they are well-posed and can be solved in a reasonable amount of computer time.

For an intercomparison exercise for system-level near-field codes, the initial phase would involve an analysis of the underlying conceptual models before benchmark tests could be specified. For valid comparisons to be made, it is essential to identify both the processes which are common to all the models and those which are different. It is also important to identify differences in model assumptions, boundary conditions or geometry, so that any divergence of benchmark results which may arise from them can be predicted.

The next phase would be to define a simplified base case that is suitable for analysis by all the participating codes. The base case should include the definition of a generalised waste form and waste package design, backfill and host rock properties, water chemistry and hydrology. It should also define the processes to be included, such that all the codes can be accommodated. For example, if not all the codes model chain decay, then the base case would specify single nuclides.

Additional cases can then be constructed, which incorporate processes included in various subsets of the models. In this way the impact of the new processes on the base case results can be determined, to establish whether they are of primary or secondary importance. In addition, cases should be included which vary the base case parameters, to determine the sensitivity of the results to those parameters.

Benchmarking by comparison with analytic solutions and by agreement between codes builds confidence that the mathematical solution is formulated without errors and that important processes have not been omitted. It cannot guarantee that incorrect results will not be obtained in future applications, for example by faulty specification of input data. An additional benefit of a benchmarking exercise is that it may uncover difficulties which occur in the practical use of the models, particularly in the areas of input and output.

A valuable part of the benchmarking exercise is comparison of the methods used to deal with uncertainties. This is particularly important in view of the long timescales over which performance assessment calculations are expected.

5.3 Validation

The ultimate test for a model is to demonstrate that the conceptual model and the derived computer code provide a good representation of the actual processes occurring in the real system. This is referred to as validation [15] and is carried out by comparison of calculations with field observations and experimental measurements. The timescales involved greatly limit even the testing of sub-models and make direct testing of integrated models impossible. An approach which can offer limited validation in such cases involves testing the models against natural analogues which closely resemble some aspects of the near field.

It is not intended that validation would form a part of the proposed model testing exercise. However, it is recognised that the better understanding of the system gained through benchmarking studies can provide ideas for suitable experiments which could be performed with validation in mind and help identify particular aspects to search for in natural analogue systems.

6. CONCLUSIONS

International collaborative exercises for testing models in other fields of repository safety assessment show they can provide a practical way to demonstrate the correctness of codes. They are also extremely valuable in catalysing communication and the exchange of information, and increasing the credibility of codes within the scientific community.

It is envisaged that an intercomparison exercise for system-level near-field models would proceed in a stepwise manner. The initial phase would comprise a review in which the capabilities and status of the current codes/models are examined and the assumptions in the conceptual models identified in order to establish a firm basis for an intercomparison exercise. The aims of such an intercomparison exercise would be to:provide a forum for the exchange of ideas and information establish the ability of current performance assessment codes to account for various phenomena identify differences in the codes assess the relative importance of different processes and environmental phenomena stimulate model development

Information gained in the identification of the most important processes and the data required to model them can then be fed back into research programmes, assisting in the direction of such programmes towards the achievement of better-defined goals.

In summary, an international forum for testing near-field models would help to improve confidence that the processes affecting radionuclide release are incorporated in their formulation, to establish their range of application, and to identify areas where further research and development may be required.

ACKNOWLEDGEMENTS

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DISCUSSION ON BENCHMARKING

Lawrence Johnson, AECL Canada

A broad spectrum of views were expressed on the issue of validation and benchmarking of codes. In spite of significant differences in opinion, it was clear that all participants felt that periodic meetings of a group dealing with near-field models would be very valuable. Such meetings would enhance the credibility of the models used by all participating nations. A starting point could be a meeting to exchange information on the models used, including challenging and assessing the basic assumptions in the models and the reasons for them. This approach would have two major advantages. The first would be to help direct research in near-field processes (both laboratory studies and theoretical modelling) into the most beneficial areas. The second would be to allow participants to explore the reason for different assumptions being used in the conceptual models (e.g. apparent disagreements between two approaches to modelling the same process may arise from different repository conditions, different data being relied upon in the two cases as a basis for the model, or different degrees of conservatism applied in selecting either the data or the modelling approach). Whatever the reasons, the discussion and clarification of these differences will improve the quality of models and our ability to explain to reviewers and the public why such differences exist and, possibly, eliminate some differences.

Progress beyond this stage, e.g. to the stage of benchmarking test cases, may be difficult to achieve in the short term. Relatively few published codes exist and it is likely that a greater number need to be developed before a broad multinational benchmarking exercise could be undertaken. In the meantime, further meetings on near-field performance assessment should be held, focusing on commonalities and differences in the models, the reasons for them and what data and models can help to advance our collective understanding and our ability to undertake high quality near-field performance assessment.

CONCLUDING REMARKS FOR THE TECHNICAL WORKSHOP ON NEAR-FIELD PERFORMANCE ASSESSMENT

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PURPOSE

The purpose of convening this Workshop was to identify and discuss the key processes within the near field of a nuclear waste repository that affect performance assessment. Furthermore; specific attention was devoted to the relative importance of these processes, integration of process models into performance assessment codes, the benchmarking/ validation of such codes, and the role of such codes in providing a defensible basis for risk analysis, as well as guidance to data collection.

ROLE OF NEAR-FIELD

Permanent disposal of nuclear waste in repositories located in deep geologic formations is being studied world-wide. The most credible release pathway is interaction between groundwater and nuclear waste forms, followed by migration of radionuclide-bearing groundwater to the accessible environment. Under certain conditions, vapor transport of volatile radionuclides is possible. The primary components of repositories that mitigate release are the near-field and the far-field subsystems. The near-field encompasses the waste packages composed of engineered barriers (e.g., man-made materials, such as vitrified waste, corrosion-resistant containers), while the far-field includes the natural barriers (e.g., host rock, hydrologic setting). Taken together, these two subsystems define a series of multiple, redundant barriers that act to assure the safe isolation of nuclear waste.

The far-field has a tremendous capability for the safe isolation of nuclear waste. Factors that affect far-field isolation capacity and performance have been the subject of extensive evaluation. Considerable international effort has been directed towards finding sites that have "favorable" characteristics (e.g., low groundwater flow, highly sorptive minerals, low redox (Eh) potential, hydrologically unsaturated regions) for geologic disposal.

There are, however, certain advantages in achieving high confidence and reliability in isolation of nuclear waste by the engineered barrier subsystem (EBS).

—the geologic setting can only be partially characterized with unavoidably large uncertainties because of natural heterogeneities; in contrast, EBS components can be designed and constructed with well-described and highly uniform properties.

—the evaluation of the performance of the far-field must be based on ambient characteristics of the geologic site. The ability to examine site performance under alternate conditions is extremely limited, both in control of test conditions and in the spatial portion of the host rock that can be tested. In contrast, the performance of individual and assembled components of the EBS can be tested readily over a wide range of controlled conditions.

—the "favorable" characteristics of a site often reflects current conditions. The constancy of these site characteristics over time periods of tens and hundreds of thousands of years can be problematical. Components of the EBS can be designed to provide acceptable performance over a wide range of conditions.

—the radionuclide releases from the EBS represent a limiting source-term that is required to evaluate to the performance of the far-field.

These advantages are implicitly acknowledged in past and planned assessments of the total repository system. Typically, the far field is assumed to consist of 100 meters or less of rock between the EBS and the nearest major fracture zone; therefore, the performance of the near field is central to demonstrating the feasibility and safety of geologic disposal. This reality does not obviate the need for understanding and evaluating the performance of the natural barriers. A balanced isolation strategy, based on both subsystems, must be encouraged.

MASS-TRANSFER ANALYSIS OF THE NEAR FIELD

Mass-transfer analysis has played a central role in prediction of near-field performance assessment by Swedish, Swiss, French, U.S., Canada, Japanese and other national repository programs. The most notable applications are in evaluation of containment by canisters and the subsequent release of radionuclides from the waste package to the host rock. Calculations based on mass-transfer theory have several advantages over approaches based on more empirical models. Mass transfer is a mechanistic theory based upon well-understood governing equations. When combined with conservative bounding values for boundary conditions, it can provide a realistic, reliable, and technically defensible approach for calculating performance of the EBS. Mass-transfer theory places no reliance on adjustable coefficients or arbitrary parameters developed from empirical "fits" to data. It provides a clear indication of the functional relationship among chemical, physical, and design parameters and what data are required for performance assessment. Furthermore, performance models based on mass-transfer theory are readily validated because they are exact, mathematical formalisms of physico-chemical processes and require knowledge of a limited number of directly measured parameters.

Mass-transfer models for release require a boundary condition for the concentrations of radionuclides at the waste-form surface. The concentration at the waste form surface will be controlled by the relative rates of waste-form dissolution and diffusional-transport of dissolved radionuclides. If transport rate is fast relative to the dissolution rate, a mass-flux rate must be applied at the waste-form surface; this rate may or may not be constant with time. Conversely, if the transport rate is slow relative to the waste-form dissolution rate, then a solubility limited concentration must be applied. This value also may or may not be constant with time. The assumption of constant flux or constant solubility concentrations seems justified, however, given that the change in chemical and thermal characteristics of the near field are small after the first several hundred years following emplacement.

Previous analyses indicate that most radionuclides will be limited by the formation of solubility-limiting phases, rather than by the dissolution rate of waste forms, for expected near-field conditions. This prediction has been confirmed by the ubiquitous formation of secondary reactions products in waste-form tests of reasonable duration, although waste-form testing under open-system conditions would help to further test this conclusion. The results of performance assessment analyses indicate studies should be re-directed from waste-form "leaching" tests to the study of radioelement solubilities under expected repository conditions.

The determination of realistic solubilities for radioelements is not, however, a straight forward application of thermodynamic calculation of the most stable solid containing a given radionuclide.

First, formation of metastable (more soluble) phases occurs commonly at temperatures below 200°C, as seen in natural geologic systems. Second, thermodynamic data base for phases composed of radioelements is limited. Third, the radioelement-bearing phases for which data are available tend to be oxides or hydroxides, and less frequently carbonates or phosphates, whereas silicates and alumino-silicate phases may as likely to form (e.g., cesium alumino-silicate, pollucite). Fourth, not every radioelement will form it's own solubility-limiting phase. Most radioelements will be incorporated ("co-precipitated") as trace components in solid solution with alteration phases.

Mass-transfer analysis can also be used to demonstrate the relative importance of transport characteristics of near-field barrier materials. Diffusional transport of radionuclides through compacted bentonite "buffers" surrounding the waste container must be evaluated by separate measurement of porosity, retardation, and tortuosity factors. In addition, the mass-transfer resistances of corrosion layers of failed containers and the encompassing host rock (porous or fractured) have also been shown to strongly affect the release of radionuclides from the EBS. Furthermore, the effect of neighboring emplacement tunnels and major fracture zones may change the relative direction and rate of radionuclide release. Realistic mass-transfer models must incorporate this significant degree of spatial inhomogeneity within the near field.

INTEGRATED NEAR-FIELD ASSESSMENT

The reliable prediction of the behavior of high-level waste emplaced in a deep geologic repository is the goal of performance assessment. Performance assessment has three key functions:

—demonstrate compliance with performance requirements that assure public safety,

—provide a quantitative and scientific basis for waste-isolation strategies, including waste-package design optimization, and

—efficiently guide data collection activities.

A hierarchy of performance assessment models match these three functions and are based on the physical scale of the system to be evaluated. For the near-field region of a nuclear waste repository, three different systems and levels of performance models can be established: Engineered Barrier System model, Waste Package model, and Component model. These different models are described in the following paragraphs.

Engineered Barrier System Model

An Engineered Barrier System (EBS) model addresses the behavior of a system composed of the natural and engineered components of the underground repository. This behavior is evaluated as a function of temporal and spatial variation of physicochemical parameters within this extensive system. The objective of an EBS model is to demonstrate safe isolation for a range of possible future conditions (PA function #1), often on the basis of a probabilistic risk assessment. Because of the need to assess the performance of hundreds to thousands of separate waste packages from arrays of stochastic inputs, the process models contained in an EBS model are usually simplified descriptions of the dominant processes that affect the overall EBS performance. In particular, the calculation of radionuclide releases are based on analytical or numerical solutions to a set of mass-transfer equations. These solutions are computationally efficient and easily integrated with arrays of data that represent distributions of parameter values. Convolution of these parameter distributions and simplified process models provides a basis for quantifying both the expected performance of the EBS and the relative uncertainty in that estimation.

In extreme cases, an EBS code can be used to evaluate the relative importance of processes and parameters that may affect the release rate of radionuclides from an individual waste package. This application, however, stretches their original scope and intent. For a more realistic analysis of the relative importance of near-field processes and associated parameters, including design parameters, a Waste Package model is preferred.

Prominent EBS codes include SYVAC/ Vault, AREST, STRENG, MELODIE, and PANDORA. It must be noted that ranges of parameters, boundary conditions, and geometries have been used to develop different conceptual models to describe the waste package and near field. In some cases these EBS codes have, in turn, been incorporated into larger codes for the purpose of performance assessment of the total repository system.

Waste Package Model

Integrating the performance of multiple barriers is the objective of a Waste Package model. This model is based on mechanistic descriptions of the chemical, thermal, hydrological, mechanical, radiological, biological, and transport processes that occur within a system defined as the nuclear waste package. A Waste Package model considers synergistic effects among these processes, as well as their effect on the performance of the components of the waste package and surrounding host rock. The objective of a Waste Package model is to provide a scientific understanding, as well as relative importance (sensitivity), of the processes affecting waste package performance (PA function #2). In addition, a Waste Package model can be used to confirm the technical basis for the more simplistic process model descriptions contained in an EBS model.

Numerical models of a single waste package and surrounding rock provide a particularly useful tool for analysing interactions between the physical and chemical phenomena occurring in the near-field. For example, the CALIBRE code was used to analyse the release of radionuclides into discrete fractures and the effect of redox front motion on radionuclide release in the recent Swedish Project-90 assessment of spent fuel disposal in crystalline rock. Future extensions could include calculation of release through localized failures in containers, estimation of the effect of spatial heterogeneities in sorption and porosity on release, analysis of adjoining, low-porosity tunnels in creating preferential migration pathways, optimization of the waste-package design and materials selection, and the linkage of numerical models used for thermal-mechanical-hydrological analysis.

Component Models

At the most fundamental level are Component models for the performance of individual barrier materials, including both engineered and natural barrier materials. Each such model defines the basic parameters needed to assess the performance for a system defined as a single component. Accordingly, such models can be used to evaluate the relative importance (sensitivity) of parameters as a guide to data collection (PA function #3). Examples of Component/ Process models include the dissolution rate of borosilicate glass, the corrosion rate of overpack/ container materials, the solubility of radioelements, the reversible sorption of radioelements on barrier materials, and the diffusion of dissolved species through compacted bentonite or partially saturated rock rubble.

The natural tendency of Component models is to pursue a complete understanding of a process. Not only is this goal illusionary, but is it potentially dangerous if it results in open-ended experimentation. The initiation and termination in the development of Component models must originate not with the individual researcher, but from integrated assessments of the waste package and engineered barrier system.

BENCHMARKING OF CODES

A key role of performance assessment is to provide sensitivity analyses to guide testing and data collection. It is prudent, therefore, to establish the credibility of existing performance assessment codes, as well as codes for modeling the thermal-chemical-hydrological-mechanical-radiological environment of the near field. One approach to establishing this credibility is through benchmarking studies.

Benchmark analyses have been conducted for various thermal-chemical-hydrological-mechanical-radiological codes that provide supporting data and constraints for near-field performance assessment. Such codes have applications that go beyond assessment of geologic disposal of nuclear waste, and are generally well-accepted within the scientific community.

Performance assessment codes for the near field are being developed by most national repository programs. These codes are fundamentally similar (being based on mass-transfer theory), despite requirements to evaluate different waste-package geometries, engineered barrier materials, and waste forms. Preliminary comparison of the SYVAC-Vault and AREST codes, for example, demonstrated an encouraging consistency in predicted releases for a reference waste package using different conceptual models and geometries.

Before embarking on an extended benchmarking exercise, it would be prudent to develop a plan for conducting such a program. It was a recommendation from this Workshop that a small number of researchers meet to assess the assumptions and calculation bases of current waste-package release codes. From this comparison, a viable plan for conducting meaningful benchmarking of codes can be developed. Current plans are to convene such a working group during 1991.

SUMMARY

There are advantages in achieving high confidence and reliability in isolation of nuclear waste by the engineered barriers system of the near field. The long-term capability of engineered barrier materials to contain and control the release of radionuclides can be thoroughly tested and quantified on the basis of well-accepted models based on geochemical principles and mass-transfer theory. In addition, a "source-term" of radionuclides released from the near field is necessary for credible predictions of the performance of the natural barriers of the far field.

Several important topics in near-field performance assessment were reviewed at this Workshop. Other topics were omitted from this Workshop, including corrosion of waste containers, radiolysis, colloidal transport to name but a few. Conversely, the inclusion of so many different topics led to a larger number of participants than optimal for an informal workshop. Future workshops on near-field performance assessment would do well to limit the agenda to a narrower set of issues and participants.

Nonetheless, occasional meetings among a broad spectrum of scientists is of value in determining the state of integration in near-field performance assessment. Mutual collaboration and criticism promote this integration. This applies to the integration of experimentalists and modelers, who need to shape an overall research program that is directed and efficient. But it also applies to expanded coordination among national repository programs, as well as separate national programs focusing on the disposal of high-level and low-level radioactive wastes. The acknowledged differences among types of host rocks, designs, and materials cannot be allowed to obscure fundamental similarities in the performance assessment models and data requirements.

DISCUSSION ON FUTURE DIRECTIONS AND NEEDS

Patrik Sellin, SKB Sweden

The importance of radionuclide reactions with aluminum silicates was discussed. Sorption and co-precipitation of radionuclides with clay are very important processes for limiting their release, but data for such reactions are not available. It was agreed that this was a field for further research.

The question whether the near-field should be given more attention because it is easier to characterize, model and provides much more safety was raised. The conclusion was that we have to study the near-field/geosphere interaction more closely. The near-field behaviour is very much dependent on the geological environment. The near-field consists of engineered barriers, which, although they can easily be studied in laboratory experiments, never have been tested for the time-periods considered. The gradients in the near-field (thermal, chemical) are initially much steeper than those in the far-field. Although, the normal behaviour of the near-field may be simple to model is it very difficult to predict the unanticipated behaviour (human intrusion, faults ...).

The modelling of the behaviour of a repository in salt is very different compared to granite, clay and tuff modelling. In a salt repository, the salt itself has the best capacity of limiting radionuclide release to the biosphere. Therefore, it is impossible to make comparisons of codes used in near-field performance assessment in salt to those used in other concepts. However, for the other concepts, could a benchmarking exercise be valuable, if host rock and design are similar.

The release rate of radionuclides from the waste package is governed either by the alteration rate of the matrix (spent fuel or glass) or by the solubility of the nuclide and the waterflow. It is important to understand the mechanisms of matrix alteration to be able to determine which of the to processes that dominates. Today, we have acceptable data for the solubilty of pure actinide phases, but data is lacking for some of the fission products, which may account for a high percentage of the dose release. Data is also lacking for the solid solutions that may form and give much lower release rates for some radionuclides.

There was some discussion about the time dependence of the environment and the use of natural analogues in near-field performance assessment. Natural analogues studies are very important for the understanding of the processes that take place in a repository, but it is very difficult to get any valuable quantitative data from such studies.

There was agreement among the participants that international co-operation in the field of Near-Field Performance Assessment is important and valuable, but a pure code-intercomparison exercise seems premature today. A discussion forum on conceptual models with a limited number of participants (10) is a better idea and such group could also discuss future forms of cooperation.

MONDAY, OCTOBER 15

9:00-9:45	Coffee/Introductions by Organizing Committee (Informal)	
9:45-10:00	Opening of Workshop Welcoming Address by ENRESA	Gago/ Spain Ulibarri/ Spain
10:00-11:00	Technical Presentations on National HLW Programs for Near-Field Performance Assessment Sweden - P. Sellin/ SKB Canada - L. Johnson/ AECL Belgium - G. Volckaert/ CEN/SCK Japan - S. Masuda/ PNC France - S. Voinis/ CEA	Gago/ Spain
11:00-11:30	*Break*	
11:30-13:00	Technical Presentations on National Programs(con't) Switzerland - I. McKinley/ Nagra Finland - T. Vieno/ VTT Spain - M. Cuñado/ENRESA United States - R. Levich/ USDOE Germany - R. Storck/GSF United Kingdom - S. Manton/ BNFL NEA - H. Wanner/ NEA	Sellin/ Sweden
13:00-15:50	INDEPENDENT ACTIVITIES	
15:50-16:00	Introduction to Technical Sessions	Apted/USA
16:00-16:45	INVITED TALK "Post-Emplacement Environment"	Murphy/ USA
16:45-17:30	Open Discussion	Sharland/ UK
17:30-18:00	INVITED TALK "Benchmarking"	Grogan/ UK
18:00-18:30	Open Discussion	Johnson/Canada
18:30	END OF FIRST DAY	

TUESDAY, OCTOBER 16

9:00-9:30	INVITED TALK "Glass Release"	Grambow/Germany
9:30-10:15	Open Discussion	Petit/France
10:15-10:45	INVITED TALK "Spent-Fuel Release"	Garisto/ Canada
10:45-11:30	Open Discussion	Vieno/ Finland
11:30-11:45	*Break*	
11:45-12:15	INVITED TALK "Solubility"	Nitsche/ USA
12:15-13:00	Open Discussion	Bruno/ Spain
13:00-16:00	INDEPENDENT ACTIVITIES	
16:00-16:30	INVITED TALK "Near-Field Transport Processes"	Neretneiks/ Sweden
16:30-17:15	Open Discussion	Conca/USA
17:15-17:45	INVITED TALK "Coupled Processes"	Jamet/France
17:45- 18:30	Open Discussion	Park/USA
18:30	END OF SECOND DAY	
20:30	*WORKSHOP BANQUET (All Invited)*	

WEDNESDAY, OCTOBER 17

9:00-9:30	INVITED TALK "Integrated Near-Field Assessment"	McKinley/ Switzerland
9:30-10:15	Open Discussion	Cernes/France
10:15-10:45	INVITED TALK "Sensitivity Analyses and Validation"	Umeki/ Japan
10:45-11:30	Open Discussion	McGrail/USA
11:30-11:45	*Break*	
11:45-12:30	INVITED TALK "Future Directions and Needs"	Apted/ USA
12:30-14:00	Open Discussion	Sellin/ Sweden
14:00-14:10	Closing Remarks	Gago/ Spain
14:10	END OF WORKSHOP	
14:10-16:30	**Meeting on Proceedings Volume**	**Speakers and Discussion Leaders**

WORKSHOP ON NEAR-FIELD PERFORMANCE ASSESSMENT

Madrid, Spain
October 15-17, 1990

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Stefan Sehlstedt, Tomas Stark
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1. The application of PIE techniques to the study of the corrosion of spent oxide fuel in deep-rock ground waters
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R S Forsyth
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January 1991

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Plutonium solubilities
I Puigdomènech[1], J Bruno[2]
[1]Enviromental Services, Studsvik Nuclear, Nyköping, Sweden
[2]MBT Tecnologia Ambiental, CENT, Cerdanyola, Spain
February 1991

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Kaj Ahlbom[1], Sven Tirén[2]
[1]Conterra AB
[2]Sveriges Geologiska AB
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Eva Hakami[1], Anders Ekstav[2], Ulf Qvarfort[2]
[1]Vattenfall HydroPower AB
[2]Golder Geosystem AB
January 1991

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Impact from the disturbed zone on nuclide migration – a radioactive waste repository study
Akke Bengtsson[1], Bertil Grundfelt[1], Anders Markström[1], Anders Rasmuson[2]
[1]KEMAKTA Konsult AB
[2]Chalmers Institute of Technology
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Björn Lindbom, Anders Boghammar, Hans Lindberg, Jan Bjelkås
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[1]Starprog AB
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[1]KEMAKTA Consultants Co
[2]Chalmers Institute of Technology

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Royal Institute of Technology, Stockholm, Sweden
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Department of Chemical Engineering,
Royal Institute of Technology, Stockholm, Sweden
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MBT Tecnologìa Ambiental, Cerdanyola, Spain
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August 1991

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Trygve E Eriksen, Daquing Cui
Royal Institute of Technology, Department of
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Department of Chemical Engineering, Royal
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December 1991

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November 1991

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Kaj Ahlbom[1], Jan-Erik Andersson[2],
Rune Nordqvist[2], Christer Ljunggren[2], Sven Tirén[2],
Clifford Voss[3]
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October 1991

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Per Vallander, Jan Eurenius
VBB VIAK AB
December 1991

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C-L Axelsson[1], J Byström[1], Å Eriksson[1],
J Holmén[1], H M Haitjema[2]
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September 1991

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Veijo Pirhonen, Petteri Pitkänen
Technical Research Center of Finland
December 1991

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Karsten Pedersen, Susanne Ekendahl,
Johanna Arlinger
Department of General and Marine Microbiology,
University of Göteborg, Göteborg, Sweden
December 1991

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Kaj Ahlbom
CONTERRA AB

Part B: A numerical study of the combined effects of salinity gradients, temperature gradients and fracture zones
Urban Svensson
CFE AB

Part C: A three-dimensional numerical model of groundwater flow and salinity distribution in the Finnsjö area
Urban Svensson
CFE AB
November 1991

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Björn Lindbom, Anders Boghammar
Kemakta Konsult AB, Stockholm
December 1991