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The feasibility of modelling coupled processes in safety analysis of spent nuclear fuel disposal

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ABSTRACT

The potential of applying coupled modelling in the Finnish safety analysis programme has been reviewed. The study focused on the migration of radionuclides escaping from a spent fuel repository planned to be excavated in fractured bedrock. Two effects that can trigger various couplings in and around a spent fuel repository in Finland were studied in detail; namely heat generation in the spent fuel and the presence of deep, saline groundwaters. The latter have been observed in coastal areas.

A systematic survey of the requirements of coupled modelling identified features that render such migration calculations a challenging task. In groundwater flow modelling there appears to be wide ranging uncertainty related to conceptualisation of flow systems and to the corresponding input data. In terms of migration related chemistry there appear to be large gaps in the underlying thermodynamic database for geochemical systems. Rock mechanical predictions are heavily dependent on knowing the location, structure and properties of dominant fractures; information which is extremely difficult to obtain. Conduction and convection of heat is understood well in principle.

On the basis of this review, it appears that coupled migration modelling may not yet be at the stage of development that would allow its use as a standard modelling tool in performance assessments. However, a firmer basis for the conclusions reached can only be obtained after a systematic modelling exercise on a relevant and real migration problem has been carried out.

FOREWORD

This study forms part of the Public Sector's Research Programme on Nuclear Waste Management in Finland which is funded jointly by the Ministry of Trade and Industry and the Radiation and Nuclear Safety Authority. Performance assessment related issues were covered by Kari Rasilainen. Groundwater flow and heat transfer were reviewed by Auli Niemi. Migration related chemistry was covered jointly by Ari Luukkonen and Markus Olin. Finally, rock mechanics was addressed by Jukka Pöllä. The authors are grateful to David Read for his careful review of the manuscript and for his valuable comments.

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1. INTRODUCTION

The Finnish concept for final disposal of spent nuclear fuel is based on geological isolation deep in the crystalline bedrock (Teollisuuden Voima 1992). The potential radiological impact of disposal is being assessed quantitatively in advance by computational safety analyses. Owing to the long time periods (of the order of hundreds of thousands of years) that must be covered in these analyses, mathematical simulations are the only quantitative way to assess the radiological impact; experimental studies over this time scale are not possible. An additional aspect necessitating the use of mathematical simulations is that the system as a whole is so complicated that it can be approached experimentally only by dividing it into subsystems. However, the simulations require input data that are based on experimental studies.

The credibility of a safety analysis obviously depends on how well the physico-chemical system being modelled is understood and on how well this understanding is represented in the numerical analysis. Both require well-grounded simulation models and input data derived from experiments. Numerous model verification and validation exercises at the subsystem level have helped create confidence in our modelling capabilities. In this report the term ‘verification’, refers to the arithmetical accuracy of the model, i.e. that it solves the basic mathematical equations correctly, whereas the term ‘validation’ refers to the realism of the model, i.e. how well the equations actually represent the physico-chemical system being modelled. Verification of a model is, of course, a necessary part of its validation. The international verification/validation exercises conducted to date have covered, for example, groundwater flow modelling (NEA 1992), radionuclide transport modelling in the geosphere (SKI 1984, 1986, and NEA 1996), and radionuclide transport modelling in the biosphere (QuantiSci 1996).

One factor that makes it difficult to construct a model system that is a true reflection of the real repository-bedrock system, is that, in the real system, subsystems may be coupled. Coupling means that changes in one subsystem cause subsequent changes in other subsystems. In many cases coupling occurs in both directions, i.e. the subsystem affected in turn affects the first system. The induced changes in a subsystem may be direct or indirect whereby a third subsystem acts as a link. For spent nuclear fuel disposal, there are two main features that can “trigger” coupled effects. The first is the relatively long-term heat generation by the waste. The second, characteristic of Finnish latitudes, is that future glaciations will inevitably affect the repository-bedrock system.

In this report, coupled processes are discussed from the perspective of the required safety analysis of final disposal of spent nuclear fuel. An attempt is made to analyse the role of coupled processes in the transport of radionuclides from the repository via groundwater along water-carrying fractures. Since this transport depends on both groundwater flow and on the prevailing geochemical conditions, the information needed for transport modelling is substantial. A schematic description of the dominant interactions is given in Fig. 1.

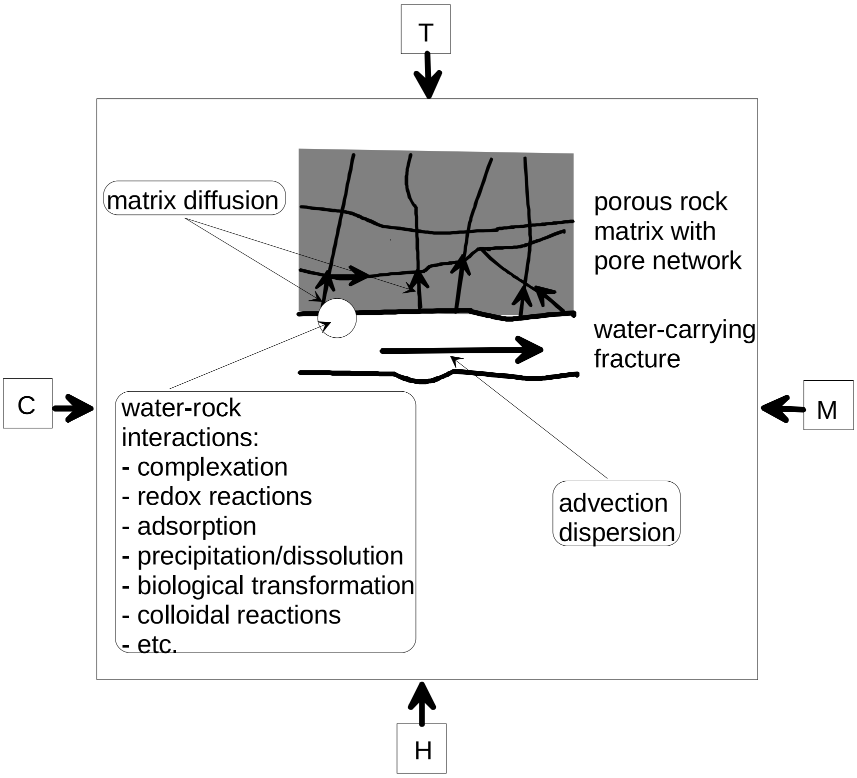
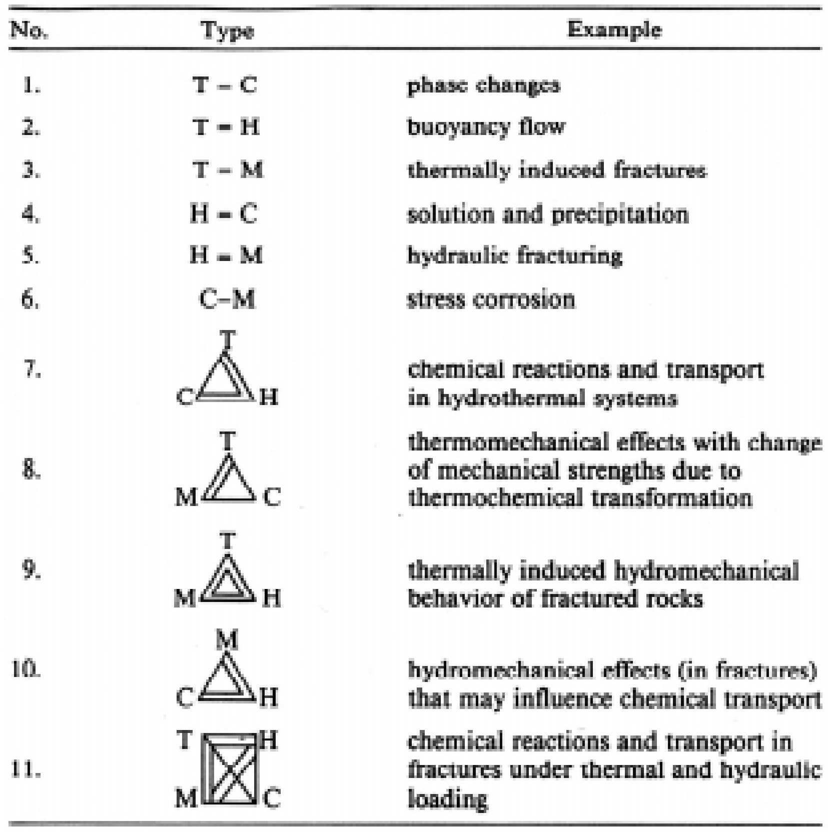


Fig. 1. A schematic view of how thermal (T), mechanical (M), hydrological (H), and chemical (C) effects act on a radionuclide transport system in fractured bedrock. Note that water-rock interactions in the rock matrix are not necessarily the same as in the fracture.

Coupled processes relevant to the behaviour of a repository-bedrock system are thought to arise from four main perturbations: thermal (T), hydrological (H), mechanical (M), and chemical (C) (Tsang 1987). These effects can be combined into eleven types of coupling of varying strength (Table 1). The phenomena included are, for the most part, well known. For example, the coupling T->C includes chemical thermodynamics (e.g. thermally induced phase changes), T->H includes thermally induced buoyancy flow of groundwater (i.e. convection), and T->M includes thermomechanical effects in the bedrock (e.g. thermally induced cracking).

Table 1. Types of coupled processes; T is thermal, M is mechanical, H is hydrologiacl and C is chemical coupling. A single line indicates weak, and double line strong coupling (Tsang 1987).



No.	Type	Example
1.	T – C	phase changes
2.	T = H	buoyancy flow
3.	T – M	thermally induced fractures
4.	H = C	solution and precipitation
5.	H = M	hydraulic fracturing
6.	C–M	stress corrosion
7.	T C H	chemical reactions and transport in hydrothermal systems
8.	T M C	thermomechanical effects with change of mechanical strengths due to thermochemical transformation
9.	T M H	thermally induced hydromechanical behavior of fractured rocks
10.	M C H	hydromechanical effects (in fractures) that may influence chemical transport
11.	T H M C	chemical reactions and transport in fractures under thermal and hydraulic loading

The objective of this work is to review present capabilities in modelling coupled processes relevant to radionuclide transport. We will focus on approaches that have been developed sufficiently such that a significant improvement in safety analyses can be expected from applying them. Thus, we emphasise the practical issues of defining boundary conditions in model validation and the availability of reliable input data. Specific objectives are:

- to describe relevant couplings in a systematic way,
- to address where the simplified direct couplings currently used in performance assessments are defensible and where a more detailed analysis is required,
- to address whether there are prerequisites for these more detailed analyses, e.g the feasibility of obtaining sufficient data.

Even though a large number of sophisticated and powerful coupled models have been developed during the last decades, their current applicability to field scale radionuclide transport modelling depends on how well the issues of model validation and provision of sufficient data can be addressed.

This report is structured as follows. In Chapter 2 a general description is given of the final disposal of spent nuclear fuel according to the Finnish concept together with the main features of the safety analysis. In Chapter 3 a brief overview is given of the basic thermal, hydrologic, mechanical and chemical processes in the repository-bedrock system. In Chapter 4 couplings between the basic effects that are most relevant to safety analysis are discussed in quantitative terms. Understanding these couplings is a prerequisite for understanding the final stage of radionuclide transport modelling. In Chapter 5 the application potential of relevant coupling methods in support of a safety analysis for spent nuclear fuel disposal is discussed. This includes the availability of suitable codes and input data. Experience gained from participating in international coupled model validation projects such as CHEMVAL (Falck & Read 1996) and DECOVALEX (Jing et al. 1996) are central. Recommendations for future work are given in Chapter 6.

2. FINAL DISPOSAL OF SPENT NUCLEAR FUEL

2.1 DISPOSAL CONCEPT

The aim of disposal is to isolate the wastes from the biosphere by placing them into a deep repository excavated in a stable geological unit (Teollisuuden Voima 1992). Isolation results from the granitoid bedrock itself and the technical release barriers constructed around the waste in the repository.

Geological disposal is meant to be final in the sense that after placing the wastes in the repository there is no plan to retrieve them. Retrieval is technically possible but at high cost. Geological disposal is also meant to be final in the sense that the radiological safety of the disposal is based on passive ”laws of nature” rather than continuous human activity. The fact that spent fuel is radioactive means, in practice, that the radiological impact of the waste decreases with time, thus also lowering the isolation requirements of the barrier system with time.

All spent fuel produced in Finland, both in the Loviisa[1] and Olkiluoto nuclear power plants, is planned to be disposed of in a single repository excavated at a depth of approximately 500 m in granitoid bedrock. A disposal depth of 500 m prevents direct radiation to the ground surface and also maintains stable geochemical conditions around the repository e.g. during future glaciations. In addition, the chosen disposal depth protects the repository against mechanical erosion of the surface of the bedrock caused by repeated glaciations and also against the effects of human activity (e.g. accidental intrusion).

Because the repository for spent fuel will be excavated below the water table, the main transport route for radionuclides released from the repository will be along water-carrying fractures. Individual fractures form a network of inter-connected fractures that eventually will intersect fracture zones which act as ”highways” for radionuclides migrating towards the biosphere. Highly conductive fracture zones possess high flow velocities (m/a) as well as high volumetric flows (m^3/a). The main role of the technical release barriers in the repository is to limit the migration of released radionuclides along water-carrying fractures and fracture zones. In actuality, the siting of the repository is, to a considerable degree, determined by the need to avoid highly conductive fracture zones.

According to the current Finnish disposal concept, eleven spent fuel bundles will be placed intact inside a copper-steel canister (Vieno & Nordman 1996). The inner steel layer provides the mechanical strength required, and the outer copper layer the necessary corrosion protection; an ”eternal” canister will not be needed

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[1] The reactors of the Loviisa nuclear power plant were acquired from the former USSR. The owner of Loviisa NPP, Imatran Voima Oy, made initially contractual arrangements for the whole fuel cycle service from USSR, including the return of spent fuel. The Finnish Parliament issued an Amendment of the Nuclear Energy Act in 1994 requiring domestic final disposal of all nuclear wastes produced in Finland, and spent fuel shipments to Russia were halted after 1996.

because the activity of the waste decreases with time. The canisters will be placed one by one into vertical deposition holes drilled from the underground tunnels of the repository. The canisters will be surrounded by blocks of compacted bentonite. The bentonite acts mainly as a mechanical release barrier because it will swell when wet, thereby closing any proximal water-carrying fractures. Therefore, migration through the bentonite will take place by diffusion. Finally, after the canisters have been placed in the deposition holes, the repository tunnels will be filled with a mixture of crushed rock and bentonite to limit groundwater flow along the tunnels. The last release barrier for radionuclides is the bedrock itself with its potential dilution and retardation properties. This system of multiple, subsequent barriers (multibarrier system) is shown schematically in Fig. 2.

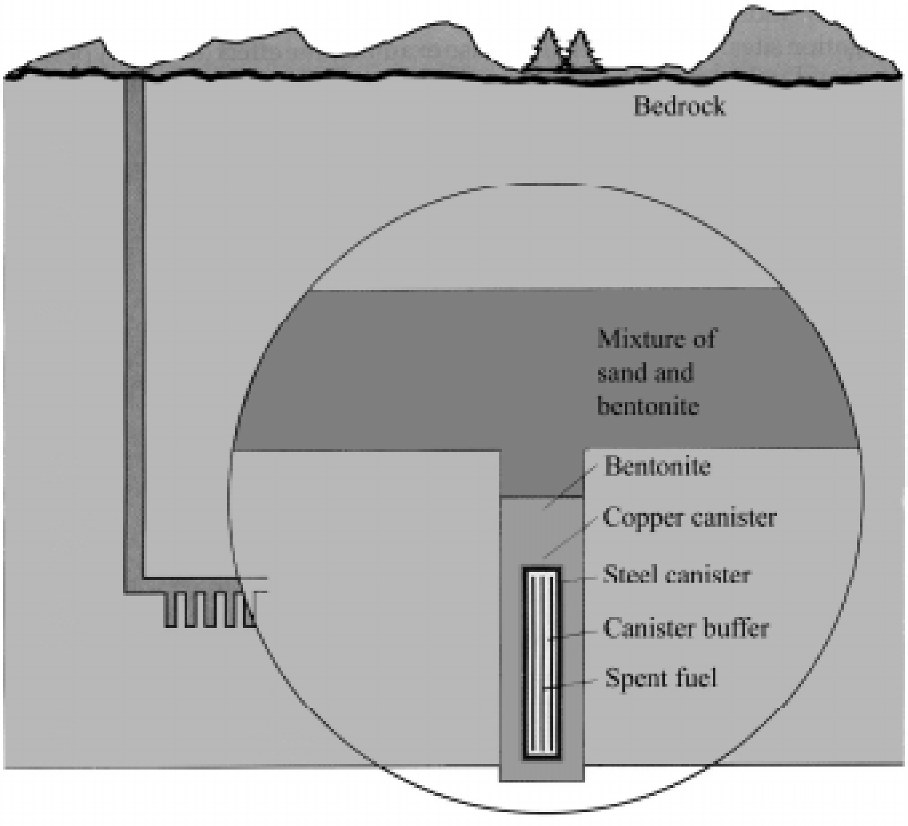

Fig. 2. The multibarrier concept for spent nuclear fuel disposal (Teollisuuden Voima 1992).

2.2 SAFETY ANALYSIS OF THE DISPOSAL OF SPENT FUEL

Methodology

Analysis of the radiological safety of spent fuel disposal is performed prior to the disposal. This approach offers a rational basis for authorities to evaluate the acceptability of the suggested disposal concept. Also, repeated safety analyses provide a quantitative basis for technical ”fine-tuning” of the disposal concept.

Quantitative assessment of radiological safety (or radiological impact) is conducted in consecutive steps. The most important step in the Finnish approach is the determination of calculation scenarios, i.e. outlining a representative set of possible evolutionary futures of the repository-bedrock system. Formal methodologies have been developed for the purpose of constructing scenarios by systematically combining individual ”features, events, processes”, or FEP’s (e.g. Eng et al. 1994, Chapman et al. 1995). After the scenarios have been determined, the radiological consequences are calculated for each scenario. The reliability of this consequence simulation step depends mainly on two factors. First, on the representativity and reliability of the input data and second, on validation of the simulation models and the modelling concepts. The final step of a safety analysis comprises comparison of the results obtained with the safety criteria set by the authorities. Fig. 3 shows the approach used in the Swedish SITE-94 safety analysis and illustrates the methodology as well as the accumulation of uncertainties through the different steps of the analysis.

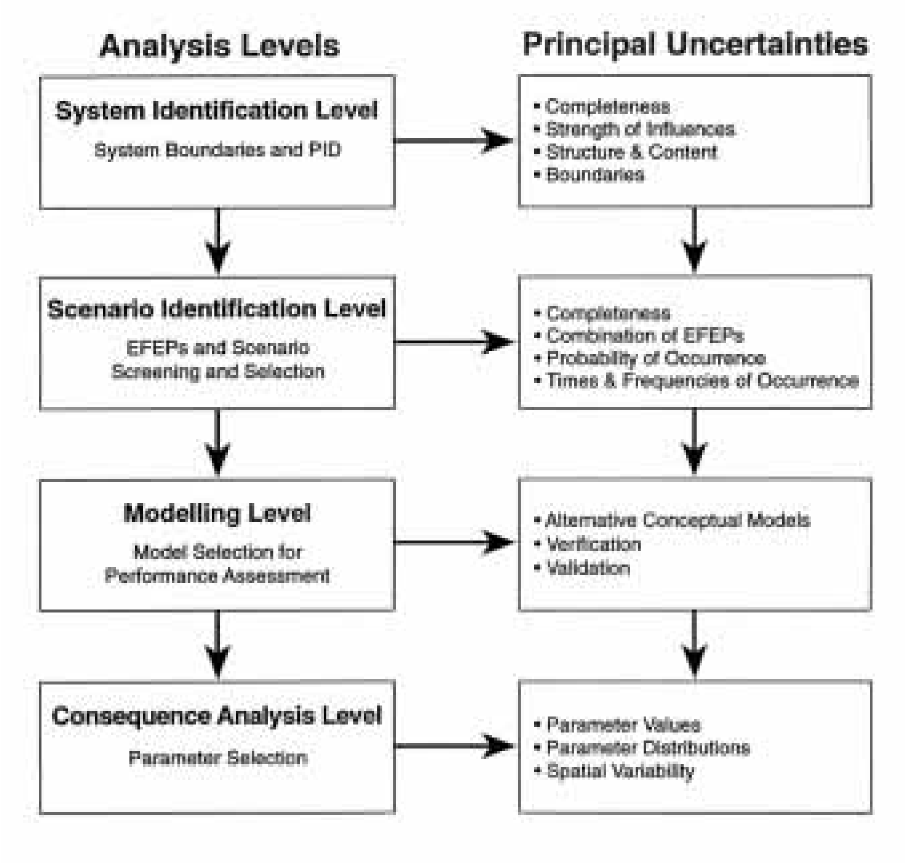

Fig. 3. Schematic description of analysis methodology and the accumulation of uncertainties in SITE-94 safety analysis (Chapman et al. 1995).

The calculation models used in safety analyses are by necessity simplified representations of the repository-bedrock system. The simplifications are intended to be conservative, i.e. in a manner that over-predicts the radiological impact. The general approach to simplification means that only the most essential mechanisms are included in the analysis. The conservativity principle, in turn, means that all those processes that can contribute to radionuclide release and transport must be discussed, whereas those possibly contributing to additional radionuclide retention can be ignored. Accordingly, the inclusion or exclusion of a particular process in a performance assessment depends on its overall potential in accelerating or retarding migration, rather than on the level of current understanding of the process.

The conservative simplification logic, although reasonable as such, is not without problems. One extreme outcome of excessive application of the logic is that the simulations become over-simplified and, thus, fail to reproduce the real behaviour of the repository-bedrock system. The ultimate cause of this is that the system being modelled is so complicated that it is not always easy to see whether the inclusion or exclusion of a particular modelling concept, which may be conservative in a subsystem, will also be conservative at the whole system level.

The conservativity principle is applied throughout a safety analysis, which means in practice that scenarios, modelling concepts and input data for the calculation models are chosen systematically in such a way that the release of radioactivity to the biosphere will be over-predicted. Applying this principle is justified because, owing to the long time scales that must be considered, there will inevitably be uncertainties in the analysis and also, because of the complexity of the system being modelled, it must be simplified in any case. As a result, the main aim of a safety analysis is not to produce a prediction of the highest possible accuracy and probability (as in, for example, a weather forecast), but rather to extrapolate alternative, internally consistent evolutionary histories of the repository-bedrock system into the future. In other words, a safety analysis is essentially based on “if … then” -logic.

Main mechanisms in the migration of radionuclides

The most central features of the disposal system affect both the definition of scenarios and the validation of simulation models. Heat production in the spent nuclear fuel, and phenomena affecting the water-borne migration of radionuclides are particularly important.

Spent nuclear fuel contains a considerable amount of short-lived fission products which means that the radioactivity and the induced heat production are functions of time. Immediately after the spent fuel is removed from the reactor, heat production decreases almost two orders of magnitude in few days as the very short-lived fission products decay, but after this period heat production decreases more slowly (Anttila 1992). Fig. 4 shows heat production as a function of time for one burn-up value of spent fuel. Heat production of the spent fuel is one factor that affects the planned packing density of the waste within a repository. The starting point in thermal optimisation is that the temperature of the compacted bentonite surrounding a spent fuel canister should not exceed 100 °C for long periods of time (Raiko 1996).

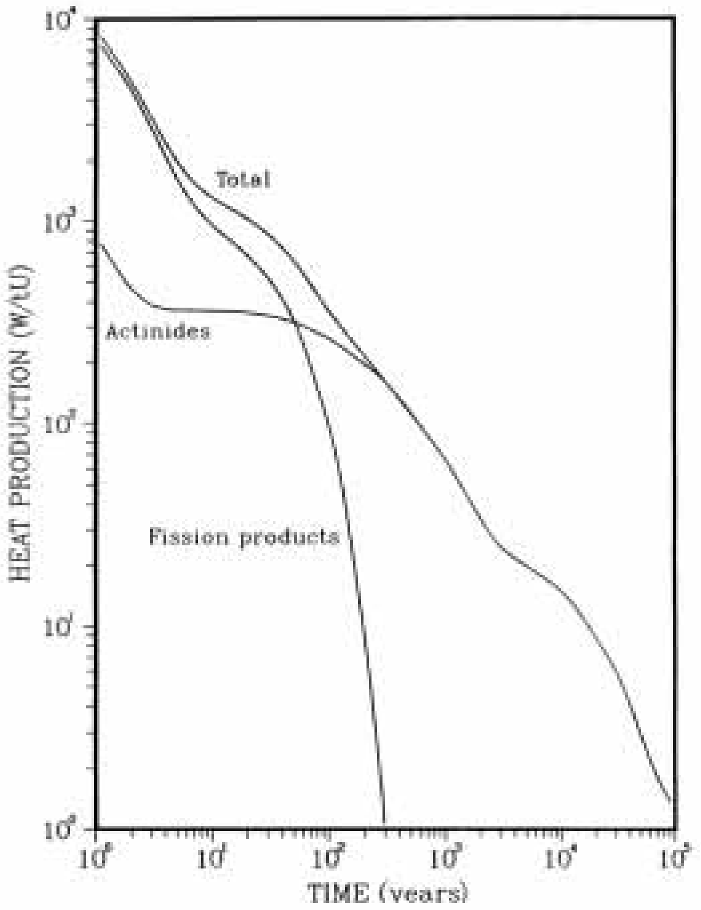

Fig. 4. Heat production of spent fuel (burn-up 36 MWd/kgU) as a function of cooling time (modified after Anttila 1992). The extremely rapid decrease in heat production immediately after the spent fuel is removed from the reactor is not shown in the graph.

Assessment of the migration of radionuclides from the repository into the biosphere is conducted in several consecutive steps. Determining the source term is the first step. Mass flows of corroding agents, carried by groundwater advection in the bedrock and by diffusion through the bentonite onto the canister largely define the lifetime of the canister. After the canister has been corroded, the release rate of the radionuclides depends mainly on two factors: the elemental solubility (g/m^3) and the volumetric flow of groundwater (m^3/a). The nuclide-specific release rate (g/a) is directly the product of these two parameters. The release rate depends also on the dissolution of the waste form.

When assessing the migration of radionuclides through the technical release barriers and in the bedrock, one must know the advection and dispersion of groundwater that acts as the carrier for the radionuclides and the retardation mechanisms of the radionuclides in the bedrock-groundwater system. Knowing advection and dispersion means knowing the flow field of the water, which in turn requires detailed groundwater flow modelling of the system. The retardation mechanisms considered in the safety analyses relevant to this programme are sorption and matrix diffusion.

Sorption is a non-specific term for the various physico-chemical mechanisms that bind radionuclides onto the minerals along the transport route, for example, ion exchange and surface adsorption (e.g. Banwart 1997). The ability of sorption to attach nuclides onto mineral surfaces depends on the radionuclide itself, or more precisely, on its species, the minerals, and the geochemical conditions, e.g. Eh, pH, and ionic strength. To quantify sorption one must know the prevailing chemical conditions as these will control the partitioning of a radionuclide between the solid and water. This, in turn, requires a geochemical interpretation of the bedrock-groundwater system since geochemical conditions determine speciation. To date, Finnish safety analyses have only considered reversible sorption, i.e. the nuclides are not assumed to attach permanently onto mineral surfaces, which is intended to accord with the conservativity principle.

Matrix diffusion (~microdispersion) is essentially molecular diffusion of the substances in the porewater of the rock matrix. Being a physical phenomenon it acts on all aqueous species. As a result of matrix diffusion, the radionuclides, initially only in the flowing groundwater, will be dispersed into stagnant porewater. Ideally, the huge pore surface of the porous rock matrix will gradually be exposed for sorption to occur. Sorption, itself, retards the diffusion process by binding radionuclides onto the newly exposed pore surfaces: the higher the sorption, the slower the diffusion. As a result of these retardation mechanisms, the concentration of radionuclides in the flowing groundwater decreases and the net effect is retention of the migrating radionuclides.

2.3 COUPLED PROCESSES IN THE SAFETY ANALYSIS

The treatment of coupled processes in Finnish safety analyses has also followed the overall conservativity principle. To date the analyses (Vieno et al. 1992, Teollisuuden Voima 1992, Vieno & Nordman 1996) have mostly been based on direct one-way coupling. For example, the effect of temperature on advection has been taken into account in this manner (Vieno & Nordman 1996). Another example is the effect of groundwater chemistry on the retardation of radionuclides where a change in chemistry is described by a change in sorption. The effects on flow pathways due to changes in stress field after excavation have been taken into account by means of sensitivity studies (Vieno & Nordman 1996).

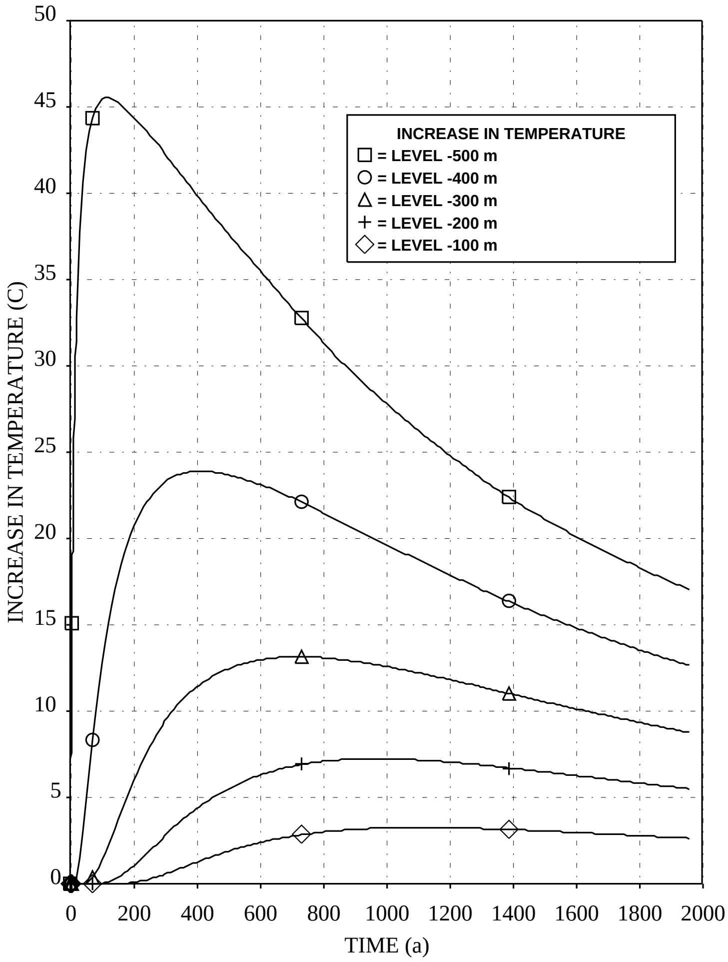

Fig. 5. Temperature rise in bedrock at repository level and at four depths directly above the repository. The reference point is the middle of the repository which represents the maximum temperature (modified after Raiko 1996).

The repository for spent nuclear fuel produces considerable amounts of heat. Thermal coupling has already been considered in safety analyses, although in a simplified manner. For a more detailed analysis of thermal coupling, two factors are noteworthy. First, temperature is clearly a function of time, which in practice means that temperatures are at their maximum while the canisters are probably still intact. In other words, thermal coupling is strongest for special release cases in which individual canisters start leaking earlier than overall corrosion rate studies would indicate. Another essential point in thermal coupling is that temperature is also a function of space in the sense that the highest temperatures are within the repository or in the immediate vicinity, i.e. in the near field, whereas the temperature rise in the far field is quite limited (Raiko 1996). Fig. 5 shows the temperature rise in bedrock at different depths directly above the repository; the middle of the repository was chosen as the reference point because at this point the simulated temperature is at a maximum at the repository level. In Fig. 5 one can see that the temperature rise in the bedrock is at most 45 °C, and that the closer to the repository the point of observation is the sooner this maximum will be reached. According to the figure, the maximum temperature will, however, always be reached within the first 1 000 years after closing the repository.

Groundwater flow and, hence, transport, as described by advection and dispersion processes, takes place in water-conducting fractures. These are highly heterogeneous in nature. In addition, this heterogeneity is subject to changes due to the coupled processes involved. Most notably, changes in stress field due to repository construction are likely to alter the pathways. The order of magnitude of these hydro-mechanical couplings in relation to other issues in radionuclide transport - e.g. the uncertainty in the pathway prediction in general - is of considerable interest when coupled processes are addressed.

The current candidate sites for a spent fuel repository in Finland comprise two inland sites and two coastal sites on the Baltic Sea; the site is planned to be selected by the year 2 000. Investigations at both coastal sites, Olkiluoto and Loviisa, have shown the presence of deep, saline groundwaters. The coastal sites rose above the sea as islands about 2 600 and 4 000 years ago, respectively; at both sites there is a continuing land uplift after the last glaciation, of 6 and 3 mm/a, respectively. There is an aspect of hydro-mechanical coupling in this gradual “opening” of the fractured bedrock.

At coastal sites it is usual to have layered groundwaters with the more recently infiltrated fresh water lying on top of the older saline water. The chemical coupling the saline groundwaters bring about must be taken into account when considering the migration of radionuclides. The salinity of the water affects advection because the density of saline water is higher and also, possibly, retardation via sorption, because for some elements sorption is lower in saline than fresh water (Hakanen & Hölttä 1992). Salinity also affects the speciation of aqueous components and the solubility of solids, though the extent to which this occurs depends on the type of brine considered.

3. OVERVIEW OF COUPLED PROCESSES

3.1 BACKGROUND AND TERMINOLOGY

Transport modelling depends on the many preceding analyses which provide the necessary understanding and input data, and, therefore, these should be considered first. The most important are modelling of the groundwater flow field and calculations of radionuclide solubility in groundwater. These factors, in turn, depend on hydrologic, chemical and mechanical processes that can be affected by the elevated temperature of the repository. Solute transport equations will be discussed separately in section 3.3 after the basic processes have been described.

A schematic representation of the various physico-chemical interactions present in the repository-bedrock system is given in Fig. 6.

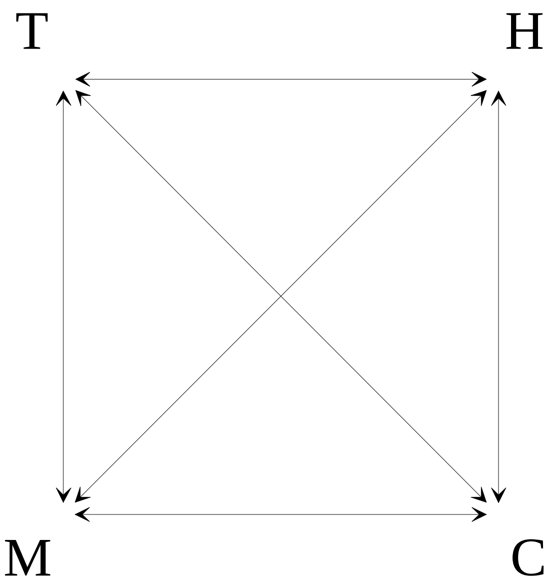

Fig. 6. Potential coupled interactions affecting the transport of radionuclides from a leaking repository (modified after Tsang 1987). T is thermal, H is hydrological, C is chemical, and M is mechanical system.

3.2 BASIC PROCESSES IN A REPOSITORY CONTEXT

The fundamental physico-chemical processes represented in the corners of Fig. 6 are described briefly below. The basic equations are presented in one dimension (where possible) to simplify the notation and the subsequent introduction of possible couplings. These equations are derived from the principles of non-equilibrium thermodynamics, in which it is assumed that a certain flux is always caused by a corresponding thermodynamic driving force. If the flux depends linearly on the force, it is quite straightforward to develop general theories. Most generalised driving forces are gradients of some intensive quantities like pressure, density, temperature or chemical potential; fluxes are typically linearly dependent on these gradients (cf. Fick's and Darcy's laws). For small changes in the gradients, the assumption of linearity appears sensible. For a more detailed discussion on this topic, the reader is referred to de Marsily (1987).

Important departures from linear dependence occur in the case of chemical reactions, in which the driving force is chemical affinity. In most cases geochemical reactions are so far away from equilibrium that the flux may depend exponentially on the affinity. In addition to this theoretical problem, the lack of kinetic rate coefficients makes it difficult to apply the principles of non-equilibrium thermodynamics in practice. Therefore, chemistry, unlike the other phenomena included in Fig. 6, is typically described by assuming chemical equilibrium during any short period of time. When conditions change due to other forces, a new equilibrium state is calculated.

3.2.1 Groundwater flow

The governing equation for saturated groundwater flow is often written in terms of hydraulic head as (e.g. Huyakorn & Pinder 1983):

$$\frac{\partial}{\partial x_i} K_{ij} \frac{\partial h}{\partial x_j} = S_s \frac{\partial h}{\partial t} \tag{1}$$

where h = hydraulic head (m), x_i, and x_j = spatial coordinates (i, j=1,2,3) K_{ij} = components of the hydraulic conductivity tensor (m/s), and S_s = specific storage coefficient of the medium (1/m). Equation (1) gives the distribution of hydraulic head in space and time as a function of the transmissive and storage properties of the system. Hydraulic head is a derived quantity that assumes constant density of the flowing fluid and is defined as:

$$h = \frac{p}{\rho g} + z \tag{2}$$

where p = fluid pressure (Pa), ρ = fluid density (kg/m^3), g = acceleration due to gravity (m/s^2), and z = elevation from a reference level (m).

The hydraulic conductivity of a medium (K) is a product of the properties of both the medium and of the fluid flowing through it (e.g. Freeze & Cherry 1979, Domenico & Schwarz 1990):

$$K = \frac{k\rho g}{\mu} \tag{3}$$

where k = intrinsic permeability describing solely the medium (m^2), μ = dynamic viscosity of the flowing fluid (kg/m·s).

The specific storage coefficient of the medium, expressing how much water can be released or stored in unit time per unit change in hydraulic head, is a sum of the compressibility of the medium and of the fluid according to (e.g. Freeze & Cherry 1979, Domenico & Schwarz 1990):

$$S_S = \rho g(\alpha + n\beta) \tag{4}$$

where n = porosity of the medium (-), α = compressibility of the rock ($m \cdot s^2/kg$), and β = compressibility of the fluid ($m \cdot s^2/kg$).

Hydraulic head distribution can be solved from Eq. (1), and, hence, the average linear groundwater flow velocity $\bar{v}_i$ in the direction i can be expressed as:

$$\bar{v}_i = \frac{K_i}{n_e} \frac{\partial h}{\partial x_i} \tag{5}$$

where n_e = effective flow porosity, i.e. the fraction of porosity allowing flow.

Equation (1) is commonly used in hydrogeological transport calculations. The assumptions employed in its derivation are those of constant density and viscosity, assumptions that are not true in the case of, for example, non-isothermal flow or flow with variable density due to large concentration differences. The formulation is also not valid for cases where mechanical changes alter the pore space i.e. cases with hydromechanical coupling.

Therefore, when modelling coupled processes where the assumptions of constant density, viscosity and porosity are not valid, the flow equation is expressed in terms of pressure rather than hydraulic head. Thus, the corresponding continuity equation for saturated groundwater flow is (Kipp 1987):

$$\nabla \rho \frac{k}{\mu}\left(\nabla p + \rho g\right) = \frac{\partial(\rho n)}{\partial t} \tag{6}$$

The expressions listed above were originally developed for porous media. In the case of fractured rocks, flow is usually governed by the highly conductive fractures, whereas the rock matrix with a large volume but low overall conductivity acts primarily as a storage component. When describing flow in fractures, equations (1) and (6) are solved either in one or two-dimensional form, separately for each fracture. The earliest and simplest description of flow in individual fractures used the parallel plate analogy, assuming that the fracture can be presented by means of an open space between parallel wall surfaces. Then, for laminar flow conditions, the permeability can be derived to follow the so-called cubic law (Witherspoon et al. 1980)

$$k = \frac{b^2}{12} \tag{7}$$

where b = aperture[1] of the fracture (m).

The assumption of parallel-wall, open apertures is not true in the case of natural fractures. These have rough walls resulting in variable apertures with alternating open and closed sections. The cubic law expression has been modified to include the effects of surface roughness and aperture contact (see e.g. National Research Council 1996 for detailed references). For open fractures with rough walls the expression is modified to (e.g. National Research Council 1996):

$$k = \frac{1}{f}\frac{b^2}{12} \tag{8}$$

where f = 1 for fractures with smooth walls, and f > 1 for fractures with rough walls. With fracture walls partly in contact, the expression has been further modified (Brown 1987) to:

$$k = \frac{1}{f}\left(\frac{(1-d)}{(1+d)}\right)\frac{b^2}{12} \tag{9}$$

where d = ratio of surface area in contact with the opposite wall to the total fracture surface area. Determination of values for f and d is a major obstacle for field studies, where a large number of fractures need to be modelled and the critical factor for their overall conductivity is their connectivity.

Some recent studies also use a one-dimensional formulation for flow in individual fractures. In doing so the heterogeneous flow within the fracture plane is ‘collapsed’ into a one-dimensional channel or pipe (e.g. Cacas et al. 1990, Nordqvist et al. 1996 etc.).

How well is groundwater flow understood?

In characterising groundwater flow in fractured media difficulties exist both in conceptualising the system, in choosing an adequate model to represent it and in obtaining meaningful model parameters.

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[1] The term ‘b’ for aperture is used here in line with standard usage in hydrology. Later in the migration discussion, ‘2b’ will be used for aperture, in line with standard usage in performance assessments.

When modelling microscopic flow at the scale of individual fractures, full Navier-Stokes equations have been used (e.g. Mourzenko et al. 1997) though other workers have employed assumptions of, for example, a locally valid cubic law and the Darcy approximation (Tsang 1984, Thompson & Brown 1991). Selection of the appropriate microscopic flow equation becomes relevant when constitutive relations are derived from the starting point of detailed flow geometry in individual fractures.

At larger scales, Darcy type approximations are commonly used. In such cases the main difficulty arises in predicting complicated flow paths i.e. in obtaining parameters for the flow and transport models. The present 'state-of-the-art' in modelling field scale flow reduces to three basic approaches; the equivalent porous medium, fracture network and stochastic continuum approaches. As the relative significance of local heterogeneities decreases with increasing scale, the range of applicability of each approach depends on both the characteristics of the medium and the scale of interest.

The porous medium approach - where the fractured medium is approximated by homogeneous average properties - is applicable at the largest scales where, for example, the effect of major fracture zones is of interest. In fracture network modelling the bedrock is assumed to consist of a network of individual fractures usually generated statistically. Owing to computational constraints, fracture network models are restricted to scales of at most a few hundred metres. The stochastic continuum approach is appropriate at intermediate scales. Variability in borehole hydraulic conductivity data is introduced directly into Monte Carlo type simulation models by using the scale of field measurements as a guide to the scale of the model permeability zones.

Regardless of the model chosen, the fundamental difficulty is in identifying and describing the flow paths using representative model parameters. This is a parameter estimation problem, i.e. how can the global properties of the heterogeneous networks be estimated from local observations. Owing to the roughness of fracture surfaces, there is heterogeneity in the flow and transport paths inside individual fractures and from one fracture to another.

Therefore, the number of parameters to be estimated in describing this heterogeneity becomes extremely large. Usually the properties are given through their statistical characteristics and the resulting modelling predictions are also probability distributions rather than single values. The uncertainty or spread in these estimates is probably one of the largest encountered in radionuclide transport modelling. Subsequently, any refinement in these parameters, due to e.g. coupled hydromechanical or other processes, must be compared against this significant background variation.

3.2.2 Migration related chemistry

In this section we discuss the broad topic of geochemistry from a migration point of view, and, therefore, concentrate mainly on solubility and sorption. However, to obtain a more general starting point, we first briefly describe chemical processes in natural systems from the perspective of reaction kinetics. An introduction to aqueous equilibria is given in the Appendix.

The solubility of a radioelement, for example U, depends on many factors including the composition and properties of the dissolving solid phase, the composition of the solution (pH, Eh etc.) the concentrations of various complexing ligands and the concentrations of other competing metal ions.

The term ‘sorption’ is used loosely in this report to denote adsorption, ion-exchange and a range of other surface interaction processes. In performance analyses, the distinction between various sorptive processes is rarely made and experimentally derived ‘distribution coefficients’ are used which has the effect of lumping all sorption processes together.

Classification of chemical processes

Radionuclides migrate in a reactive manner, i.e. they interact with the water-rock system and go through several chemical and microbiological reactions during transport. These reactions may retard or transform the migrating components.

Chemical reactions that affect the concentration of species may take place solely in the aqueous phase or they may involve both aqueous and solid phases (Fig. 7). Possible reactions can be classified to successive levels (e.g. Rubin 1983). The first level divides reactions in terms of fast and reversible (local equilibrium assumption applies) and slow and/or irreversible (kinetic approach required). Both groups are then further divided into homogenous (aqueous phase) and heterogeneous (aqueous and solid phases) reactions.

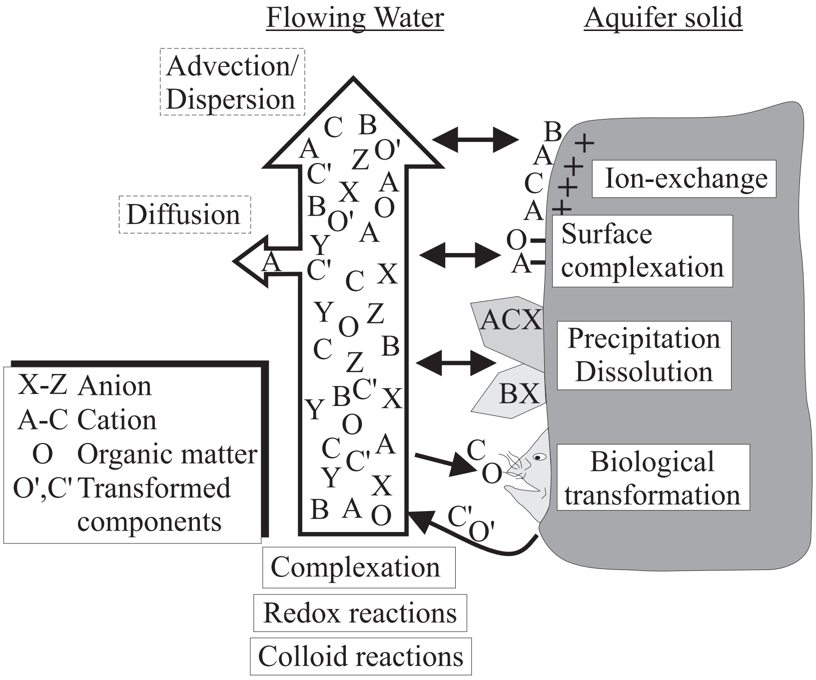

Fig. 7. Possible reactions during the migration of species in a water carrying fracture (modified after Engesgaard 1996).

We may describe the net effect of various reactions with a single equation. The total reaction rate R_i (mol/m^3 s) of a nuclide i is split into heterogeneous, precipitation-dissolution *(min)*, surface complexation *(sclx)*, ion-exchange *(ex)*, and biological transformation *(bio)* terms, and into homogenous, redox *(red)* and complexation *(clx)* terms, such that (cf. Fig. 7)

$$R_i = \left(R_i^{\min} + R_i^{sclx} + R_i^{ex} + R_i^{bio}\right)^{het} + \left(R_i^{red} + R_i^{clx}\right)^{\mathrm{hom}} \qquad (10)$$

If biological activity is disccounted (a possibly major simplification), and if homogenous and surface sorption processes are combined into the aqueous term *(aq),* we obtain an equation where all reactions collected into term R_i^{aq} are considered reversible and all reactions in the term $R_i^{m\,n}$ irreversible.

$$R_i = R_i^{aq} + R_i^{min} \qquad (11)$$

The net rate R_i^{aq} rapidly becomes zero in equilibrium reactions (i.e. the aqueous term reaches equilibrium) and can be eliminated from the total rate considerations. However, the dissolution of a solid species ($R_i^{m\,n}$) is often an irreversible process. For example, with silicate reactions, time spans of tens of thousands of years may be needed to approach zero-level net rate in $R_i^{m\,n}$ (e.g. Steefel & Lasaga 1994).

In performance assessments the main emphasis is on how migrating radionuclides react with the water-rock system and in order not to over-estimate the retardation brought about by these reactions, only reversible adsorption reactions are considered. For example, irreversible precipitation on fracture walls is neglected.

Factors controlling the solubility of migrating species

According to chemical thermodynamics, a system is defined if the following parameters are known:

- temperature,
- pressure,
- total activity of each element,
- any constraint inhibiting the attainment of equilibrium.

Temperature is much more important than pressure in most geochemical systems and affects equilibrium constants, activity coefficients, pressure (≈ fugacity) of gases, and redox reactions. Pressure corrections are usually omitted in geochemical models.

Constraints (e.g. gas fugacity, temperature, Eh, pH, reaction kinetics) are important because they expand the application range of equilibrium chemistry to systems which are only partly in equilibrium (a very common case in nature). A constraint may follow some slow kinetics: a mineral is not formed under given conditions or reactions are too slow.

In heterogeneous systems, a solid phase may be in equilibrium with an aqueous phase. In order to maintain this equilibrium as the conditions in the aqueous phase change, total concentration of a dissolved element must change accordingly. The presence and properties of solid phases (e.g. UO_2, $USiO_4$, $UO_2 \cdot 2UO_3$) limit the solubility of an element: if this element is added to the aqueous phase, it will precipitate and if its concentration is reduced in the aqueous phase, the solid will tend to dissolve. The existence of equilibrium is tested with solubility constants; if the ion product for the dissolution reactions is larger than the solubility constant, precipitation of the solid is thermodynamically possible.

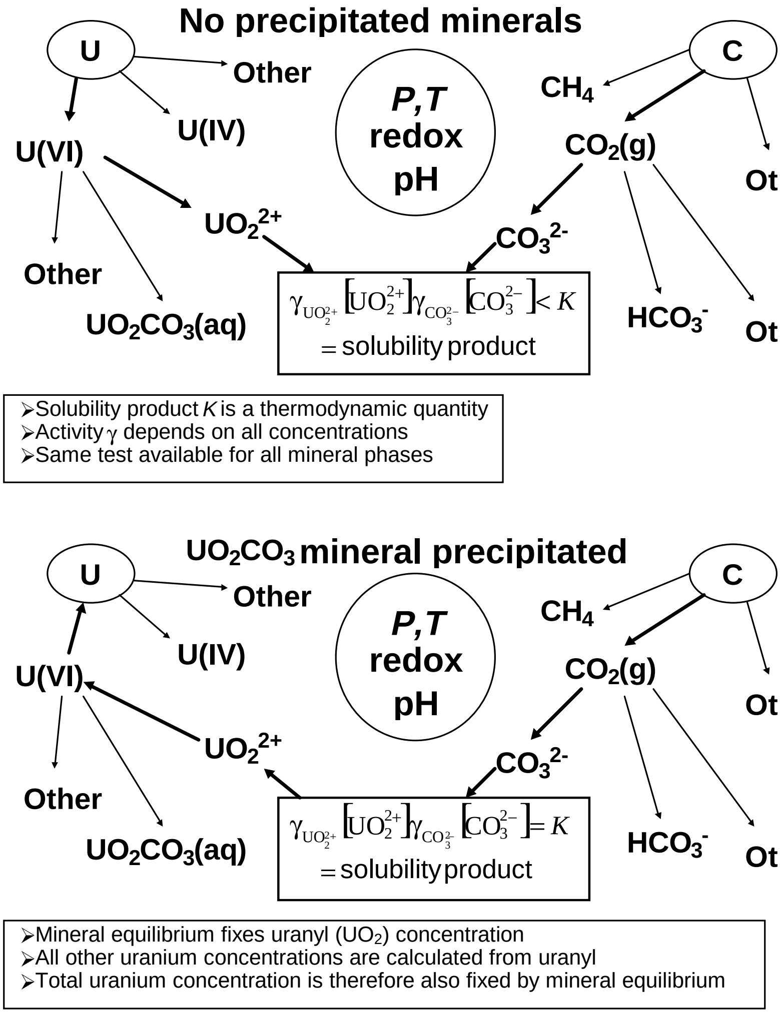

Fig. 8. Uranium solubility and the meaning of solubility product. Physical parameters, temperature and pressure affect the concentrations of all species; activity coefficients and solubility products with temperature being the most important factors. Total concentration affects solubility via the activity coefficients.

The solubility concept is shown in Fig. 8 where under-saturation (above) and saturation situations (below) are shown. The chemical system in Fig. 8 is strongly coupled, and temperature, for example, influences the complete system. Transport processes always affect total concentrations in the system but the ability of a nuclide to migrate is defined via other elements distributed in mobile aqueous species, immobile sorbed species and in solid phases.

Specifically, in the case of uranium, once redox-conditions begin to favour the more soluble U(VI) state rather than the less soluble U(IV), pH becomes an important variable which controls the behaviour of uranium (Ollila 1995, Brookings 1988). Common dissolved complexes are formed with ligands such as carbonate and the anions of organic acids (Grenthe et al. 1997a). In the Finnish candidates for spent fuel repository sites these ligand groups have been observed in the groundwater (cf. Pitkänen et al. 1996, 1999a, 1999b) and are considered relevant.

Approaches to sorption

The following discussion applies mostly to reactions at amphoteric hydrous oxide mineral surfaces because these are known to act as sorbing sinks for migrating radionuclides, and also because the models for these systems are relatively well advanced (e.g. Banwart 1997). Hydrous surfaces obtain negative charge with relative ease, due to H^+ release, and, thus, become attractive to positively charged cations, e.g. UO_2^{2+}.

As compared to the comparatively exact theory for inorganic aqueous chemistry, which is derived from the laws of thermodynamics, mechanistic sorption models have a number of shortcomings. However, they offer a useful means of explaining the properties of species sorbed on surfaces. Present models may be used to at least fit experimental data and there is also some evidence of their predictive power. A report is being prepared within the NEA Sorption Forum on the potential of mechanistic sorption modelling to support performance assessments, see also Olin & Lehikoinen (1997).

In essence, *ion exchange* can take place on any solid surface though it is most often considered in conjunction with interlayer clays. Any replacement of one adsorbed, readily exchangeable ion by another can be called ion exchange (Stumm 1992). This definition excludes mineral transformation reactions on a solid surface, e.g. alteration of calcite ($CaCO_3$) to strontianite ($SrCO_3$). Fine grained minerals having a large specific surface area, such as montmorillonite clays and micas, are especially efficient cation exchangers (Appelo & Postma 1993).

Ion exchange reactions may be described by chemical mass action equations, assuming that the activities of the ions on the solid phases can be approximated, for example, by their mole fractions. In order to calculate the impact of ion-exchange processes on solution composition, the CEC (cation exchange capacity), Ns (sorption site surface density) values for adsorbents, the amount of adsorbents, and selectivity coefficients or binding constants ("equilibrium constants") for each exchange reaction are needed. Anion exchange processes are handled in a manner similar to cation exchange reactions.

There are several options for defining mass-balances and equivalent fractions for selectivity constants (e.g. Appelo & Postma 1993). Vanselow and Gaines-Thomas models are accurate for reactions involving cations of the same valence ($NaX \rightarrow KX$), whereas the Gapon model tends to work better with monovalent-bivalent ($NaX \rightarrow CaX$) exchange reactions (Read & Falck 1997). However, the Gapon Equation does not perform well when several heterovalent cations are present and, thus, the Gaines-Thomas or the Vanselow conventions are generally preferred (Appelo & Postma 1993).

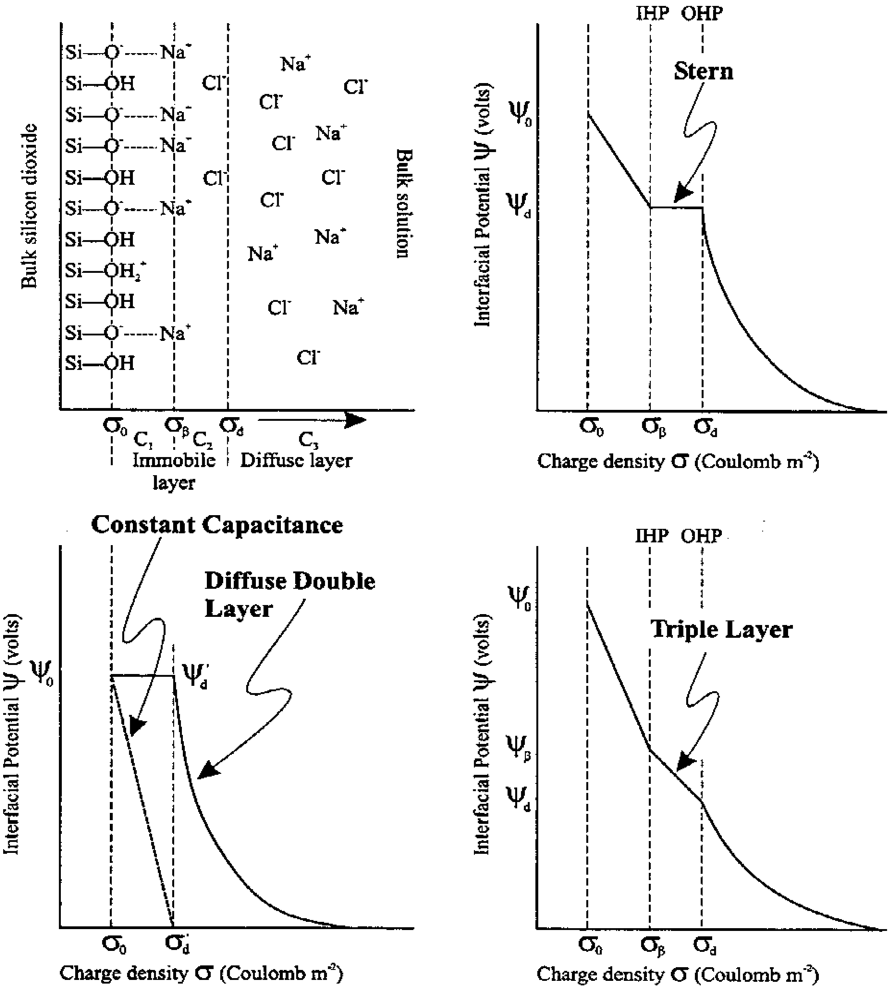

Fig. 9. Schematic illustration of various surface complexation models for an idealised planar quartz–water–sodium chloride interface (modified from Dove 1995, Stumm 1992, Ewart et al. 1992, Davis & Kent 1990). Each layer has an associated interfacial potential, ψ_i, and charge density, σ_i, that determine the inner (C_1), outer (C_2) and diffuse layer (C_3) capacitances (Faraday m^{-2}) by the relationship $C_j = \Delta\sigma_i(\Delta\psi_i)^{-1}$. The magnitude of these parameters decreases with distance from the mineral surface into the solution side of the interface and finally to the bulk solution. In the diffuse double layer, Stern and triple layer models the bulk uncharged solution is beyond the diffuse layer. In the constant capacitance model the bulk solution is considered to start immediately after the immobile layer. IHP = inner Helmholz plane, OHP = outer Helmholz plane.

Surface complexation theories consider adsorbed ions to be located at one or more planes in the interfacial region between a solid oxide and the aqueous phase (Fig. 9). The Gibbs free energy (driving force of chemical reactions - [kJ/mol]) of a surface reaction (sorption) is then defined as a combination of a chemical and a Coulombic term:

$$\Delta G_{sorb} = \Delta G_{chem} + \Delta G_{Coul} \qquad (12)$$

Several approaches to surface complexation modelling have been described (Fig 9). Owing to the complexity of natural systems, empirical approaches have been used widely in geochemical applications (Davis & Kent 1990).

(1) At its simplest level the concentration relationship between an aqueous species and the same species adsorbed on a surface can be described in terms of an isotherm. This assumes that the adsorbed concentration of a species depends solely on the concentration of that species in solution. In the vast majority of cases, measured distribution coefficients represent the low concentration portion of the isotherm where the adsorbed amount depends approximately linearly on the concentration in the solution, see e.g. McKinley & Hadermann (1985). The shapes of adsorption isotherms are often convex, indicating that adsorption sites tend to saturate at higher concentrations. In these cases, the data may be fitted to a multicomponent Langmuir Equation or a generalised exponential isotherm, such as the Freundlich isotherm, see e.g. NEA (1983), McKinley & Hadermann (1985).

(2) Mechanistically, the simplest way to model surface complexation processes is to omit the effect of surface charges and to use ‘intrinsic constants’ [K_{int}, cf. Eq. (12)] as apparent equilibrium constants (unmodified mass action or non-electrostatic modelling). A surface site is then treated in a similar way to an aqueous species. There is an on-going discussion about the need and usefulness of electrostatic corrections (e.g. NEA 1997), because formulations without electrostatic corrections are simpler and, therefore, a smaller set of system constraining parameters is needed. However, there are several electrostatic correction methods available. Constant capacitance and diffuse double layer (DDL) models (Stumm 1992) assume a single charged surface (Fig. 9). In addition to the surface layer, the DDL model also assumes a gradually vanishing diffuse layer, representing the closest distance of approach for all dissociated counter ions (Davis & Kent 1990). Constant capacitance and DDL layer models are combined in the Stern model (Fig. 9). Even more detailed three and four layer approaches have been developed to model electrostatic potential decrease across the solid-water interface.

Sorption in performance assessments

To date, performance assessments have applied experimentally derived parameters that describe the net partitioning of migrating substances between the solid and water phase. A mass-based distribution coefficient K_d (m^3/kg), see e.g. Vandergraaf et al. (1992), is defined as:

$$K_d = \frac{adsorbed\, inventory\, /\, mass\, of\ solid}{inventory\, in\, water\, /\, water\, volume} \tag{13}$$

A surface area based distribution coefficient K_a (m^3/m^2), see e.g. Vandergraaf et al. (1992), is defined as:

$$K_a = \frac{adsorbed\,inventory\,/\,surface\,area\,of\;solid}{inventory\,in\,water\,/\,water\,volume} \qquad (14)$$

In line with the general conservativity principle, sorption in performance assessment is defined to cover rapid attachment of migrating substances on mineral surfaces. Slow and irreversible reactions, e.g. mineralisation and precipitation, are clearly excluded from the term. The parameters used to describe sorption are further assumed to represent solely reversible adsorption.

The conceptual drawback of these experimental K_d values is that they give only the net result, they do not give any direct information about the sorption mechanisms that were taking place in the experiment. All we can say is that they were rapid on the timescale of the experiment. Sorption isotherms have the same shortcoming.

The advantage of the distribution coefficient approach is that, provided the geochemical conditions (or their variability) along the migration route are known, this method offers a feasible way of characterising sorption for a large number of elements, species and conditions. The distribution coefficient describes the net partitioning of the tracer even if we do not understand all of the sorption mechanisms involved. If, on the other hand, the geochemical conditions are not known[2], or if the experimental conditions do not replicate those encountered in the field, then the approach will not provide a meaningful description of migration.

How well is migration related chemistry understood?

From a modelling point of view, all of the approaches discussed above have inherent pros and cons.

The advantage of distribution coefficients is that the concept is simple and the experimental method is well established. A distribution coefficient, however, refers to strictly equilibrium conditions at the constant temperature used in the experiment. It assumes that all aqueous species of a solute have equal affinity for the surface and that all surfaces have equal affinity for aqueous species. The coefficient is highly dependent on the conditions under which it is measured, e.g. pH, Eh, background electrolyte composition, concentrations of dissolved ions and, possibly, competing adsorbents. Thus, one distribution coefficient cannot realistically predict the response of solute adsorption to changes in an aqueous system (Davis & Kent 1990). For this reason ranges of distribution coefficients, measured under different conditions, have been applied in performance assessments.

The advantage of mechanistic models is that they utilise the current thermodynamic understanding of sorption. The models take into account changes

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[2] If the geochemical conditions are not known, then all approaches to model sorption are equally "meaningful".

in aqueous systems. There are differences, however, among the models. The constant capacitance model tends to overestimate ionic mobility in the interfacial region, and strictly, it is applicable only to systems at high, relatively constant ionic strength (Davis & Kent 1990). The DDL model should be applicable at variable and dilute ionic strengths (Davis & Kent 1990). The detailed models are accurate, if they are correctly adjusted, but as a model becomes more complicated, more and more adjusting parameters will have to be defined and measured (cf. Fig. 9).

Rigorously speaking, fitting experimental data to a distribution coefficient, an isotherm model, or a mechanistic adsorption model does not guarantee that adsorption is the only mechanism that accounts for the loss of the solute from water (Stumm 1992). In certain cases precipitation, coprecipitation and other mineralisation reactions may also remove material from water.

Surface complexation modelling is used mainly to justify distribution coefficients obtained from empirical studies. If only for reasons of data availability, mechanistic sorption modelling cannot, in most cases, replace the empirical distribution coefficient approach. In well defined cases, it can be used as a tool to predict adsorption on solid phases, e.g. hydrous ferric oxides (Dzombak & Morel 1990). Many geochemical modelling codes like HYDRAQL (Papelis et al. 1988) contain all of the modelling methods presented above. Hydrogeochemically coupled codes usually implement non-electrostatic or DDL approaches, e.g. reactive transport codes like OS3D and GIMRT take surface reactions into account via a non-electrostatic model (Steefel & Yabusaki 1996), while PHREEQC implements both non-electrostatic or DDL models (Parkhurst 1995).

Concerning practical site-specific applications, it should be noted that surface complexation and ion-exchange modelling requires experimental data on material from the study site for appropriate model parameterisation (Parkhurst 1995). With a performance assessment for many elements and the many possible geochemical conditions that must be covered, these data will be extremely difficult to obtain.

3.2.3 Transport of heat

The governing equation for the transport of heat in a water saturated porous medium can be expressed as:

$$(\rho c)_s \frac{\partial T}{\partial t} = \nabla (K_H \nabla T) + (\rho c)_f \bar{q} \nabla T \tag{15}$$

where T = temperature (°K), $(\rho c)_s$ and $(\rho c)_f$ are density weighted heat capacities of the solid and fluid (joule/(m^3·°K)), K_H = effective heat conductivity of the rock-water mixture (joule/(m·s·°K)), and $\bar{q}$ = water flux (volumetric flow rate per unit area) (m/s). The first term on the right hand side presents the conductive flux of heat, i.e. transfer of heat through the material, and the second term the convective flux, i.e. transfer of heat with moving water.

How well is transport of heat understood?

The transport of heat in fractured crystalline rock is understood relatively well in principle. Heat can be conducted through the bedrock and convected via the flowing groundwater away from a heat source. In practical modelling, the problem is thus reduced to a pragmatic effort to obtain reliable heat capacities for the rock and water. Considering the relatively high heat conductivity in rock and the limited amount of groundwater available in deep bedrock, conduction is probably the dominating effect. Of course, for the convection problem, knowing groundwater flow is a critical requirement.

3.2.4 Rock Mechanics

The mechanical behaviour of solid material must satisfy requirements for both static equilibrium and strain compatibility. The way in which stresses and strains are related in a material under load is described by its constitutive behaviour. Elasticity is the most commonly used constitutive property of engineering materials including many rocks. Elasticity also provides a useful basis for understanding more complex behaviour.

The most general statement of linear elastic behaviour is a generalised form of Hooke's Law which can be expressed in matrix form as:

$$[\varepsilon] = [\mathrm{S}]\,[\sigma] \tag{16}$$

The generalised Hooke's Law can be expressed in component representation:

$$\begin{bmatrix} \varepsilon_x \\ \varepsilon_y \\ \varepsilon_z \\ \gamma_{xy} \\ \gamma_{yz} \\ \gamma_{zx} \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16} \\ S_{21} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26} \\ S_{31} & S_{32} & S_{33} & S_{34} & S_{35} & S_{36} \\ S_{41} & S_{42} & S_{43} & S_{44} & S_{45} & S_{46} \\ S_{51} & S_{52} & S_{53} & S_{54} & S_{55} & S_{56} \\ S_{61} & S_{62} & S_{63} & S_{64} & S_{65} & S_{66} \end{bmatrix} \begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \\ \tau_{xy} \\ \tau_{yz} \\ \tau_{zx} \end{bmatrix} \tag{17}$$

where ε_x, ε_y and ε_z = strain components in x-, y- and z-directions (-), σ_x, σ_y and σ_z = stress components in x-, y- and z-directions (N/m^2), γ_{xy}, γ_{yz} and γ_{zx} = shear strains (-) due to shear stresses τ_{xy}, τ_{yz} and τ_{zx} (N/m^2), and coefficient matrix [S] (N/m^2)$^{-1}$ depends on material properties. Each of the elements S_{ij} of the matrix [S] is called an elastic modulus. The theoretical background for the elastic behaviour of a rock mass is given, for example, by Jaeger & Cook (1984).

Stresses and displacements caused by an underground opening can be calculated analytically or numerically. Analytical solutions can be found in several texts, for example, Jaeger & Cook (1984), Brady & Brown (1985), and Jussila (1997). Numerical solutions are based on continuous or discontinuous material models. Numerical methods and computer codes used in coupled thermo-hydro-mechanical processes are described, for example, by Stephansson et al. (1996).

Excavation of an underground space redistributes the in-situ stresses. Depending on the type of rock, the magnitude of in-situ stresses and the method of excavation, the stress redistribution may produce more or less damage to the rock structure and an associated change in the resistance to fluid flow. The region damaged due to stress redistribution is called the Excavation Damaged Zone (EDZ) or Disturbed Rock Zone (DRZ). The phenomena inside an EDZ formed in a jointed rock involve complex thermo-hydro-mechanical-chemical coupling relationships of the three-dimensional joint network. More detailed discussion on the properties of an EDZ is given by Martino & Martin (1996).

How well is rock mechanics understood?

In a fractured rock mass, estimating the state of stress is complicated due to the fact that displacements take place along fractures. The orientation of fracture surfaces and their properties determine the stress behaviour of the rock mass. A review of laboratory tests and development of models for rock joints is given by Stephansson & Jing (1995). As a conclusion they point out that there still remain several uncertainties surrounding joint behaviour, including:

- roughness, which is the dominant factor affecting all aspects of mechanical and coupled behaviour of rock joints, such as the scale effect, anisotropy, stress-dependency, the dynamic effect and hydraulic conductivity,
- the effect of gouge material is practically unknown,
- the coupled behaviour of rock joints, especially during heated shear tests, is the most complex, but experimentally least studied,
- the available models are still not capable of predicting joint behaviour with a reasonable level of confidence. The major difficulty is the lack of an unique and quantitative mathematical representation of joint roughness, asperity damage and the influence of gouge material.

3.3 TRANSPORT OF RADIONUCLIDES

Solving the transport equation requires knowledge of the groundwater flow field, including advection (average flow) and dispersion (a measure of the variation of flow due to different flow paths). The traditional way of solving the transport problem is to solve Eq. (1) first, then solve the flow velocities from the calculated head field using Eq. (5), and then to substitute the velocities so obtained into the transport equations. When doing so, it is assumed that the composition of the water and interactions of the substance being transported do not affect the groundwater flow equation. In other words, the transport equation is assumed to be a strictly one-way (H->C) coupling in which water-rock interactions of the migrating substances are simply “added” onto the groundwater flow. It is generally considered a realistic assumption. In principle, exceptions might arise where the concentrations of the substances become high enough to affect the properties of the flowing fluid, e.g. density and viscosity. Another possibility is if minerals precipitate in pores or flow channels.

Assume transport of radionuclides belonging to a decay chain along a water-carrying fracture in the x-direction. The nuclides interact instantaneously with the fracture surface and diffuse into the rock matrix along a continuous pore network in the z-direction, perpendicular to the direction of water flow (x-direction). While diffusing, the radionuclides interact with pore surfaces they come into contact with. The water-rock interaction of the radionuclides is simplified to instantaneous reversible sorption described by mass-based distribution coefficients, K_d, (in the rock matrix) and area-based distribution coefficient K_a (on fracture surfaces). The transport of radionuclides in the fracture is described by Eq. (18), and within the rock matrix by Eq. (19). The coupling between the two transport equations is provided by the matrix diffusion term; matrix diffusion is the mechanism that allows the groundwater flowing in the fracture to communicate with the stagnant pore water in the rock matrix (cf. Jakob et al. 1989, SKI 1991).

$$R_{f,i}\frac{\partial c_{f,i}}{\partial t} = -v\frac{\partial c_{f,i}}{\partial x} + \frac{\partial}{\partial x}\left(D\frac{\partial c_{f,i}}{\partial x}\right) + \frac{2}{2b}D_e\frac{\partial c_{p,i}}{\partial z}\Big|_{z=b} - \lambda_i R_{f,i}c_{f,i} + \lambda_{i-1}R_{f,i-1}c_{f,i-1} \tag{18}$$

$$R_{p,i}\frac{\partial c_{p,i}}{\partial t} = \frac{\partial}{\partial z}\left(D_p\frac{\partial c_{p,i}}{\partial z}\right) - \lambda_i R_{p,i}c_{p,i} + \lambda_{i-1}R_{p,i-1}c_{p,i-1} \tag{19}$$

where $c_{f,i}$ = concentration of the dissolved migrating nuclide i in the flowing water (atoms/m^3), D = dispersion coefficient in the x-direction (m^2/s), $R_{f,i}$ = retardation coefficient of nuclide i in the fracture (-), v = groundwater velocity in the fracture (m/s), D_e = effective diffusivity in the rock matrix (m^2/s), λ_i = radioactive decay constant of nuclide i (1/s), $R_{p,i}$ = retardation coefficient of nuclide i in the rock matrix (-), and D_p = diffusivity in the rock matrix (m^2/s). The equations apply for both sorbing ($R_{f,i} > 1$, $R_{p,i} > 1$), and non-sorbing (conservative) radionuclides ($R_{f,i} = 1$, $R_{p,i} = 1$).

The two diffusivities in the rock matrix (D_e and D_p) are inter-linked, and can both be derived from molecular diffusivity (assumed equal for all nuclides), see e.g. Rasilainen (1997), Olin (1994):

$$D_p = \frac{\delta_D}{\tau^2}D_w \tag{20}$$

$$D_e = \varepsilon_p D_p \tag{21}$$

where δ_D = the constrictivity of the pore network (-), τ^2 = the tortuosity of the pore network (-), D_w = molecular diffusivity in free water (m^2/s), and ε_p = porosity of the rock matrix (-). The factor $\delta_D/(\tau^2)$ is called the geometric factor, and it takes into account the fact that molecular diffusion does not take place in free water, but in a complicated network of irregular pores.

The two concentrations of nuclide i ($c_{f,i}$ and $c_{p,i}$) are linked to each other by assuming that the distribution of the concentration from the flowing water in the fracture into the pore water in the rock matrix is continuous:

$$c_{p,i}(z = b, t)\big|_x = c_{f,i}(x,t) \tag{22}$$

The concentration $c_{f,j}$ at the beginning of a fracture can be derived from the solubility of nuclide j. The above assumption is valid even if there is interaction between pore surfaces and aqueous species. Pore surfaces generally carry some net negative charge and in small pores (aperture < 50 nm), the charge on the surfaces can lead to a decrease in anion concentrations and an increase in surface cation concentrations. This may be the reason for reported observations of anion exclusion and surface diffusion of cations (e.g. Olin et al. 1997).

The retardation factor expresses the ratio of water velocity to the radionuclide velocity. The inverse of the retardation factor represents the fraction of the total radionuclide inventory that is dissolved in the water and considered mobile. The retardation factors in a fracture ($R_{f,i}$) and in the rock matrix ($R_{p,i}$) are given by:

$$R_{f,i} = 1 + \frac{2}{2b} K_{a,i} \tag{23}$$

$$R_{p,i} = 1 + \frac{\rho_s (1 - \varepsilon_p) K_{d,i}}{\varepsilon_p} \tag{24}$$

where 2b = fracture aperture (m), $K_{a,i}$ = area-based distribution coefficient of nuclide i (m^3/m^2), $K_{d,i}$ = mass-based distribution coefficient of nuclide i (m^3/kg), and ε_p = porosity of the rock matrix (-). K_d can be derived from K_a by multiplying by the specific surface area of the rock:

$$K_{d,i} = K_{a,i} a_f \tag{25}$$

where a_f (m^2/kg) is the specific surface area of the rock.

The first three terms on the right hand side of Eq. (18) represent advection, dispersion and matrix diffusion, respectively. The coefficient 2/(2b) in the matrix diffusion term in Eq. (18) represents the surface to volume ratio in a fracture

(m^2/m^3), assuming that the whole fracture surface is in contact with the water. The last two terms on the right hand side represent radioactive chain decay. Equation (19) describes matrix diffusion together with chain decay. The two equations are coupled via the matrix diffusion term and must be solved simultaneously with the total number of equations equalling the number of radionuclides in the decay chain.

Advective transport takes place in the mean direction of flow and with a mean velocity $v/R_{f,i}$ in the fracture, whereas the dispersive term incorporates all effects due to flow path heterogeneity, i.e. route dispersion. It also includes the spreading of substances by molecular diffusion in the fracture due to chemical concentration gradients. The dispersion coefficient can be expressed as (see e.g. Grisak & Pickens 1980):

$$D_l = \alpha_l v_l + D_w \tag{26}$$

where α_l = dispersivity (m), v_l = mean groundwater velocity (m/s), and D_w = molecular diffusion coefficient (m^2/s). Advective and dispersive transport are dependent on the same factors as described earlier for groundwater flow.

3.4 DIFFERENT APPROACHES TO COUPLED MODELLING

Strictly speaking, the term coupled model is used for models in which the solution of one process equation is taken into account in the parameters of another process equation, the solution of which in turn is taken into account in the parameters of the first equation etc. When simulating the two inter-linked processes, the two equations need to be solved in an iterative manner until convergence is achieved.

In the nuclear waste management community, the following types of coupled models have been used:

- coupled hydrogeochemical (H-C) models solving simultaneously the flow and transport equation with the geochemical process equations,
- coupled thermo-hydro-mechanical (T-H-M) models that solve simultaneously the fluid flow, heat flow and rock mechanical equations or two of the above simultaneously,
- density dependent models that solve the flow and transport equations in a coupled manner by taking into account the solution of the transport equation in the solution of the flow equation and vice versa.

In the present work, we try to get an overview of all these processes and couplings, which traditionally are looked at separately and by different scientific communities.

The “zeroth order” approach to coupled modelling is that the processes identified in the corners of Fig. 6 are solved independently as individual governing equations. When a strong coupling exists between two processes, i.e. the development of one process in space and time affects the development of another, both equations need to be solved simultaneously. Consequently, the quantitative effect of one equation on the other one must be taken into account through an appropriate mathematical function.

Deriving the coupling function between two or more processes is the key question in coupled modelling. After it has been established, it is technically straightforward to develop coupled codes. The robustness of the coupled code in describing reality, however, depends strongly on the accuracy of the coupling function. Another equally important factor for a successful coupled description of the system is that reliable input data for the function are available.

Different approaches are available for coupling processes which differ in their respective computing requirements. The simplest and computationally least demanding is to use a constant, e.g. K_d to include all chemical water-rock interactions in transport equations. The most detailed and computationally demanding method is to employ a fully coupled set of hydrologic, thermal, chemical and rock mechanical equations. More detailed models, naturally, need more data and this often necessitates correspondingly demanding experimental work.

As stated previously, a more detailed approach is an improvement over simpler methods only if the coupling function in the more detailed model is correct. A conceptual improvement thus brings about a better founded interpretation and more detailed description of the system than uncoupled or qualitatively coupled models. Practical improvement can be obtained, however, only where there are reliable input data available for the range of cases to be discussed. One important aim of the current work is to study whether there are real possibilities to improve the simplistic way of handling coupled processes currently used in safety analyses.

4. COUPLINGS RELEVANT TO SAFETY ANALYSIS

4.1 RELEVANCE OF A COUPLING

In this chapter we discuss potential couplings between the basic components reviewed in the previous section. In describing the effect of chemistry on other processes and also on migration in general, we consider the major components in groundwater as those causing a possible effect on other processes. In other words, the migrating substances that normally are assumed to be at trace element concentrations are not assumed to have much effect on the surroundings.

We can define a coupling as relevant if its effect on the system variables is essentially stronger than the effects caused by natural variability of the system parameters. If the effect of coupling is small when compared to natural variability, the actual improvement in the description brought about by including the coupling is also small, as it is always added to the original variability. Against the background of general uncertainty in a performance assessment, only essential couplings are worth taking into account explicitly.

Couplings regarded as being of minor importance do not require explicit treatment. It is first necessary, however, to demonstrate that a particular coupling has only an insignificant effect on the system variables.

In the following we will investigate couplings between the basic processes described in the previous section. The emphasis will be on the effects on radionuclide transport in fractured crystalline rock. Two important effects in the Finnish disposal plan are studied in more detail, namely temperature and groundwater salinity.

4.2 THE EFFECT OF TEMPERATURE ON RADIONUCLIDE MIGRATION

The following discussion considers potential couplings triggered by heat. We first consider direct couplings with temperature (T-H, T-C, T-M), and after that indirect couplings in the C-M-H plane, see Fig. 10.

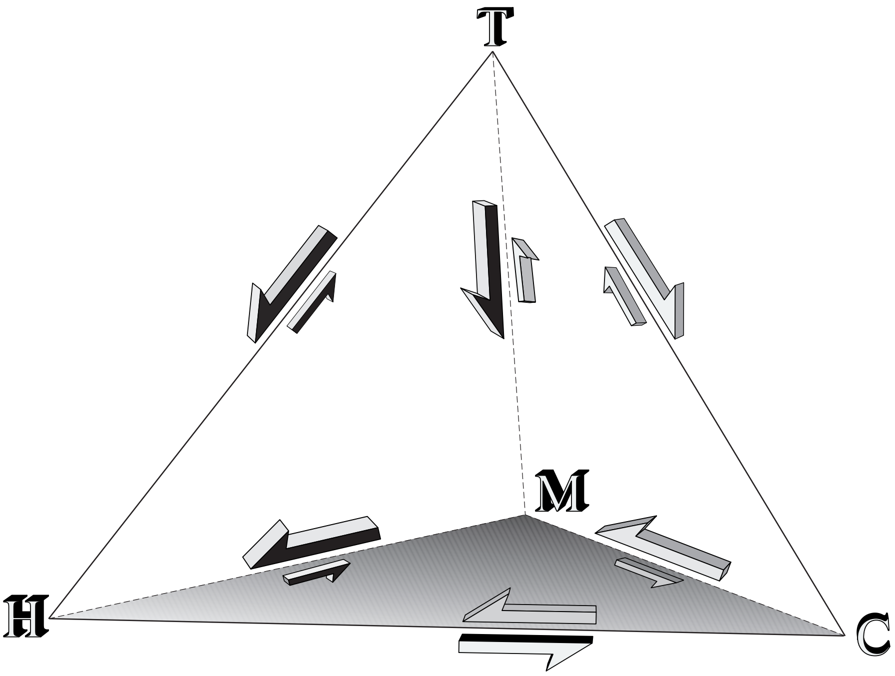

Fig. 10. Potential coupled interactions affecting the transport of radionuclides from a leaking repository (modified after Tsang, 1987). H is hydrological, C is chemical, T is thermal, and M is mechanical system. The couplings usually considered most significant are shown by large arrows, and those considered insignificant with small arrows. Note that a coupling is not necessarily equally strong in both directions, e.g. the effect of temperature on chemistry (T->C coupling) is strong, whereas chemistry is not expected to affect the temperature distribution much (C->T coupling is weak).

4.2.1 Direct thermo-hydraulic coupling

The effect of heat on groundwater flow (T->H coupling)

Temperature affects the flow equation (T->H coupling in Fig. 10) through fluid properties, namely viscosity and density. With increasing temperature, the density of water decreases, and these density gradients create a convective flow. The viscosity of water also decreases clearly with increasing temperature. These two phenomena are also called buoyancy effects.

In terms of mathematical modelling, this effect is taken care of by using a temperature dependent formulation for the groundwater flow equation [Eq. (6)], by taking into account the fact that fluid properties vary with location depending on temperature at a given time, i.e. $\rho=\rho(T)$ and $\mu=\mu(T)$. Fig. 11 shows the dependence of these parameters on temperature in the range of interest for a nuclear waste repository environment.

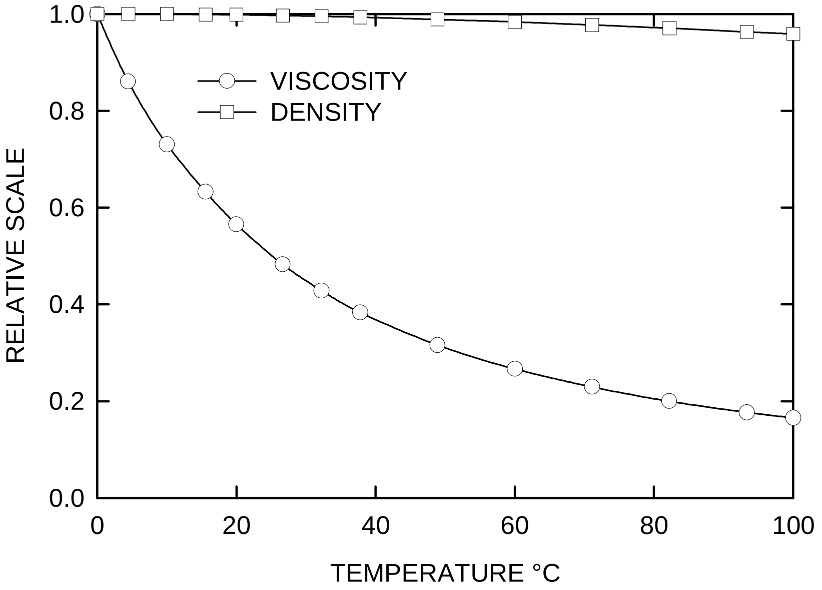

Fig. 11. Temperature dependence of water viscosity and density in the temperature range 0-100°C (White 1974).

The effect of hydrology on temperature distribution (H->T coupling)

The basic effect of groundwater flow on temperature distribution is relatively well understood and is represented through the convection term in Eq. (15). The groundwater flux q used in this expression is determined from the flow equation; after the head or pressure distribution has been solved [Eqs. (1) and (6)] fluxes can be determined from the Darcy expression and the solution is inserted into the heat flow equation [Eq. (15)]. Simultaneously, the solution of the heat equation is taken into account in the parameters of the flow equation as described above (cf. also Chan et al. 1987, Ahola et al. 1996).

The effect of temperature on dispersion

The dispersion coefficient in transport equation [Eqs. (18-19)] is indirectly dependent on temperature, in the sense that elevated temperature may change the flow paths, i.e. channelling of groundwater flow. This indirect dependence results from the fact that dispersion is simply a measure of the variability in the groundwater flow field. The molecular diffusion coefficient (D_w) is, in contrast, a directly temperature dependent quantity, the dependency varying with the solute and properties of the liquid. These dependencies have been tabulated for numerous substances.

Considering dispersion in a fracture, molecular diffusion is likely to be less important than route dispersion. In the rock matrix on the other hand, matrix diffusivity depends directly on molecular diffusivity D_w. Table 2 gives an example of the temperature dependence of molecular diffusivity.

Table 2. Temperature dependence of molecular diffusion coefficient D_w (Frick 1996). The dependency is derived from viscosity changes with temperature.

Temperature (°C)	Relative molecular diffusivity D_w
5	$0.55 \cdot D_{25\,°C}$
10	$0.65 \cdot D_{25\,°C}$
15	$0.75 \cdot D_{25\,°C}$
20	$0.87 \cdot D_{25\,°C}$
25	$1.00 \cdot D_{25\,°C}$
35	$1.28 \cdot D_{25\,°C}$
50	$1.76 \cdot D_{25\,°C}$
70	$2.54 \cdot D_{25\,°C}$

4.2.2 Direct thermo-chemical coupling

Temperature dependence of chemical reactions (T->C coupling)

Temperature has a strong effect on all kinetic reactions. As a simple rule it can be said that every 10 degree increase in temperature doubles reaction rates. There are exceptions to this rule, but on the whole the temperature dependence of the reaction rate can be expressed well enough with the Arrhenius expression. Because rate constants for reactions are normally reported at 25°C, the Arrhenius expression can be presented in the form:

$$k = k_{25} \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \tag{27}$$

where E_a = the activation energy (kJ/mol) and k_{25} = the rate constant at 25°C (1/s for first order reactions), R = the gas constant (kJ/mol·°K), and T = temperature (°K).

As temperature rises, local chemical equilibrium and kinetic formulation for crystal growth and dissolution may approach each other. As an example, for an infinite timespan it can be shown that for simple one step (first order) reactions, the following relation applies between the equilibrium constant K and growth and dissolution constants k_m and k_{-m}:

$$K = \frac{k_m}{k_{-m}} \tag{28}$$

For a second or higher order reaction that is a consequence of several reaction steps, this formulation is not usually valid and more complex relations between chemical equilibrium and rate constants must be considered. However, if the reactions are relatively fast and if reaction rates are further accelerated by temperature increase, the system will move faster towards equilibrium and the assumption of local equilibria for heterogeneous reactions in a low fluid velocity environment may become valid.

The effect of temperature on speciation

Temperature affects aqueous, surface and solid species in several ways. First, there is a direct effect of temperature on the balance of a chemical reaction and these changes affect the speciation of the aqueous phase. A temperature change also has an effect on activity coefficients and electrostatic potentials as discussed in more detail below.

The direct effect of temperature on chemistry is modelled via temperature dependent thermodynamic data. For an equilibrium constant this dependence is taken into account via heat capacities and enthalpies for the species and reactions in question. The formation of a compound is expressed with relations between the equilibrium constant (*K*), Gibbs free energy (*ΔG* - kJ/mol), entalphy (*ΔH* - kJ/mol) and entropy (*ΔS* - kJ/mol·°K) as follows:

$$\Delta G = -RT \ln K = \Delta H + T\Delta S \tag{29}$$

Both enthalpy and entropy are temperature dependent. At constant pressure, where only aqueous and solid phase reactions occur (i.e. no gas phase considered) the following relations can be written for enthalpy and entropy (e.g. Helgeson et al. 1978):

$$\begin{gathered} H_{f,T} - H_{f,298} = \int_{298}^{T} C_p dT \\ S_{f,T} - S_{f,298} = \int_{298}^{T} \frac{dH}{T} = \int_{298}^{T} \frac{C_p}{T} dT \end{gathered} \tag{30}$$

where C_p is heat capacity (kJ/mol·°K), and subscripts *f* and *298* imply formation and a temperature of 298.15 °K, respectively. Therefore, knowledge of the differential behaviour of heat capacity as a function of temperature gives the temperature dependence for an equilibrium constant studied. In practice, several values of either heat capacity or, especially at higher temperatures, the heat content ($H_{f,T}$ – $H_{f,298}$, e.g. Robie et al. 1978) are measured and are fitted to polynomials.

Extensive studies exist on mineral, gas and aqueous species equilibria as a function of temperature and pressure. In addition to classical aqueous (SiO_2-TiO_2-Al_2O_3-Fe_2O_3-CaO-MgO-FeO-K_2O-Na_2O-H_2O-CO_2) systems (e.g. Helgeson 1969, Helgeson et al. 1978, Robie et al. 1978, Hemingway et al. 1983, Berman 1988, Gottschalk 1997) quite extensive data are available for aqueous organic, metal-organic and rare earth element complexes (e.g. Wolery et al. 1990, Johnson et al. 1992, Shock 1992, 1993, 1995, Schulte & Shock 1993, Shock & McKinnon 1993, Shock & Koretsky 1993, 1995, Haas et al. 1995). A good deal of these data are suited for modelling chemical and mineralogical interactions in geochemical systems over the range 0–300°C, which is well in the relevant temperature range for a spent fuel repository.

The effect of temperature change on ionic strength is accounted for by the common activity expressions, γ, itself being temperature dependent. The effect of temperature on electrostatic activity corrections for surface species may be calculated in a similar fashion though the lack of experimental data is a problem.

The effect of chemistry on temperature distribution (C->T coupling)

The effect of chemistry on temperature distribution is usually considered negligible (see e.g. Tsang 1987) and certainly is likely to be much less than heat generation in a spent nuclear fuel repository. The heat of hydration of cements may be an exception, but this heat generation is limited by the relatively small amount of cement in the Finnish repository concept for spent fuel.

4.2.3 Direct thermo-mechanical coupling

The effect of temperature on rock mechanics (T->M coupling)

The effect of temperature variation on rock mechanical properties is relatively well understood and can be described through the temperature dependence of Young's modulus coefficient E(T) and strain ε(T).

The strain ε caused by the change in temperature ΔT in an uniaxial stress situation is

$$\varepsilon = \alpha \Delta T \tag{31}$$

where α = linear thermal expansion coefficient (1/ ^{0}C).

Rock mass prevents free displacements and, therefore, the stress caused by temperature change in an uniaxial stress situation is:

$$\sigma = \mathrm{E}\alpha \, \Delta \mathrm{T} \tag{32}$$

Thermally induced strains can be coupled to strains caused by mechanical stresses by simply adding the two strains.

In a plane stress condition, $\sigma_x \neq 0$, $\sigma_y \neq 0$ $\sigma_z = 0$, the stress changes due to temperature changes are:

$$\Delta\sigma_x = \frac{E}{1-\upsilon}\alpha\,\Delta T \qquad (33)$$

$$\Delta\sigma_y = \frac{E}{1-\upsilon}\alpha\,\Delta T$$

where υ = Poisson's ratio (-). It is also known that E, υ and strength properties of intact rock are temperature dependent (Jaeger & Cook 1984).

In a scale of kilometres, the effect of heat produced by spent nuclear fuel on the mechanical behaviour of the rock mass has been considered e.g. by Reivinen et al. (1996).

The effect of rock mechanics on temperature distribution (M->T coupling)

Mechanical effects on temperature distribution are usually considered insignificant (see e.g. Tsang 1987). Friction creates heat but compared to the heat production in a spent nuclear fuel repository, this source is considered negligible.

4.2.4 Indirect hydro-mechanic-chemical couplings

HYDRO-MECHANIC SEQUENCE OF H-M-C COUPLINGS

The effect of rock mechanics on groundwater flow (M->H coupling)

The ambient stress field affects groundwater flow in fractured rock primarily by opening and closing fractures which are the pathways to flow. This can be seen, for example, in the statistically observed trend of hydraulic conductivity decreasing with depth in bedrock, as increasing lithostatic pressure closes fractures (e.g. Niemi 1994). The excavation of repository tunnels will alter the existing stress distribution and, therefore, these effects need to be understood (see e.g. Tanai et al. 1994). Since the internal geometry of the fractures is usually highly irregular due to surface roughness, these effects are not straightforward and the effects of shear stress on the flow and transport characteristics of the fractures are not yet fully understood.

In principle, the release of long term anisotropic stress fields in bedrock (see e.g. Chandler & Martin 1994, Apotria et al. 1994) may produce a completely new fracture zone in or around the near field of a repository. This largely unpredictable incident may have profound effects on the groundwater flow field depending on the dimensions of the incident, fracture orientations and hydraulic conductivities related to the new fracture zone.

An excavation disturbed zone (EDZ) around tunnels with enhanced hydraulic conductivity and, thus, enhanced groundwater flow has been taken into account in Finnish performance assessments by increasing the hydraulic conductivity by two orders of magnitude (Vieno 1994, Vieno et al. 1992).

In a discontinuous rock mass containing fractures, displacements can theoretically take place in both intact rock and in fractures which can close, open, and slide. Usually, deformations and stresses in intact rock can be handled with linear elasticity theory. However, deformations taking place in fractures are highly non-linear and irreversible. Deformations normal to fracture walls are caused by normal stress σ_n (MPa) and are called normal displacements v (mm). Deformations along the fracture wall are caused by shear stress τ (MPa) and are called shear displacements u (mm).

Shear stress τ is a function of normal stress σ_n and fracture surface roughness

$$\tau = \sigma_\mathrm{n} \tan(\varphi + \mathrm{i}) \tag{34}$$

where φ = a basic friction angle ($^\circ$) and i describes the roughness of a fracture surface ($^\circ$). Barton (1973) has proposed that, when φ equals the residual friction angle φ_r, the term i ($^\circ$) is given by:

$$\mathrm{i} = \mathrm{JRC} \log_{10}\left(\frac{\mathrm{JCS}}{\sigma_\mathrm{n}}\right) \tag{35}$$

where JRC = dimensionless joint roughness coefficient on a scale from 1 (smoothest) to 20 (roughest) for various surfaces. JCS is joint wall compressive strength ($\mathrm{MN/m^2}$).

If the stress component σ_n acts normal to the fracture walls, then the normal displacement, i.e. closure, v (mm) of the fracture can be assumed to be (by analogy to Hooke's Law)

$$\mathrm{v} = \frac{\sigma_\mathrm{n}}{\mathrm{K_n}} \tag{36}$$

where K_n = normal stiffness (MPa/mm). However, there is a hyperbolic relation between normal stress vs. normal displacement behaviour of fractures meaning that K_n is not a constant but a function of stress. Goodman (1974) has given the following relation:

$$\frac{\sigma_n - \xi}{\xi} = A\left(\frac{v}{V_{mc} - v}\right)^t \tag{37}$$

where V_{mc} = maximum possible closure (mm), ξ = a seating pressure defining the initial conditions for measuring normal displacement (MPa) and A and t = experimentally determined dimensionless constants. The normal stiffness K_n is the tangent to the σ_n - v -curve and is highly stress dependent, see Fig. 12.

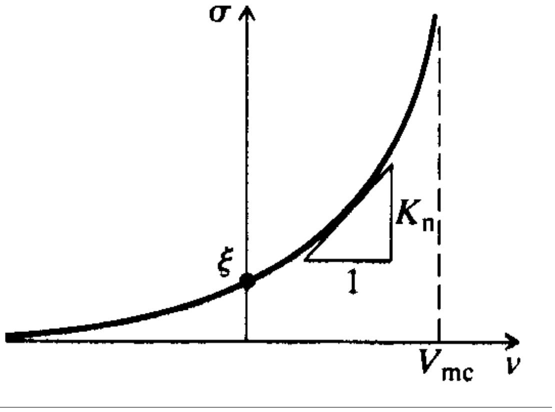

Fig. 12. Hyperbolic normal stress vs. normal displacement curve for discontinuity (after Goodman 1974).

The shear displacement u (mm) of a fracture is:

$$u = \frac{\tau}{K_s} \tag{38}$$

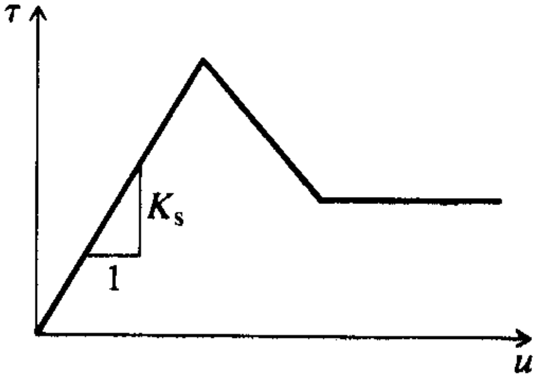

Fig. 13. Idealised tri-linear shear stress vs. shear displacement curve for discontinuity (Brady & Brown 1985).

The shear stiffness K_s (MPa/mm) is calculated from the slope of the τ vs. u -curve, but it is highly variable and very difficult to predict. It varies with the disturbance of the discontinuity, testing technique, specimen size and normal stress. Often it is assumed that K_s is constant in the pre-peak range, i.e. prior to the yield point (Fig. 13).

In principle, all displacements that take place in a fracture due to changes in mechanically or thermally induced stresses affect the water conductivity of the fracture. The thermo-mechanical coupling of stresses is theoretically known for solid material. However, in discontinuous material the coupling is only partly known because the actual displacements are very difficult to predict and the magnitude of displacements affect the stress level. The hydraulic aperture of the fracture is related to the mechanical aperture of the fracture. The prediction of hydraulic aperture based on the mechanical closure is, however, very difficult due to the highly complex surface geometry and characteristics of discontinuity. In a rough surface discontinuity there may still be open flow paths (channels) even if the mechanical closure has reached its maximum value. Shear displacements can simultaneously open and close flow paths depending on surface geometry. Also, gouge formed during shearing can block flow paths.

In mathematical terms, stress (σ) influences both the hydraulic conductivity and porosity terms of the flow equations [Eqs. (1-6)] by altering the aperture and pore space distribution of the fracture, i.e. $k = k(\sigma)$ and $n = n(\sigma)$. The M->H coupling is much more complicated than the T->H coupling. The effect depends on the properties of the fractures, known to be highly variable and heterogeneous, unlike material properties in the T->H coupling.

There are a large number of laboratory studies documenting changes in fracture transmissivity due to changes of both normal and shear stress. These studies are largely constrained to greatly simplify the characteristics of a natural fracture. Changes in shear stress may cause both an increase and decrease in permeability and are sensitive to fracture surface characteristics and loading conditions. Relations between hydraulic properties of a fracture and effective normal stress has been presented, for example, by Gangi (1978), Gale (1982) and Swan (1983). These expressions are based on at least one experimental flow test (Zhao & Brown 1992). However, large variations in model parameters cause difficulties when applied to predictions of water flow. For example, Zhao & Brown (1992) found that parameters in Gangi’s model had a variation of an order of magnitude. Pöllä et al. (1996) made tests and analysed results with the above mentioned models by assuming that a cubic relationship between fracture aperture and hydraulic conductivity is valid. Calculations indicated that there are no significant deviations between measured values and modelled results. The models, however, are empirical and are basically best-fit functions of noisy data sets. Therefore, the predictive power of these models is somewhat questionable.

Hakami & Larsson (1995) carried out flow experiments and aperture measurements on the same specimen of a single natural fracture in order to compare measured flow with predicted flow based on a geometrical description of the fracture void space. The predicted and measured flow through the fracture specimen were in good agreement.

As the effects of stress on fracture flow are not well understood, only a limited number of numerical codes exist to handle this coupling. Some examples can be found in the summary report of the DECOVALEX project (Jing et al. 1996).

The effect of hydrology on rock mechanics (H->M coupling)

Hydrology affects mechanical behaviour through water pressure p, solved in Eq. (6). In principle, this effect on the stress distribution is taken into account through the concept of effective stress $\sigma_{eff} = \sigma - p$. Changes in water pressures prevailing in fractures and pores of the rock mass may affect the fracture apertures and, with high enough hydraulic pressure, there may be hydraulic fracturing (see e.g. Norishaad & Tsang 1987, 1996, Rummel 1991).

CHEMICAL-MECHANICAL SEQUENCE OF H-M-C COUPLINGS

The effect of chemistry on rock mechanics (C->M coupling)

Chemical corrosion and other chemical events that possibly affect rock mechanical properties, e.g. precipitation and dissolution of minerals, have often been considered negligible. However, near field simulations indicate that quartz dissolves and calcite precipitates in the vicinity of a canister but that gradually away from the canister the fate of these minerals is inverted (e.g. Carnahan 1987, Langmuir 1987, Vaughan 1987). According to de Marsily (1987) mechanical modification of the flow field due to mineral transformations (e.g. bentonite swelling), mineral dissolution/precipitation processes (e.g. silica, gypsum, calcite, serpentine) and flocculation of colloids are among first major processes affecting nuclide transport. Both repository backfill material and the host rock are affected by such processes. Steefel & Lasaga (1994) touched on this topic by simulating changes in porosity, fracture aperture and permeability as a function of time in a porous rock by utilising quartz, K-feldspar, albite reaction rate changes subject to a temperature gradient. Also on the basis of numerical simulations, Lichtner (1996) has illustrated propagation of rock weathering and “ghost zones” as a function of time. Alteration products of porous rock and along water-carrying fractures have lower strength and density than the original rock minerals and, thus, the strength of repository walls may change slowly in time.

The effect of rock mechanics on chemistry

There are few quantitative studies or observations on the effect of rock mechanics on chemistry. In principle, it is possible that fluid inclusions inside the rock matrix or, more likely, within fracture minerals, can break and release their contents into groundwater if the rock is subjected to stress. The overall effect on groundwater chemistry is unknown. Nordstrom et al. (1989) studied the influence of fluid inclusions on groundwater chemistry in the Proterozoic Stripa granite, central Sweden. According to their studies, the “residual porosity” (caused by fluid inclusions) of fracture quartz and calcite is about 1 - 2%. However, Nordstrom et al. (1989) point out that only a small number of fluid inclusions need to break to account for variations in the groundwater chemistry.

HYDRO-CHEMICAL SEQUENCE OF H-M-C COUPLINGS

The effect of hydrology on chemistry (H->C coupling)

Hydrology has relatively little effect on the chemistry of migrating substances but strongly affects the groundwaters, themselves. New waters mix with older waters and react to changes in the system. Depending on the head field gradients and fracture zone properties, advective cells of groundwater extend to various depths in the bedrock and discharge groundwaters of varying ages at topographical lows.

Observed groundwater compositions along a flow path can be used to deduce geochemical reactions which occurred in the past. The method is called inverse modelling and gives insights into the history of current groundwater compositions (e.g. Parkhurst & Plummer 1993).

The effect of chemistry on groundwater flow (C->H coupling)

The effect of chemistry on groundwater flow is usually not significant. There are, however, exceptions to this. First, if the concentration of a solute is high enough it can alter the properties of the fluid, i.e. viscosity and density. Second, if chemical dissolution and precipitation take place along the walls of rock fractures, they can alter the permeability of the fractures and, thus, indirectly groundwater flow.

A special case where the effect of chemistry on groundwater flow will have to be addressed is saline groundwater in which the increased density makes the water less mobile. In principle, when solving density dependent flow [Eq.(6)], one solves the flow and transport equations simultaneously taking into account the effect of concentration on flow properties during each time-step. Thorough presentation and implementation of the topic has been described, for example, by Kipp (1987).

Considering indirect C->M coupling induced effects, chemical dissolution or precipitation may affect the aperture and, consequently, the permeability distribution of fractures. Since mass balance applies, dissolution at one site may be accompanied by precipitation at another down the hydraulic gradient. Therefore, dissolution and precipitation may locally increase or decrease permeabilities, respectively.

The overall temperature-induced effect on radionuclide transport

In summary, temperature-induced effects on radionuclide migration, described in detail above, can be broadly divided into two categories:

- the effect of temperature on flow, i.e. the viscosity and density parameters in the flow equation, temperature on mechanics (and eventually on flow) and, through these processes, to
    - ◊ flow velocities,
    - ◊ dispersivities,
    - ◊ molecular diffusion and
- the effect of temperature on chemistry, through the effects on:
    - ◊ sorption,
    - ◊ matrix diffusion,
    - ◊ overall retardation.

Chemistry has a decisive role in all non-physical water-rock interactions described in Eqs. (18-19) by simple retardation factors that are based on K_d and K_a concepts. The role is not explicit in the transport equations but, in reality, however, the K_d/K_a values are "loaded" with chemistry. First, groundwater chemistry determines the species of the dissolved radionuclides and second, it affects water-rock interfaces where the radionuclide-water-rock interactions take place, and, thus, the intensity of the interactions.

It is important to see that migration modelling is the final step in the modelling chain and all processes that affect the previous modelling steps will implicitly affect migration modelling. In other words the effect is active although not always explicitly shown in the transport equation.

4.3 THE EFFECT OF GROUNDWATER SALINITY ON RADIONUCLIDE MIGRATION

In Finnish site investigations for a spent fuel repository, deep saline groundwaters have been observed at the two coastal candidate sites, Loviisa and Olkiluoto. The salinity of the groundwater can affect the transport of radionuclides in two ways. First it may affect groundwater flow and second it may affect water-rock interactions of the migrating radionuclides.

Concerning groundwater flow, the density of water increases with salinity which, in turn, makes saline waters less mobile. With regard to the transport equation, this change in flow field is reflected in velocity v and dispersivity D. The molecular diffusion coefficient (D_w) is also likely to be affected by groundwater salinity.

The salinity of water will also affect water-rock interactions, e.g. sorption and, by this means, the overall retardation of radionuclides in the bedrock. The effect of salinity on sorption has been reviewed for performance assessment purposes in Finland (Hakanen & Hölttä 1992). These effects will be discussed in more detail below.

The effects of high ionic strength on the chemistry of migrating nuclides

The salinity of groundwater is represented in terms of its ionic strength. Chemical equilibria are particularly dependent on temperature and background electrolyte concentration and, to a lesser extent, on pressure (Read & Falck 1997). The background electrolyte concentration has a significant effect on the activities of reacting species. Most coupled models employ databases that are designed for low ionic strength conditions. Conversion algorithms for thermodynamic parameters are necessary for extrapolating data to high ionic strength conditions.

In low ionic strength solutions (I < 0.1) mean activity coefficients can be evaluated with the Debye-Hückel Equation. The Davies equation (Davies 1962) is a simple extension of the Debye-Hückel Equation and is of the form:

$$\log \gamma_i = -Az^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \tag{39}$$

where A = 0.509 at 25 °C.

As ionic strength increases in dilute solutions, the activity of ions decrease: ions are hydrated with water molecules. In solutions with moderate or strong ionic strength (I > 0.3) activity coefficients may either increase or decrease depending on the ions present in the solution. Both specific interaction theory (SIT) and the Pitzer approach attach additional terms into the Debye-Hückel equation to take into account interactions among ions. Owing to its relative simplicity and the limited number of parameters required for activity correction calculations, Read & Falck (1997) consider SIT as more suitable for waste disposal studies. The more complex Pitzer approach is, however, the most commonly used method for calculating activity coefficients in saline waters. The main benefit of the Pitzer approach is that activity coefficient calculations can be extended to very high salinities. The major drawback of the method is the high number of parameters required which besides problems of data availability makes calculations increasingly cumbersome in multicomponent cases.

Activity coefficients of individual ions in a multicomponent system (SIT approach) can be formulated as follows (Read & Falck 1997):

$$\log \gamma_i = -z_i^2 \cdot \frac{A\sqrt{I}}{1+B\mathring{a}_i\sqrt{I}} + \sum_j \varepsilon_{i,j}(I) \cdot m_j \tag{40}$$

where ε = a coefficient of interaction between cation *M* and anion *X* **(**kg/mol**)**, and m = total concentration of a species **(**mol/kg H_2O**)**. *A*, *B* and *å* = parameters from the Debye-Hückel theory (e.g. Grenthe et al. 1997b).

Sorption

For monovalent and bivalent cations it can be shown that, in dilute solutions, reacting surfaces prefer the higher charged cations (Appelo & Postma 1993). This trend is gradually reversed as ionic strength increases. Somewhat similar behaviour may be expected for more highly charged cations. Ions in solution compete with radioactive species for sorption sites and the number of available sites per aqueous ion is less in saline than in dilute solutions. Theoretically this should decrease the sorption of radionuclides and this can be reproduced by codes such as HYDRAQL (Papelis et al. 1988). There is also experimental evidence of the salinity of water leading to a decrease in sorption (e.g. Hakanen & Hölttä 1992). In general, however, interactions related to surface complexation are poorly known because cases where several ions/complexes are competing for the available surface sites have not been considered.

Solubility

Saline waters have higher ligand concentrations than non-saline waters and, therefore, complexation tends to be more pronounced (Fig. 8). Conversely, high salinity may decrease the activity of certain ligands so much that the effect of higher ligand concentrations is compensated for, thus leading to similar or lower solubility than in fresh waters. In principle, high salinity solutions can be modelled by the Pitzer Equation but current databases (e.g. Wolery et al. 1990) are limited to 25 °C, oxic conditions and for relatively few species.

Matrix diffusion

Salinity may have an effect on matrix diffusion via sorption, anion exclusion and surface diffusion. At high salinity all these phenomena should diminish considerably, if it is assumed that negative surface charge is the source of the phenomena. Dominating cations of highly saline waters fill up available binding sites on the surface (cf. Fig. 9) and the electric double layer is compressed (e.g. Stumm 1992, Davis & Kent 1990).

5. MODELLING CAPABILITIES FOR COUPLED PROCESSES

5.1 EXPERIENCE WITH MODEL VALIDATION

The best known international model validation programmes for coupled models are the CHEMVAL and DECOVALEX projects. The first (Falck & Read 1996) concentrated on coupling between chemistry and transport (C-H), whereas in the latter (Jing et al. 1996) the focus was on coupled hydro-thermo-mechanical (T-H-M) processes.

5.1.1 CHEMVAL

CHEMVAL II aimed at verification and, where possible, validation of predictive models describing groundwater speciation and geochemical transport. The second phase of CHEMVAL (1991 - 1994) aimed to build on the earlier study by considering six discrete modelling and experimental programmes rather than the more general use of chemical models in risk assessment. The programmes were

- modelling the effects of elevated temperatures on groundwater chemistry,
- modelling the effects of high ionic strength on speciation and solubility,
- characterisation and modelling of sorption processes,
- modelling of complexation by high molecular weight organics,
- simulation of trace metal coprecipitation,
- modelling of coupled chemical transport processes.

In the following, all programmes relevant for this report are discussed, thus excluding the organics and coprecipitation tasks. The discussion is based on the final report of CHEMVAL II (Read & Falck 1997).

Modelling the effects of elevated temperatures on groundwater chemistry

After conducting a review of methods available for describing the effects of temperature on chemical equilibria, the working group accepted that a rigorous thermodynamic approach to modelling should include the variation of both enthalpies and heat capacity with changes in temperature. However, there are few heat capacity data available, in particular for reactions involving the radioelements of interest in waste disposal. For practical reasons it was recommended, therefore, that a simplified Van't Hoff Equation be used to obtain the temperature-related variation of log K. This approach assumes that heat capacities, and hence, enthalpies of reaction are constant over small temperature intervals.

A set of model cases was designed to test this constant-enthalpy approach. The test cases were modified from tests performed in the previous CHEMVAL Project supplemented by representative field data for hydrothermal systems. Participants in the modelling exercises used the geochemical codes EQ3/6, CHIMERE, and modified versions of PHREEQE to perform the calculations. The results for the verification test cases were obtained using a standardised thermodynamic database (based on the CHEMVAL 4.0 Database), which included constant enthalpy data. These results were compared with those obtained using the EQ3/6 temperature grid with both its own database (r 3245), compiled by Lawrence Livermore National Laboratory (LLNL), which is based on the thermodynamically more realistic variable enthalpy approach.

The model results indicate that the simplified Van't Hoff equation, in which the temperature dependence of the heat capacity is assumed to be negligible, gave reasonable results in the majority of cases for temperatures less than or equal to 100 °C, regardless of the code used to perform the calculations. This holds with the exception of certain aqueous species and solids, including carbonates, where the change in enthalpy with temperature is known to be significant. The main divergence in results using different codes seems to be related to weakly buffered redox reactions with very low concentrations of redox-sensitive elements, such as uranium. This divergence tends to be magnified at higher temperatures.

Modelling the effects of high ionic strength on speciation and solubility

A review of modelling options for calculating activity coefficients of aqueous species, in waters having ionic strengths from 0.3 to 2 molal, identified the Specific Interaction Theory (SIT) as the most suitable method for application to radioactive waste disposal systems. The strengths of the model include its relative simplicity and the limited number of parameters required for activity correction calculations. These factors facilitate future database extension to include additional aqueous species.

A matrix of interaction coefficients, required to support SIT calculations, was compiled following a literature review. This matrix represents the most complete compilation of SIT interaction coefficients to date. The SIT approach has been tested against experimental results and compared with the Davies, Truncated Davies and Pitzer approaches; the SIT model shows good agreement with the Pitzer model and experimental data for simple electrolytes.

Following implementation, the SIT approach was tested in more complex solutions, using a seawater test case and again compared favourably with the Pitzer model; the latter representing the most extensively tested model for major aqueous species. Thus, a sound basis has been established for use of the SIT model, with its supporting databases, for low to moderate ionic strength groundwaters.

Application of the SIT model is critically dependent on the availability of specific ion interaction coefficients. For a significant number of aqueous species these coefficients are not currently available. Additional coefficients can be derived from published experimental work in which equilibrium constants have been measured at different ionic strengths.

Where an ionic strength dependence of the interaction parameter has been observed, as is the case for certain 2:1 electrolytes, a single interaction coefficient was used in the CHEMVAL SIT implementation, based on optimisation at 1.5 molal. The sensitivity of this simplification should be assessed, however. As ionic strength exceeds 2 molal, SIT model predictions begin to deviate increasingly from experimental results even for simple electrolyte solutions. The deviations are species-dependent. In future applications of the model, there will be a need to define confidence limits in the speciation predictions in a rigorous and systematic way. As for the Finnish candidate sites for a spent fuel repository, the highest ionic strength found so far (1.7 molal) is from Olkiluoto, see Pitkänen et al. (1999a).

Characterisation and modelling of sorption processes

Initial verification exercises in CHEMVAL II demonstrated that the sorption theory is generally coded and implemented correctly in the codes being used. The predictive capacity of electrostatic models (double layer model [DLM] and triple layer model [TLM], cf. Fig. 9) for sorption on single mineral surfaces given changes in pH, ionic strength, and concentration is quite good. It has not been possible to identify where one model works more effectively than another, although the TLM seems more flexible for fine tuning when considering complex surface reactions. However, the variation in the way the systems were modelled by the participants indicates that good agreement may not necessarily reflect modelling of the correct reactions. Additionally, electrostatic models do not always give good results (Am on silica test case, parts of the Ni on silica test case). Where this is the case, additional experimental data are needed for model testing.

Comparatively few modelling studies in the literature fit surface data and many researchers use surface parameters from different experiments. CHEMVAL II showed that the errors introduced by this assumption are often acceptable (Co on silica, U on silica), but confidence is needed that the surfaces in the experiments are similar. This is especially important when transferring data from single mineral experiments to natural systems.

In the St Bees Sandstone system, the results could be modelled assuming that Fe-oxides dominated the sorption behaviour. This suggests that sorption to mineralogically complex rocks might be predicted on the basis of single phase data from laboratory experiments. It may prove to be the case that iron oxides are the dominant sorbing phase in many natural systems and that electrostatic models of this mineral can be widely applied.

Modelling of coupled chemical transport processes

When the CHEMVAL Project was launched in 1986, several speciation and coupled codes had been developed, but few, if any, intercomparison studies had been carried out. Since different physical, chemical and transport concepts and often very different numerical approaches were employed in these codes, choosing appropriate and representative calculation procedures for performance assessment purposes was not easy.

The overall objective of CHEMVAL was to pool European scientific skills on geochemical and coupled modelling, define standard procedures for the comparison of the codes and, finally, provide the European Community with verified and validated tools for modelling work related to radionuclide speciation and migration in the geosphere.

As the four stages of the CHEMVAL Project (verification and validation of speciation codes, verification and validation of coupled codes) proceeded, the importance and size of the task to be tackled gradually became clear. The CHEMVAL Project was built as a multi-disciplinary forum where specialists from geochemistry, thermodynamics, hydrology, geology and numerical methods exchanged ideas on modelling problems. This led to considerable enhancement of the modelling methodologies but, at the end of the project, only stages I and II (related to speciation modelling) were completed. The coupled codes still needed to be addressed fully. In addition, the CHEMVAL Project demonstrated the need for reliable data for validation.

Thus, on the one hand, the CHEMVAL II Project consisted of the continuation of the CHEMVAL activities, especially focusing on coupled codes. On the other hand, it consisted of the use or the design of appropriate experiments to support validation studies. Moreover, CHEMVAL II provided the opportunity of thorough scientific debates on the physical and chemical concepts developed to represent homogeneous and heterogeneous processes occurring in porous media. In CHEMVAL all participants addressed the problems together, depending on the availability of codes. However, it was felt that a more efficient structure was required for CHEMVAL II, taking account of the various specialist working areas.

For the reasons mentioned above, it was decided to restructure the CHEMVAL Project. The chosen structure for CHEMVAL II consisted of (i) five topics, where the selection of suitable geochemical and physical concepts to introduce into the codes was to be performed and (ii) a technical workshop for coupled modellers. CHEMVAL II collaborators, however, were free to participate in any of these groups. In addition, it was decided to assign, if possible, experimental activities to each group. Finally, a database project was maintained throughout the duration of CHEMVAL II in order to provide the codes with consistent thermodynamic data.

The working group on coupled codes (Topic F) was placed at the focal point of the CHEMVAL II activities since the other topical groups worked on subjects directly linked to the modelling of experimental and field work. Results and advice from the other working groups were fed back to the group working on coupled processes. In this sense, in addition to its specific objective (validation of coupled codes), the remit of Topic F was also to consolidate the specialised activities of all other groups.

The CHEMVAL II work on coupled codes was more than a simple intercomparison of existing codes and their validation against existing or specifically designed experiments. First, it made it possible to document the characteristics of the codes, in terms of:

- the set of physical and chemical concepts on which they are based,
- the numerical methodologies for the solution of the transport and geochemistry equations and the coupling procedures,
- the parameters required to perform the calculations.

This was a necessary step prior to the development of the verification or validation test-cases.

The nine codes that were used provided an excellent coverage of the diversity within these three aspects. In general, this diversity is not a major factor in discerning discrepancies between the various modelling results. Hence, code design does not need standardising. However, the numerical methods used in some models appear to be more efficient than others. This seems to be the case, for example, for the direct solution method of coupling in one-dimensional configurations and when sharp fronts occur. The results from the random-walk procedure generally diverge from the other methods. There is no evidence, however, that this deviation is due to the method itself.

In short, one of the major results of the coupled modelling work is that it demonstrated the importance of the conceptual approaches selected by either the experimentalists or the modellers, for instance the proper identification of processes which will influence the experimental results.

A number of validation and verification cases were helpful in the improvement of coupled models. The exercises provided the opportunity to compare the results of the model simulations with analytical solutions to the test cases. They also allowed the different models to be compared with each other. This systematic test of the models against each other is necessary to check the reliability of the numerical method.

The first four verification exercises (quartz dissolution by NaOH injection, diffusion involving Ca/Na ion exchange in a bentonite barrier, cement dissolution by "clayey water" and, copper/pyrite reaction) have been used to improve the codes. The agreement between the different modelling attempts was good and demonstrates an acceptable internal consistency between the various codes. This is a significant improvement over CHEMVAL after which noticeable discrepancies remained.

Two validation test-cases were investigated by a number of participating teams. They consist of two experimental data sets involving migration of radionuclides.

The Winfrith test case (migration of uranium through a sandstone core) led to a qualitative agreement between modelling and experimental results. This was very encouraging, since the modelling attempts were performed "blind". The ability of the codes to deal with sorption phenomena, given adequate supporting data was demonstrated, at least, qualitatively.

Unfortunately, this was not the case for the Grenoble test case, which showed marked discrepancies between the modelling and the experimental results. More precisely, the codes should have predicted caesium retention onto the columns and a strontium breakthrough but generally failed even on a qualitative level. However, a conceptual misunderstanding of the processes actually occurring in the Grenoble material cannot be ruled out. Calculations with a simple retardation model seem to indicate that the experimental parameters derived from the batch experiments were not compatible with the observed results. It is possible that coprecipitation phenomena involving strontianite occur whereas ion-exchange was expected as the major geochemical phenomenon. The set of Grenoble experiments was aimed at being simple enough to address elementary geochemical phenomena. It was surprising to see that even such a simple system retains an internal complexity with which the modelling groups could not cope.

The above demonstrates the need for future work covering a range of experimental systems in order to establish the capabilities and limitations of coupled chemical transport codes.

The division of CHEMVAL II into a number of manageable topics resulted in genuine progress being made over a wide range of technical areas. In future work, progress on these topics should be taken forward and applied more directly to coupled models as these represent the essential foundation of the performance assessment process.

In the area of coupled modelling, close collaboration between experimentalists and modellers is particularly important. Even under the coordination of the CHEMVAL II Project, shortfalls in experimental data were noted. In future work, it is essential that data requirements for modelling are identified and communicated to experimentalists at the earliest possible design stage.

Uncertainties surrounding the processes operating in some test cases restricted the success of the modelling studies. This problem could be minimised if test cases are planned as an iterative process. Early modelling allows testing of the conceptual understanding and, hence, modification of both the modelling and the experimental work.

A coherent long-term study of one (e.g. Palmottu, see Blomqvist et al. 1998) or several natural cases could harness the conceptual and modelling activities within CHEMVAL. Such a study could resemble the natural analogues programme within MIRAGE. It would require simultaneous treatment of basic geochemical field data using models developed in, for example, CHEMVAL II topic areas. The expertise from these would then be the starting point for any further coupled geochemical modelling.

International model intercomparison exercises such as CHEMVAL II provide a forum in which model strengths and weaknesses can be identified. Future research projects in this area should preserve features which provide a focus for international collaboration and promote multidisciplinarity.

5.1.2 DECOVALEX

The DECOVALEX (DEvelopment of COupled models and their VALidation against EXperiments in nuclear waste isolation) Project is an international effort to develop mathematical models, numerical methods and computer codes for coupled thermo-hydro-mechanical (T-H-M) processes. Emphasis is placed on fractured rocks and buffer materials for geological disposal of spent nuclear fuel and other radioactive wastes; the aim being to validate the models against laboratory or field experiments.

The overall goal of DECOVALEX is to increase our understanding of the various coupled T-H-M processes of importance in the release and transport of radionuclides from the repository to the biosphere, and how those processes can be described by mathematical models. Results from different phases of the DECOVALEX Project have been published by Jing et al. (1993, 1994, 1995, 1996).

The DECOVALEX Project was organised around numerical simulations of a number of problems, called Bench-Mark Tests (BMT) and Test Cases (TC), by international research teams using different mathematical models and computer codes. The BMT's were hypothetical problems defined specifically to represent all or part of coupled T-H-M processes of a repository in fractured rocks as either a near or far field problem. The TC's were finalised or ongoing laboratory experiments. Both were defined as initial-boundary value problems with proper thermal, hydraulic and mechanical initial-boundary conditions. The aim was to compare, validate and improve the prediction capabilities of the mathematical models and computer codes. A description of the BMT's and TC's studied are shown in Table 3.

Table 3. Summary of Bench-Mark Tests (BMT's) and Test Cases (TC's) studied in DECOVALEX (Jing et al. 1996). In T-H-M problems the aim was to calculate mechanical stress, temperature, thermal stress, and groundwater flow. In H-M problems the aim was to calculate mechanical stress and groundwater flow.

Problem	Brief Description	Scale	Processes	Remarks
BMT1	Fractured rock with 2 orthogonal sets of persistent fractures and a heat-releasing waste repository	3000 x 1000 m	T-H-M	2D far field problem
BMT2	Fractured rock with a 4 discrete fractures and a finite length heat source	0.75 x 0.5 m	T-H-M	2D near-field problem
BMT3	Fractured rock with a realistic fracture network of 6580 fractures from Stripa site data	50 x 50 m	T-H-M	2D near-field problem
TC1	Laboratory shear-flow test on a rock core sample with a single joint	8 cm (length)	H-M	Fundamental law of HM behaviour of an isolated fracture
TC2	Field experiment in fractured rock at Fanay-Augeres, France	12 x 10 x 5 m	T-H-M	3D problem; unsaturated rock; mainly TM
TC3	Large-scale laboratory experiment in engineering buffer material (Big Ben)	5 (high) x 6 (diameter) m	T-H-M	3D radial; unsaturated medium; bentonite blocks
TC4	Laboratory triaxial stress-flow experiment on rock cores with fracture	10 (high) x 8.6 (diameter) cm	(T)-H-M	Fundamental law of HM behaviour of rock joint under triaxial loading
TC5	Laboratory shear-flow experiment of a rock block with a single joint	20 x 10 cm	H-M	To study HM in unsaturated to saturated media
TC6	Field experiment of injection hydraulic test on fractures at 81 m depth and deeper in fractured rock	15 m (radius of influence)	H-M	Comparative study of flow results with constant and pulse injection using packers

The main results achieved in DECOVALEX are summarised below (Jing et al. 1996).

1) Thermal processes in fractured and continuum media are well understood. The temperature predictions made by the different approaches and computer codes for all TC and BMT problems with thermal processes involved are very consistent among themselves and in reasonable agreement with the experimental

measurements. The agreement is better for fractured rocks than for the buffer materials. As a conclusion, the models and codes utilised in DECOVALEX can be used as tools for predicting temperature distribution within and around repositories for nuclear wastes.

2) Stress-deformation predictions for the rock masses are quite consistent among the numerical approaches and codes, themselves, and in fairly good qualitative agreement with the experimental data. Models and codes applied in DECOVALEX can be used for predictions of stress-deformation behaviour of the rock matrix surrounding a nuclear waste repository, particularly for design purposes during excavation and support measures.

The major drawback in the stress-deformation predictions is the fact that predictions of the aperture and stress variations across and along rock joints during complex deformation paths are not in good agreement with the experimental results.

3) Unlike thermal and mechanical results there are significant discrepancies in hydraulic results, in pressure heads as well as in flow rates, from one conceptual approach to another and between models (codes) using the same conceptual approach. The discrepancies are mainly due to the difficulty in adequately representing fractures, their connectivity, aperture changes caused by thermo-mechanical processes and the lack of proper homogenisation schemes for continuum analysis.

4) Many of the basic parameters associated with the fundamental laws and geometric features of the fractured medium cannot be measured directly. New measurement methods, especially those in-situ, are needed. Additionally, appropriate models should be developed where the parameters they use can be measured directly and monitored in situ. These model parameters may be an average or a combination of basic parameters.

5) The required level of characterisation and data acquisition, as well as the choice of appropriate modelling approaches for particular regions or problems has to be investigated carefully.

Dewiere et al. (1996) point out that future research is necessary to build up experience and capability in coupled T-H-M processes for the performance assessment of an underground waste repository. Some of the topics to be studied are:

- Fundamental or constitutive laws of hydromechanical behaviour for a single fracture. The constitutive laws for predicting mechanical behaviour, in general, and the changes of conductive aperture complex deformation path, in particular, are not satisfactory at present.
- Representation of the far-field hydraulic and mechanical behaviour of fracture networks in an homogenised manner. It is not yet clear how to represent hydromechanical coupling behaviour in equivalent continuum media.
- Characterisation strategy for measuring hydraulic and mechanical parameters as a function of distance from thermal or mechanical sources of disturbance.
- Strategy for the choice of models or codes for particular performance assessment objectives for the near field and far field region, respectively.

DECOVALEX II is a direct continuation of the DECOVALEX Project. The objective is to apply the mathematical models and computer codes developed and validated during DECOVALEX to large scale field experiments of coupled T-H-M processess for fractured rocks and engineered buffer materials. The project involves four tasks:

- shaft sinking project involving H-M process in fractured rock,
- an in situ T-H-M experiment of buffer material surrounded by fractured rock,
- review of constitutive models for rock joints,
- preparation of state-of-the-art statements on coupled T-H-M processes for safety analysis and performance assessment for nuclear waste repositories.

The original DECOVALEX Project ran from 1992 to 1995. The project was extended at the end of 1995. DECOVALEX II will end in 1999.

5.2 AVAILABILITY OF INPUT DATA

Assuming the coupling function has been validated and incorporated into a model, the next task in applying the model to a real problem is to obtain reliable input data. The input requirements vary considerably from model to model depending on how detailed and elaborate the model is. The simple codes normally used in performance assessments have the advantage of also having simple input data requirements. In fact, much of the current site investigation studies are designed to specifically provide input data for these models.

Considering a field scale application, such as a performance assessment, a distinction must be made between the input data that are truly site-specific and data that are generic in nature. Groundwater flow field and groundwater chemistry are among the most frequently required site-specific data. Generic data, on the other hand, need not be measured if suitable information has already been measured under similar conditions elsewhere. For example, thermodynamic values can be obtained from the literature.

At the moment there are six main sites in Scandinavia where data collation and/or studies are in progress. Detailed investigations for the four spent fuel repository candidate sites are supervised by Posiva Oy (Romuvaara in Kuhmo, Kivetty in Äänekoski, Olkiluoto in Eurajoki, and Hästholmen in Loviisa). In accordance with the co-operation agreement between Posiva Oy and the Swedish Nuclear Fuel Management Co (SKB), Finnish participation in project tasks and data acquisition from the hard rock laboratory at Äspö, SE Sweden, also benefits domestic performance assessesment studies. In addition, a relatively detailed site-specific database is being collated as part of natural analogue studies at the Palmottu U-Th mineralisation in SW Finland (Blomqvist et al. 1998).

Critically evaluated groundwater chemistry data are available from 30 – 40 samples from each of the candidate Finnish repository sites (Pitkänen et al. 1996, 1999a, 1999b, Snellman et al. 1998). Supporting data sets with lower levels of quality control are also available for each site. Quite extensive sample sets from Äspö and Palmottu have been analysed and evaluated by various groups (Rhén et al. 1997 and refs. therein, Blomqvist et al. 1998 and refs. therein). Continuous sampling and analysis campaigns are underway at almost all study locations.

Generic hydrochemical data related to aqueous speciation, solubility and sorption, relies heavily on internationally accepted geochemical databases such as WATEQ4F (Ball & Nordstrom 1991, Nordstrom et al. 1990), EQ3/EQ6 (Wolery et al. 1990) and CHEMVAL (Read & Falck, 1997). Modelling with these databases normally works well in calculating speciation of major, redox, and certain trace elements in natural waters. However, there are certain areas with potential difficulties: a) high salinity solutions, b) competing sorption onto multiple mineral surfaces, c) temperature effects on trace element speciation, d) trace metal co-precipitation, e) organic complexation, f) colloidal transportation. Most of these topics have been outlined in greater detail, for example, in Read & Falck (1997). Section 5.4 considers problems related to hydrogeochemical coupling.

Data for rock mechanical analysis can be obtained easily when considering intact rock and its properties. There are many reliable laboratory test methods for parameter determination for laboratory size samples. Data for fractures are much more difficult to obtain due to the difficulties in sample acquisition and in testing. As the scale of the area affected by excavation and thermal effects is tens or hundreds of metres it is impossible at present to obtain a full data set for rock mechanical analysis. The uncertainty in the location and properties of individual fractures and the effect of these on the strength and deformation of the rock mass is too great and it is impossible to include all fractures with known properties into the rock mechanical models. This means that ‘homogenisation’ of the fractured rock mass will have to be carried out, at least to some degree. How the necessary data will be obtained and how the homogenisation will be achieved is still unresolved.

Considering a site scale migration modelling effort there will be one unavoidable limitation in the database. It stems from the fact that the site can never be drilled and sampled sufficiently. Usually the minimum distance between drill holes in Posiva's site investigations is about 100 m and the maximum depth of a drill hole is about 1 000 m. Thus, in all site specific information there is a very strong element of interpolation that affects all rock mechanical modelling, groundwater flow modelling and, ultimately, migration modelling. In this respect, the natural analogue studies at Palmottu are particularly interesting, as the distance between neighbouring drill holes within the best characterised area is only about 25 m.

Site scale interpretation is, of course, unaffected by the often very detailed but small scale studies being carried out in the laboratory. Here, the overall picture may perhaps be visualised as a very sparse network of sampling points analysed in considerable detail. What lies between the sampling points is not fully known.

5.3 CODE AVAILABILITY

There are currently a wide selection of coupled codes available at VTT for potential use, see Table 4. Of the codes presented in the table, FEFTRAN has been already used in Finnish performance assessments in order to take into account the effect of heat generation by the spent fuel in groundwater flow modelling (e.g. Vieno & Nordman 1996). PHREEQM2D has been used for a modelling exercise which studied the effects of seawater recharge into a fracture zone at Äspö (Pirhonen 1994). Similarly, qualitative H->C coupling along a 1D flow path has been implemented by utilising forward prediction tools (PHREEQE, EQ3/EQ6) together with an inverse mass-balance tool for a geochemical simulation problem (Pirhonen 1993). Additionally, tested codes can be obtained from among those that have been applied in the CHEMVAL and DECOVALEX Projects.

Table 4. Coupled codes that have been used or studied at VTT (commercially available and in-house codes). Coupling type is denoted with acronyms corresponding to those in Figs. 6 and 10.

Code name:	**Coupling type:**	**Key words**
HST3D[a)]	T-H	3D heat-solute transport, pore velocities coupled to fluid density-viscosity, single species, 2-way (T<->H) sequential transport steps in time, linear-equilibrium sorption, saturated media
FEFTRA[b)] (earlier FEFLOW)	T-H	3D transient/steady state heat-groundwater flow-transport coupling, heat transfer via conduction or advection, T->H coupling via fluid density-viscosity, transport coupling via fluid density (salinity), saturated media
UDEC[c)]	T-M-H	2D response of discontinuous media to static or dynamic loading, sequential T dependent stress change steps in time, 2-way (M<->H) sequential change steps in time, no H->T coupling
FLAC[d)]	T-M-H	2D response of various (also plastic) media to static or dynamic loading, sequential T dependent stress change steps in time, 2-way (M<->H) sequential change steps in time, no H->T coupling
TOUGH2[e)]	T-H-C	3D advective-dispersive transport, heat flow, multi-phase fluid, sequential T dependent kinetic/equilibrium reaction-transport steps in time, unsaturated and saturated media
MT3D[f)]	H-C	3D advective-dispersive transport, sequential T dependent chemical equilibrium reaction-transport steps in time, interface to a flow modelling tool (i.e. MODFLOW), saturated media
RT3D[g)]	H-C	3D sequential T dependent kinetic reaction-transport steps in time, rate-limited sorption, interfaces to advection and dispersion solver (i.e. MT3D) and to MODFLOW, saturated media
PHREEQM2D[h)]	T-H-C	2D advective-dispersive transport, sequential T dependent equilibrium reaction-transport steps in time, ion-exchange reactions, mechanistic adsorption models, saturated media
OS3D[i)]	T-H-C	3D advective-dispersive transport, sequential T dependent kinetic/equilibrium reaction-transport steps in time, unmodified mass-action sorption models, saturated media
GIMRT[i)]	T-H-C	3D advective-dispersive transport, one T dependent kinetic/equilibrium reaction-transport step in time, sorption models, saturated media
PHREEQC[j)]	T-H-C	1D advective-dispersive transport, one T dependent kinetic/equilibrium reaction-transport step in time, unmodified mass-action and mechanistic adsorption models, saturated media
CHEMTARD[k)]	H-C	1D advective-dispersive transport, one T dependent equilibrium reaction-transport step in time, ion-exchange reactions, mechanistic adsorption models, saturated media

[a)]Kipp (1987), [b)]Taivassalo et al. (1994), [c)]ITASCA (1993), [d)]ITASCA (1996), [e)]Pruess et al. (1996), [f)]Zheng (1993), [g)]Clement & Jones (1998), [h)]IF Technology (1992, 1993), [i)]Steefel & Yabusaki(1996), [j)]Parkhurst (1995), [k)]Bennett et al. (1991a,b)

5.4 PROSPECTS OF COUPLING A DETAILED REPRESENTATION OF CHEMISTRY TO TRANSPORT MODELLING

The ultimate goal of coupled model development is to use the models at the field scale for “real” applications. The majority of the cases studied up to now have concentrated on simulating reactive transport in hypothetical aquifers, column experiments and small to large scale controlled field experiments (Engesgaard 1996). Moreover, the studies in which coupled models have been applied have often been concerned with limited, well-defined, ‘special’ cases. Simulations aimed at model validation with the help of observed features at the modelling site are still rare (e.g. Narasimhan et al. 1986, Engesgaard & Traberg 1996). In contrast, model verification studies, in which a set of models is used to simulate the same case, have been conducted in a number of countries and also, for example, in CHEMVAL (Falck & Read 1996) and DECOVALEX (Jing et al. 1996).

Uncertainties in the geochemical model, i.e. distribution of reactive species, represent a major challenge in field scale transport modelling. Spatial heterogeneity in reactive species probably plays as equally important a role in the spreading of contaminants as spatial heterogeneity in physical parameters. Stochastic codes try to overcome these difficulties either by solving stochastic reactive transport equations or by utilising a Monte Carlo approach. In the former case, spatial statistical variation of the reactive species is included directly in the transport equations, whereas, in the latter case, several deterministic runs with spatially varying concentrations of reactive species gives model estimates for the species of interest (Engesgaard 1996).

Quite often the groundwater flow field is determined in a generalised manner. An average advective flux for a given volume is estimated and all flow variations are lumped into an average dispersion coefficient usually obtained by model fitting. Pore and fracture scale variations in the velocity field are “diluted” in this overall averaging. They are, however, lumped implicitly in the advection and dispersion terms according to their respective weights. Furthermore, important aquifer properties such as permeability and fracture geometry can change as a result of mineral dissolution and precipitation.

At the same time, a coupled transport model attempts to take into account all exact relations and mass transfers among homogenous and heterogeneous chemical processes. Some uncertainties linked to modelling chemical processes are discussed briefly in the following.

Thermodynamic databases used by modelling programs are based on both experimental and estimated data. Many of the values are based on extrapolation techniques for determining equilibrium constants or Gibbs Free Energies. Estimations are unavoidable, but the confidence associated with estimated values is generally not reported in detail and errors may be large at extreme temperatures and pressures.

Frequently, ion-exchange and complexation reactions on mineral surfaces are assumed to be reversible. Currently, surface complexation models are able to predict the partitioning of an inorganic species between an aqueous solution and a single solid phase. Additive adsorption of an inorganic species onto multiple phases has yet not been simulated satisfactorily. Therefore, predictive simulation of sorption on natural materials such as fracture coatings using surface complexation concepts is not regarded as reliable at its present stage of development (Basset & Melchior 1990).

The extended Debye-Hückel- or Davies Equation-based activity calculations, though frequently used, have been found to be inadequate for defining the chemistry of more concentrated aqueous solutions. Ion-interaction approaches (SIT, Pitzer) give superior fits to the simple Debye-Hückel formulations but lack an adequate experimental database for trace constituents and repeated efforts are required to back fit data as the number of components in the model expands. The interaction approach is also limited by the availability of data for elevated temperatures (Basset & Melchior 1990).

Coupled inorganic-organic codes have received growing interest because many naturally occurring high (humic and fulvic acids) and low (phenols, alcohols) molecular weight organics together with several anthropogenic compounds are capable of binding metals (Read & Falck 1997). Cellulose and its degradation products may have a similar effect. Problems may rise, however, in modelling reactive transport in a system containing humic and fulvic acids. The structure and chemistry of these macromolecules are so complex that it is almost impossible to characterise a complete molecule and, therefore, exact thermodynamic data will probably remain unavailable for modelling (Basset & Melchior 1990). The molecular weight of these weak organic acids extends to the colloidal range and this needs to be taken into account by the transport models.

6. RECOMMENDATIONS FOR FUTURE STUDIES

This overview of the possibilities of using coupled modelling in safety analysis of spent fuel disposal was mainly based on a literature survey supplemented by the authors' previous experience in performance assessments and site characterisation as well as research projects such as CHEMVAL and DECOVALEX. In order to obtain a more complete picture of the capabilities of coupled modelling in a real, site-scale migration case, a practical modelling exercise would appear to be necessary.

Such a modelling exercise would require a database detailed enough so that quantitative differences between the different modelling approaches can be seen. Currently there are two particularly interesting possibilities for a comparative modelling exercise. Both can be based on a comprehensive experimental database.

The first possibility is to carry out a performance assessment type of theoretical analysis of radionuclide migration from a spent fuel repository excavated in bedrock. This exercise could include heat generation by the spent fuel. The study could, in principle, use the existing site investigation database from one of the Finnish candidates for spent fuel disposal. In this case, the exercise would essentially entail comparing modelling results obtained by different approaches.

The second possibility is to perform an independent migration modelling exercise for the natural analogue site at Palmottu. The exercise would benefit from the migration modelling work that is currently being performed there by the various modelling teams. This exercise would allow a comparison of modelling results obtained by different approaches but, in addition, there is an extensive hydrogeological, geochemical, and mineralogical site database collated within the ambit of the Palmottu Project.

In both cases, the study would include migration modelling using models at various degrees of simplification. The independent models would range from those used in performance assessment to the most detailed coupled models at our disposal. The basic premise for the study is to apply the same database for all modelling approaches. It is acknowledged, however, that all models will not require exactly the same parameters as input. Using the same database for a real problem is considered the only means of assessing any quantitative differences in the results obtained by different modelling approaches.

In terms of the relative importance of processes, the question is: “Can we classify hydrogeochemical processes as ‘significant’ and ‘insignificant’ with these studies?” With respect to ‘validation’, the question is: “Do separate studies with the same database reflect similar basic behaviour and are the results obtained by different approaches comparable?”

Uncertainty associated to various input parameters is of crucial importance in any modelling exercise. In terms of hydrogeological modelling, there is significant uncertainty concerning e.g. hydraulic conductivity distribution. Data bases and modelling approaches do, however, exist that help to relate this uncertainty to other effects. At the moment, only limited systematic data are available concerning the accuracy of chemical analyses from the ongoing studies. Similar restrictions apply to certain chemical processes. A challenging and important task in the future will be to relate the issue of parameter uncertainty to the improved model accuracy gained by inclusion of different coupling assumptions.

From the viewpoint of site-scale thermo-hydro-mechanical exercises, the site-specific data are, at present, very difficult to obtain in practice. The mechanical properties of individual fractures and fracture zones should be included explicitly in the rock mechanical models. This complicated problem requires homogenisation of the fractured rock mass in some way, but at the moment there is no consensus about how to carry this out. Sensitivity studies addressing the spread of parameter values due to rock mechanical coupling are, however, possible to carry out. These would at least aid in relating the uncertainty due to hydromechanical coupling to the other factors discussed.

7. CONCLUSIONS

The potential of coupled modelling was reviewed with a view to its possible use in safety analysis. We focused the study specifically on the migration of radionuclides escaping from a spent fuel repository planned to be excavated in fractured bedrock.

Two basic effects that can trigger various couplings in and around a spent fuel repository in Finland were studied in more detail. Heat generation is considerable during the first thousand years after disposal. Considering the assumedly corrosion resistant copper-steel canister, it can be concluded that heat generation triggered couplings are most effective for cases with initially defective canisters, as these can release radionuclides during the high heat generation period. For longer lasting canisters heat generation is a lesser problem.

Deep, saline groundwaters have been observed at the two coastal sites among the Finnish candidates being studied for spent fuel disposal. Saline groundwaters are usually considerably less mobile than fresh waters and increasing salinity may decrease the retention of radionuclides by the rock mass.

A systematic survey of the possibilities for, and requirements of, coupled modelling, in particular those related to heat generation or groundwater salinity, has identified some features that make coupled migration modelling a challenging task. In groundwater flow modelling there appears to be a wide background uncertainty related to conceptualisation of complex flow systems. Correspondingly, input data requirements are not always apparent. In the case of migration related chemistry there seem to be areas with large gaps in the basic database for geochemical modelling. Rock mechanical predictions are heavily dependent on knowing the location, structure and properties of dominant fractures, information which is extremely difficult to obtain. Transfer of heat is understood well in principle.

Based on our survey, it appears that coupled migration modelling is not yet at the stage of development that would allow its use as a standard modelling tool in performance assessments. In other words, the potential of coupled modelling to improve the precision in the consequence analysis of performance assessment remains open. To a considerable extent this is due to the large natural variability in the background data, for instance in the groundwater flow field and in the distribution of reactive species in the rock-groundwater system.

The above conclusion must, however, be regarded as interim, because our survey was mainly based on other surveys or studies not specifically aimed at migration modelling. In this sense, a more reliable basis for conclusions can only be formed by a systematic modelling exercise considering a realistic site-scale migration problem. Also, we do not yet have a practicable methodology to incorporate coupled modelling in the performance assessment approach.

Although the present applicability of coupled modelling in Finnish performance assessment appears limited, coupled approaches could, nevertheless, prove useful. For example, systematic sensitivity studies using coupled models could be used in scenario definition. The reason is that in performance assessment the objective is to bracket the possible futures of the repository system using different scenarios, rather than to aim at the "right" scenario of maximum probability. The ultimate aim of a performance assessment is to study whether the proposed disposal concept is likely to be safe; predicting exactly what will happen in the future is, of course, impossible.

REFERENCES

Ahola, M.P., Thorvald, A. & Clowdbury, A.H. 1996. Distinct element models for the coupled T-H-M processes: theory and implementations. In: Stephansson, O., Jing, L. & Tsang, C.-F. (eds.) Coupled thermo-hydro-mechanical processes of fractured media. Amsterdam: Elsevier. P. 93 - 134.

Anttila M. 1992. Spent fuel characteristics for TVO-92 safety analysis (in Finnish). Helsinki: Nuclear Waste Commission of Finnish Power Companies, 30 p. + app. 1 p. (Report YJT-92-03.)

Apotria, T., Kaiser, C.J. & Cain B.A. 1994. Fracturing and stress history of the Devonian Antrim Shale, Michigan Basin. In: Nelson, P.P. & Lambach, S.E. (eds.) Rock mechanics, Models and measurements challenges from industry. Rotterdam: Balkema. P. 809 - 816.

Appelo, C.A.J. & Postma, D. 1993. Geochemistry, groundwater and polution. Rotterdam: Balkema.

Ball, J.W. & Nordstrom, D.K. 1991. User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters: U.S. Geological Survey Open-File Report 91-183. 189 p.

Banwart, S.A. 1997. Aqueous speciation at the interface between geological solids and groundwater. In: Grenthe, I. & Puigdomenech, I. (eds.) Modelling in aquatic chemistry. Paris: Organisation for Economic Co-operation and Development (OECD), Nuclear Energy Agency. P. 245 - 287.

Barton, N.R. 1973. Review of a new shear strength criterion for rock joints. Engng. Geol., vol. 8, p. 287 - 332.

Basset, R.L. & Melchior, D.C. 1990. Chemical modeling of aqueous systems. An overview. In: Melchior, D.C. & Basset, R.L. (eds.) Chemical modeling of aqueous systems II. American Chemical Society, Symposium Series, no. 416, p. 1–14.

Bennett, D.G., Liew, S.K., Mawbey, C.S. & Read, D. 1991a. CHEMTARD programmer’s manual, M1515/PD-WSA-6. NEA Data Bank, package: NEA-1346/01.

Bennett, D.G., Liew, S.K., Mawbey, C.S. & Read, D. 1991b. CHEMTARD user’s manual, M1515/PD-WSA-6. NEA Data Bank, package: NEA-1346/01.

Berman, R.G. 1988. Internally-consistent termodynamic data for minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. Journal of Petrology, vol. 29, p. 445 - 522.

Blomqvist, R., Kaija, J., Lampinen, P., Paananen, M., Ruskeeniemi, T., Korkealaakso, J., Pitkänen, P., Ludvigson, J.-E., Smellie, J., Koskinen, L., Floria, E., Turrero, M.J., Galarza, G., Jakobsson, K., Laaksoharju, M., Casanova, J., Grundfelt, B. & Hernan, P. 1998. The Palmottu natural analogue project. Phase I: Hydrogeological evaluation of the site. Bryssel: European Commission, Nuclear science and technology series. 98 p. (Report EUR 18202.)

Brady, B.H.G. & Brown, E.T. 1985. Rock Mechanics for Underground Mining. London: Georg Allen & Unwin.

Brookings, D.G. 1988. Eh-pH diagrams for geochemistry. Springer-Verlag, Berlin. 176 p.

Brown, S. 1987. Fluid flow through rock joints: the effect of surface roughness. Journal of Geophysical Research, vol. 92, B2, p. 1337 - 1347.

Cacas, M.C., Ledoux, E., de Marsily, G. & Tillie, B. 1990. Modeling fracture flow with a stochastic discrete fracture network. Calibration and validation, 1. The flow model. Water Resources Research. Vol. 26. No. 3. Pp. 479 - 489.

Carnahan, C.L. 1987. Simulation chemically reactive solute transport under conditions of changing temperature. In: Tsang, C.-F. (ed.) Coupled processes associated with nuclear waste repositories. Orlando: Academic Press. P. 249 - 257.

Chan, T., Reid, J.A.K. & Guvanasen, V. 1987. Numerical modelling of coupled fluid, heat and solute transport in deformable fractured rock. In: Tsang, C.-F-. (ed.) Coupled processes associated with nuclear waste repositories. Orlando: Academic Press. P. 605 - 625.

Chandler, N. & Martin, D. 1994. The influence of near surface faults on is situ stresses in the Canadian Shield. In: Nelson, P.P. & Lambach, S.E. (eds.) Rock mechanics, Models and measurements challenges from industry. Rotterdam: Balkema. P. 369 - 376.

Chapman, N.A., Andersson, J., Robinson, P., Skagius, K., Wene, C.-O., Wiborgh, M. & Wingefors, S. 1995. Systems analysis, scenario construction and consequence analysis definition for SITE-94. Stockholm: Statens Kärnkraftsinspektion, 102 p. + app. 70 p. (SKI Report 95:26.)

Clement, T.P. & Jones, N.L. 1998. RT3D tutorials for GMS users. Washington, DC: Pacific Northwest National Laboratory. (PNNL-11805.)

Davies, C.W. 1962. Ion Association. London: Butterworths.

Davis, J.A. & Kent, D.B. 1990. Surface complexation modeling in aqueous geochemistry. In: Hochella, M.F. & White, A.F. (eds.) Mineral-water interface geochemistry. Mineralogical Society of America, Reviews in Mineralogy, vol. 23, p. 177 - 260.

Dewiere, L., Plas, F. & Tsang, C.F. 1996. Lessons learned from DECOVALEX. In: Stephansson, O., Jing, L. & Tsang, C-F. (eds.). Coupled Thermo-Hydro-Mechanical Processes of Fractured Media. Amsterdam: Elsevier. Developments in Geotechnical Engineering. Vol. 79.

Domenico, P.A. & Schwarz, W.S. 1990. Physical and chemical hydrogeology. Singapore: John Wiley & Sons. New York, NY. 824 p.

Dove, P.M. 1995. Kinetic and thermodynamic controls on silica reactivity in weathering environments. In: White, A.F. & Brantley, S.L. (eds.) Chemical weathering rates of silicate minerals. Mineralogical Society of America, Reviews in Mineralogy. Vol 31. P. 235 - 290.

Dzombak, D.A. & Morel, F.M.M. 1990. Surface complexation modelling: hydrous ferrous oxide. New York, NY: John Wiley & Sons. 393 p.

Eng, T., Hudson, J., Stephansson, O., Skagius, K. & Wiborgh, M. 1994. Scenario development methodologies, Stockholm: Svensk Kärnbränslehantering, 71 p. (SKB Technical Report 94-28.)

Engesgaard, P. & Traberg, R. 1996. Contaminant transport at a waste residue deposit; 2. Geochemical transport modeling. Water Resources Research, vol. 32, p. 939 - 951.

Engesgaard, P. 1996. Multi-species reactive transport modelling. In: Abbot, M.B. & Refsgaard, J.C. (eds.) Distributed hydrological modelling. Dordrecht: Kluwer Academic Publishers. P. 71 - 91.

Ewart, F.T., Haworth, A. & Wisbey, S.J. 1992. On the derivation of a sorption database. In: Radionuclide sorption from the safety evaluation perspective, Proceedings of an NEA Workshop. Paris: Organisation for Economic Co-operation and Development (OECD), Nuclear Energy Agency. P. 163 - 183.

Falck, W.E. & Read, D. 1996. Chemval 2. A coordinated research initiative for evaluating and enhancing chemical models in radiological risk assessments. Summary report. Brussels: European Commission. 65 p. (Report EUR 16909 EN.)

Freeze, A. & Cherry, A. 1979. Groundwater. Prentice Hall Inc. Englewood Cliffs, New Jersey. 604 p.

Frick, U. 1996. An evaluation of diffusion in the groundwater of crystalline rocks. Wettingen: Nationale Genossenschaft für die Lagerung Radioaktiver Abfälle. 96 p. + app. 37 p. (Nagra Interner Bericht 92-92E.)

Gale, J.E. 1982. The effects of fracture type (induced versus natural) on the stress-fracture closure-fracture permeability relationships. Proc. of 23rd US Symp. on Rock Mech., Berkeley, California, CA.

Gangi, A.F. 1978. Variation of whole and fractured porous rock permeability with confining pressure. Int. J. of Rock Mech. and Min. Sci. and Geomech. Abstr. Vol. 15, (5).

Goodman, R. E. 1974. The mechanical properties of joints. Advances in Rock Mechanics. Proc. 3rd congr. Int. Soc. Rock Mech., Denver, 1A, 127 - 140. Washington D.C: National Academy of Sciences.

Gottschalk, M. 1997. Internally consistent thermodynamic data for minerals in the system SiO_2-TiO_2-Al_2O_3-Fe_2O_3-CaO-MgO-FeO-K_2O-Na_2O-H_2O-CO_2. European Journal of Mineralogy, 9, p. 175 - 223.

Grenthe, I., Hummel, W. & Puigdomenech, I. 1997a. Chemical background for the modelling of reactions in aqueous systems. In: Grenthe, I. & Puigdomenech, I. (eds.) Modelling in aquatic chemistry. Paris: Organisation for Economic Co-operation and Development (OECD), Nuclear Energy Agency. P. 69 - 129.

Grenthe, I., Plyasunov, A.V. & Spahiu, K. 1997b. Estimations of medium effects on thermodynamic data. In: Grenthe, I. & Puigdomenech, I. (eds.) Modelling in aquatic chemistry. Paris: Organisation for Economic Co-operation and Development (OECD), Nuclear Energy Agency. P. 325 - 426.

Grisak, G.E. & Pickens, J.F. 1980. Spolute transport through fracture media. 1. The effect of matrix diffusion. Water Resources Research, vol. 16, no. 4, p. 719 - 730.

Haas, J.R., Shock, E.L. & Sassani, D.C. 1995. Rare earth elements in hydrothermal systems: Estimates of standard partial molal thermodynamic properties of aqueous complexes of the rare earth elements at high pressures and temperatures. Geochimica et Cosmochimica Acta, vol. 59, p. 4329 - 4350.

Hakami, E. & Larsson, E. 1995. Aperture measurements and flow experiments on a single natural fracture. In: Aperture distribution of rock fractures. Doctoral thesis. Stockholm: Division of Engineering Geology, Royal Institute of Technology.

Hakanen, M. & Hölttä, P. 1992. Review of sorption and diffusion parameters for TVO-92. Helsinki: Nuclear Waste Commission of Finnish Power Companies. 62 p. + App. 17 p. (Report YJT-92-14.)

Helgeson, H.C. 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. American Journal of Science, vol. 267, p. 729 - 804.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W. & Bird, D.K., 1978. Summary and critique of the thermodynamic properties of rock-forming minerals. American Journal of Science, 278-A.

Hemingway, B.S., Haas, J.L. & Robinson, G.R. 1983. Thermodynamic properties of selected minerals in the system Al_2O_3-CaO-SiO_2-H_2O at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey, Bulletin, 1544.

Huyakorn, P.S. & Pinder, G. 1983. Computational methods in subsurface flow. New Yor, NY & Toronto: Academic Press Inc. 473 p.

IF Technology bv. 1992. PHREEQM2D, PHREEQE in a multicomponent mass transport mode, couple to HST2D. Manual and user guide version 2.0. Arnheim: IF Technology.

IF Technology bv. 1993. Calculation of adsorption with the diffuse double layer model, constant capacitance model and triple layer model in PHREEQM2D. Arnheim: IF Technology.

ITASCA. 1993. UDEC (Universal Distinct Element Code). Version ICG 1.8, Volume I: User’s manual. Minneapolis: Itasca Consulting Group, Inc.

ITASCA. 1996. FLAC (Fast Lagrangian Analysis of Continua). Version 3.3, Volume I: User’s manual. Minneapolis: Itasca Consulting Group, Inc.

Jaeger, J.C. & Cook, N.G.W. 1984. Fundamentals of Rock Mechanics, 3rd London: Chapman and Hall.

Jakob, A., Hadermann, J. & Rösel F. 1989. Radionuclide chain transport with matrix diffusion and non-linear sorption. Villigen: Paul Scherrer Institut. 64 p. (PSI-Bericht Nr. 54.)

Jing, L., Stephansson, O., Rutqvist, J., Tsang, C-F., & Kautsky, F. 1993. DECOVALEX – mathematical models of coupled T-H-M processes for nuclear waste repositories. Phase I report. (SKI Technical Report 93:31.)

Jing, L., Stephansson, O., Rutqvist, J., Tsang, C-F., & Kautsky, F. 1994. DECOVALEX – mathematical models of coupled T-H-M processes for nuclear waste repositories. Phase II report (SKI Technical Report 94:16.)

Jing, L., Stephansson, O., Rutqvist, J., Tsang, C-F., & Kautsky, F. 1995. DECOVALEX – mathematical models of coupled T-H-M processes for nuclear waste repositories. Phase III report. (SKI Report 95:80.)

Jing, L., Stephansson, O., Tsang, C.F. & Kautsky, F. 1996. DECOVALEX - Mathematical models of coupled T-H-M processes for nuclear waste repositories. Executive summary for phases I, II and III. Swedish Nuclear Power Inspectorate. 42 p. (SKI Report 96:58.)

Johnson, J.W., Oelkers, E.H. & Helgeson, H.C. 1992. SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. Computers & Geosciences, vol. 18, p. 899 - 947.

Jussila, P. 1997. Analytical solutions of the mechanical behaviour of rock with applications to a repository for spent nuclear fuel. Helsinki: Radiation and Nuclear Safety Authority. 38 p. + app. 17 p. (Report STUK-YMO-TR 136.)

Kipp, K.L. 1987. HST3D: A computer code for simulation of heat and solute transport in three-dimensional groundwater systems. US Geological Survey Water Resources Investigations Report 86-4095. 517 p.

Langmuir, D. 1987. Overview of coupled processes with emphasis in geochemistry. In: Tsang, C.-F. (ed.) Coupled processes associated with nuclear waste repositories. Orlando: Academic Press. P. 67 - 101.

Lichtner, P.C. 1996. Continuum formulation of multicomponent-multiphase reactive transport. In: Lichtner, P.C., Steefel, C.I. & Oelkers, E.H. (eds.) Reactive transport in porous media. Mineralogical Society of America, Reviews in Mineralogy, 34, p. 1 - 81.

Marsily, G. de 1987. An overview of coupled processes with emphasis on geohydrology. In: Tsang, C.-F.(ed.) Coupled processes associated with nuclear waste repositories. Orlando: Academic Press. P. 27 - 37.

Martino, J.B. & Martin C.D. (eds.) 1996. Proc. of the Excavation Disturbed Zone Workshop. Canadian Nuclear Safety, Lac du Bonnet, Canada.

McKinley, I.G. & Hadermann, J. 1985. Radionuclide sorption database for Swiss safety assessment. Baden: National Cooperative for the Disposal of Radioactive Waste. 108 p. (Nagra Technical Report 84-40.)

Mourzenko, V.V., Galamay, O., Thovert, J.F. & Adler, P.M. 1997. Fracture deformation and influence on permeability. Physical Review E. vol. 56, no. 3. 3167 - 3177.

Narasimhan, T.N., White, A.F. & Tokunaga, T. 1986. Groundwater contamination from an inactive uranium mill tailings pile; 2. Application of a dynamic mixing model. Water Resources Research, vol. 22, p. 1820 - 1834.

National Research Council. 1996. Rock Fractures and Fluid Flow - Contemporary Understandings and Applications. Washington, DC: National Academy Press.

NEA. 1996. The international INTRAVAL Project. Developing groundwater flow and transport models for radioactive waste disposal. Final Results. Paris: Organisation for Economic Co-operation and Development. 43 p.

NEA. 1992. The international HYDROCOIN Project. Summary Report. Paris: Organisation for Economic Co-operation and Development. 182 p.

NEA. 1997. International meeting on chemical modelling of sorption in the field of radioactive waste management. Linton Lodge Hotel, Oxford, UK 6 - 8 May 1997.

NEA. 1983. Sorption. Modelling and measurement for nuclear waste disposal studies. Summary of an NEA Workshop. Paris 6 - 7 June 1983. Paris: OECD/NEA. 85 p.

Niemi, A. 1994. Modeling flow in frcatured medium - Uncertainty analysis with stochastic continuum concept. Espoo: Technical Research Centre of Finland, 188 p + app. 12 p. (VTT Publications 184.)

Nordqvist, W.A., Tsang, Y.W., Tsang, C.-F., Dverstorp, B. & Andersson, J. 1996. Effects of High Variance on Fracture transmissivity on Transport and Sorption at Different scales in a Discrete model for fractured Rocks. Journal of Contaminant Hydrology. 22:39 - 66.

Nordstrom, D.K., Lindblom, S., Donahoe, R.J. & Barton, C.C. 1989. Fluid inclusions in the Stripa granite and their possible influence on the groundwater chemistry. Geochimica et Cosmochimica Acta 53, p. 1741 - 1755.

Nordstrom, D.K., Plummer, L.N., Langmuir, D., Busenberg, E., May, H.M., Jones, B.F. & Parkhurst, D.L. 1990. Revised chemical equilibrium data for major water-mineral reactions and their limitations. In: Melchior, D.C. & Bassett, R.L. (eds.) Chemical modeling in aqueous systems II: Washington, DC: American Chemical Society Symposium Series 416, p. 398 - 413.

Norishaad, J & Tsang, C.-F. 1996. Coupled thermohydroelasticity phenomena in variably saturated fractured porous rocks - formulation and numerical solution. In: Stephansson, O., Jing, L. & Tsang, C.-F. (eds.) Coupled thermo-hydro-mechanical processes of fractured media. Amsterdam: Elsevier, P. 93 - 134.

Norishaad, J. & Tsang, C.-F. 1987. Simulation of coupled thermal-hydraulic-mechanical interactions in fluid injection into fractured rocks. In. Tsang, C.-F-. (ed.) Coupled processes associated with nuclear waste repositories. Orlando: Academic Press. P. 673 - 678.

Olin, M. & Lehikoinen, J. 1997. Application of surface complexation modelling: Nickel sorption on quartz, manganese oxide, kaolinite and goethite, and thorium on silica. Helsinki: Posiva. 24 p. (Report POSIVA-97-10.)

Olin, M., Valkiainen, M. & Aalto, H. 1997. Matrix diffusion in crystalline rocks: coupling of anion exclusion, surface diffusion and surface complexation. Helsinki: Posiva. 72 p. (Report Posiva-96-25.)

Olin, M. 1994. Diffusion in crushed rock and in bentonite clay. Espoo: Technical Research Centre of Finland. 98 p. (VTT Publications 175.)

Ollila, K., 1995. Solubility of unirradiated UO_2 fuel in aqueous solutions - comparison between experimental and calculated (EQ3/6) data. Helsinki: Nuclear Waste Commission of Finnish Power Companies. (Report YJT-95-14.)

Papelis, C., Hayes, K. F. & Leckie, J. O. 1988. HYDRAQL: A program for the computation of chemical equilibrium composition of aqueous batch systems including surface-complexation modeling of ion adsorption at the oxide/solution interface. California: Stanford University, Department of civil engineering. (Technical report number 306.)

Parkhurst, D.L. & Plummer, L.N. 1993. Geochemical models. In: Alley, W.M. (ed.) Regional ground-water quality. New York, NY: Van Nostrand Reinhold. P. 199 - 225.

Parkhurst, D.L. 1995. User’s guide to PHREEQC – A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. U.S. Geological Survey, Water-Resources Investigations, Report 95-4227.

Pirhonen, V. 1993. Beforehand estimate of mass transfer in arseniferrous gold mine tailing by means of minipilot plant process water analysis and geochemical simulations. Applied Geochemistry, Suppl. Issue no. 2, p. 291 - 293.

Pirhonen, V. 1994. Intrusion of seawater into a porous fracture zone: A coupled geohydrochemical modelling exercise. In: Barkatt, A. & Van Konynenberg, R.A. (eds.) Scientific basis for nuclear waste management XVII. Materials Research Society, Symposium Proceedings. Vol. 333, p. 811 - 820.

Pitkänen, P., Luukkonen, A., Ruotsalainen, P., Leino-Forsman, H. & Vuorinen, U. 1999a. Geochemical modelling of groundwater evolution and residence time at the Olkiluoto site. Helsinki: Posiva. (to be published as Report Posiva-98-10.)

Pitkänen, P., Luukkonen, A., Ruotsalainen, P., Leino-Forsman, H. & Vuorinen, U. 1999b. Geochemical modelling of groundwater evolution and residence time at the Kivetty site. Helsinki: Posiva. 139 p. (Report Posiva-98-07.)

Pitkänen, P., Snellman, M, Vuorinen, U. & Leino-Forsman, H., 1996. Geochemical modelling study on the age and evolution of the groundwater at the Romuvaara site.Helsinki: Posiva. 125 p. (Report Posiva-96-06.)

Pitzer, K.S. 1991. Activity Coefficients in Electrolyte Solutions. 2nd ed. Boca Raton, CRC Press. 490 p.

Pruess, K., Simmons, A., Wu, Y.S. & Moridis, G., 1996. TOUGH2 Software Qualification. Lawrence Berkeley National Laboratory. (Report LBL-38383.)

Pöllä, J., Kuusela-Lahtinen A., & Kajanen, J. 1996. Experimental Study on Coupled T-H-M processes of Singlr Rock Joint with a Triaxial Test Chamber. In: Stephansson, O., Jing, L., Tsang, C-F. (eds.) Coupled Thermo-Hydro-Mechanical Processess of Fractured Media. Amsterdam: Elsevier. P. 449 - 465.

QuantiSci, 1996. BIOMOVS II. BIOMOVS - an international study to test models designed to predict the environmental transfer and bioaccumulation of radionuclides and other trace substances. An overview of the BIOMOVS II Study and its findings. 36 p + app. 1 p. (BIOMOVS II Technical Report No. 17.)

Raiko, H. 1996. Thermal optimation of the final disposal of spent nuclear fuel (in Finnish), Helsinki: Posiva. 54 p. + app. 3 p. (Report Posiva-96-03.)

Rasilainen, K. 1997. Matrix diffusion model - In situ tests using natural analogues. Espoo: Technical Research Centre of Finland. 81 p. + app. 67 p. (VTT Publications 331.)

Read, D. & Falck, W.E. (eds.) 1997. CHEMVAL 2 - A coordinated reasearch initiative for evaluating and enchancing chemical models in radiological risk assessment. Brussel: European Commission, Nuclear science and technology series. (EUR 16648.)

Reivinen, M., Freund, J. & Eloranta, E. 1996. A theoretical and numerical consideration of rock mass behaviour under thermal loading of radioactive waste repository. Helsinki: Radiation and Nuclear Safety Authority. 60 p. (Report STUK-YTO-TR 112.)

Rhén, I., Gustafson, G., Stanfors, R. & Wikberg, P. 1997. ÄSPÖ HRL - Geoscientific evaluation 1997/5. Models based on site characterization 1986–1995. Stockholm: Swedish Nuclear Fuel and Waste Management. 428 p. (SKB Technical Report 97-06.)

Robie, R.A., Hemingway, B.S. & Fisher, J.R. 1978. Thermodynamic properties of minerals and related substances at 298.15 K and 1 Bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey. Bulletin 1452.

Rubin, J. 1983. Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of reactions. Water Resources Research, vol. 19, p. 1231 - 1252.

Rummel, F. 1991. Fracture mechanics approach to hydraulic fracturing stress measurements. In: Atkinson, B.K. (ed.) Fracture mechanics of rock. London: Academic Press. P. 217 - 240.

Schulte M.D. & Shock E.L. 1993 Aldehydes in hydrothermal solution: Standard partial molal thermodynamic properties and relative stabilities at high temperatures and pressures. Geochimica et Cosmochimica Acta 57, p. 3835 - 3846.

Shock E.L. & Koretsky C.M. 1993. Metal-organic complexes in geochemical processes: Calculation of standard partial molal thermodynamic properties of aqueous acetate complexes at high pressures and temperatures. Geochimica et Cosmochimica Acta 57, p. 4899 - 4922.

Shock E.L. 1992. Stability of peptides in high temperature aqueous solutions. Geochimica et Cosmochimica Acta 56, p. 3481 - 3491.

Shock E.L. & McKinnon W.B. 1993. Hydrothermal processing of cometary volatiles. Applications to Triton. Icarus 106, p. 464 - 477.

Shock E.L. 1993. Hydrothermal dehydration of aqueous organic compounds. Geochimica et Cosmochimica Acta 57, p. 3341 - 3349.

Shock, E.L. & Koretsky, C. M. 1995. Metal-organic complexes in geochemical processes: Estimation of standard partial molal thermodynamic properties of aqueous complexes between metal cations and monovalent organic acid ligands at high pressures and temperatures. Geochimica et Cosmochimica Acta, vol. 59, p. 1497 - 1532.

Shock, E.L. 1995. Organic acids in hydrothermal solutions: Standard molal thermodynamic properties of carboxylic acids and estimates of dissociation constants at high temperatures and pressures. Amer. J. Sci. vol. 295, p. 496 - 580.

SKI, 1984. INTRACOIN. Final Report Level 1. Code verification. Stockholm: Statens Kärnkraftsinpektion. 105 p. + app. 225 p (Report SKI 84:3.)

SKI, 1986. INTRACOIN. Final Report Levels 2 and 3. Model validation and uncertainty analysis. Stockholm: Statens Kärnkraftsinpektion. 66 p. + app. 310 p (Report SKI 86:2.)

SKI, 1991. SKI Project-90. Volume 1. Stockholm: Swedish Nuclear Power Inspectorate. (SKI Technical Report 91:23.)

Snellman, M., Pitkänen, P., Luukkonen, A., Ruotsalainen, P., Leino-Forsman, H. & Vuorinen, U. 1998. Summary of recent observations from Hästholmen groundwater studies. Helsinki: Posiva. To be published as Work Report 98-44.

Steefel, C.I. & Lasaga, A.C. 1994. A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. American Journal of Science, vol. 294, p. 529 - 592.

Steefel, C.I. & Yabusaki, S.B. 1996. OS3D/GIMRT: Software for modeling multicomponent–multidimensional reactive transport. User manual & programmer's guide. Pacific Northwest National Laboratory (Report PNL-11166.)

Stephansson, O. & Jing, L. 1995. Testing and modeling of rock joints. In: Proc. of the 2nd Int. Conf. on the Mechanics of Jointed and Faulted Rock MJFR-2. Rotterdam: Balkema.

Stephansson, O., Jing, L., & Tsang, C-F. 1996. Coupled Thermo-Hydro-Mechanical Processess of Fractured Media. Amsterdam: Elsevier.

Stumm, W. 1992. Chemistry of the solid-water interface. New York, NY: John Wiley & Sons.

Swan, G. 1983. Determination of stiffness and other joint properties from roughness measurements. Rock mechanics and Rock Engineering, vol. 16, p. 19 - 38.

Taivassalo, V., Koskinen, L. & Meling, K. 1994. Groundwater flow analysis in the preliminary site investigations - Modelling strategy and computer codes. Helsinki: Nuclear Waste Commission of Finnish Power Companies. 89 p. (Report YJT-94-04.)

Tanai, A., Kaneda, T. & Mikami, T. 1994. Measurement of in-situ stress and excavation-induced changes in the vicinity of underground opening. In: Nelson, P.P. & Lambach, S.E. (eds.) Rock mechanics, Models and measurements challenges from industry. Rotterdam: Balkema. P. 377 - 384.

Teollisuuden Voima. 1992. Final disposal of spent nuclear fuel in the Finnish bedrock. Technical plans and safety assessments, Helsinki: Nuclear Waste Commission of Finnish Power Companies. 136 p. (YJT-92-31E.)

Thompson, A. & Brown, S. 1991. The Effect of Anisotropic Surface Roughness on Flow and Transport in Fractures. Journal of Geophysical Research, vol. 96, no. B13, p. 21923 - 21932.

Tsang, C.-F. 1987. Introduction to coupled processes. In: Tsang, C.-F. (ed.) Coupled processes associated with nuclear repositories. London: Academic Press, p. 1 - 6.

Tsang, C-F. 1984. The effect of tortuosity on fluid flow through single fracture. Water Resources Research, vol. 20, no. 3, p. 1209 - 1215.

Vandergraaf, T.T., Ticknor, K.V. & Melnyk, T.W. 1992. The selection and use of a sorption database for the geosphere model in the Canadian nuclear fuel waste management program. In: Proceedings of the NEA Workshop on Radionuclide Sorption from the Safety Evaluation Perspective. Paris: Organisation for Economic Co-operation and Development, Nuclear Energy Agency. P. 81 - 120. ISBN 92-64-03700-4

Vaughan, P.J. 1987. Analysis of permeability reduction during flow of heated, aqueous fluid through Westerly granite. In: Tsang, C.-F.(ed.) Coupled processes associated with nuclear waste repositories. Orlando: Academic Press. P. 529 - 539.

White, F.M. 1974. Viscous fluid flow. New York, NY: McGraw-Hill. 725 p.

Vieno, T. 1994. Safety analysis of disposal of spent nuclear fuel. Espoo: Technical Research Centre of Finland, 256 p + app. 3 p. (VTT Publications 177.)

Vieno, T., Hautojärvi, A., Koskinen, L. & Nordman, H. 1992. TVO-92 safety analysis of spent fuel disposal. Helsinki: Nuclear Waste Commission of Finnish Power Companies. 254 p. (Report YJT-92-33E.)

Vieno, T. & Nordman, H. 1996. Interim report on safety assessment of spent fuel disposal TILA-96, Helsinki: Posiva, 176 p. (Report Posiva-96-17.)

Witherspoon, P., Wang, J.S.Y., Iwai, K. & Gale, J.E. 1980. Validity of Cubic Law for Fluid Flow in a Deformable Rock Fracture. Water Resources Research, vol. 16, no. 6, p. 1016 - 1024.

Wolery, T.J., Jackson, K.J., Bourcier, W.L., Bruton, C.J., Viani, B.E., Knauss, K.G. & Delany, J.M. 1990. Current status of the EQ3/6 software package for geochemical modeling. In: Melchior, D.C. & Basset, R.L. (eds.) Chemical modeling of aqueous systems II. Washington, DC: American Chemical Society Symposium Series. Vol. 416. P. 104–116.

Zhao, J. & Brown, E.T. 1992. Hydro-thermo-mechanical properties of fractures in the Carnmenellis granite. Quarterly Journal of Engineering Geology, p. 25.

Zheng, C. 1993, Extension of the method of characteristics for simulation of solute transport in three dimensions, Ground Water, vol. 31, no. 3, p. 456 - 465.

AQUEOUS CHEMICAL EQUILIBRIUM

As an example of how dissolved species equilibrate with aqueous solution we may consider uranium speciation in an aqueous U-C-O-H system. First, we concentrate only on sub-system (1) in Fig. 1. In this sub-system chemical equilibrium is governed by three mutually dependent relations:

$$\begin{aligned} &UO_2^{2+} + HCO_3^- \leftrightarrow UO_2CO_3^0 + H^+ \\ &H_2CO_3 \leftrightarrow HCO_3^- + H^+ \\ &H_2O \leftrightarrow OH^- + H^+ \end{aligned} \tag{1}$$

The species in this system are in reversible balance, which makes it possible to reduce the number of independent concentrations. The number of independent components N_c is reduced from total number of species N_{tot} by the N_x linearly independent chemical reactions between them ($N_c = N_{tot} - N_x$). This leads to natural partitioning into N_c primary or basis species designated here as C_j and N_x secondary species, referred as to X_i (Kirkner & Reeves 1988). The equilibrium between the primary and secondary species can be written as:

$$A_i = \sum_{j=1}^{N_c} \upsilon_{ij} A_j \, , \; i = 1, ..., N_x, \tag{2}$$

where the A_j and A_i are the chemical formulas of the primary and secondary species, respectively, and υ_{ij} is the number of moles of primary species j in one mole of secondary species i. Total concentrations, U_j, for species can be defined (Kirkner & Reeves 1988)

$$U_j = C_j + \sum_{i=1}^{N_x} \upsilon_{ij} X_i \tag{3}$$

Our example system consists of species UO_2^{2+}, $UO_2CO_3^0$, HCO_3^-, H_2CO_3, H_2O, H^+, and OH^- ($N_{tot} = 7$), cf. Eq. (1). By choosing UO_2^{2+}, HCO_3^-, H^+ and H_2O as the primary species ($N_c = 4$), reactions can be written with three equations ($N_x = 3$). Reactions can be presented in a matrix form conforming Eq. (2) as:

$$\begin{bmatrix} 1 & 1 & -1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & -1 & 1 \end{bmatrix} \cdot \begin{bmatrix} UO_2^{2+} \\ HCO_3^- \\ H^+ \\ H_2O \end{bmatrix} = \begin{bmatrix} UO_2CO_3^0 \\ H_2CO_3 \\ OH^- \end{bmatrix} \tag{4}$$

From Eq. (3) and from the coefficient matrix in Eq. (4) it follows that the total concentrations for primary species are:

$$
\begin{aligned}
U_{UO_2^{2+}} &= C_{UO_2^{2+}} + X_{UO_2CO_3^0} \\
U_{HCO_3^-} &= C_{HCO_3^-} + X_{UO_2CO_3^0} + X_{H_2CO_3} \\
U_{H^+} &= C_{H^+} - X_{UO_2CO_3^0} + X_{H_2CO_3} - X_{OH^-} \\
U_{H_2O} &= C_{H_2O} + X_{OH^-}
\end{aligned}
\qquad (5)
$$

In all, sub-system (1) in Fig. 1 can be governed with alkalinity, pH and UO_2^{2+} concentration, and the mutual equilibria among the dependent reactions in Eq. (4). UO_2^{2+} concentration, in turn, depends on the availability and solubility of crystalline UO_2. There is also an additional factor affecting the UO_2^{2+} concentration, namely crystalline UO_2CO_3(c) which we did not take into account above for the sake of simplicity (cf. Fig. 1).

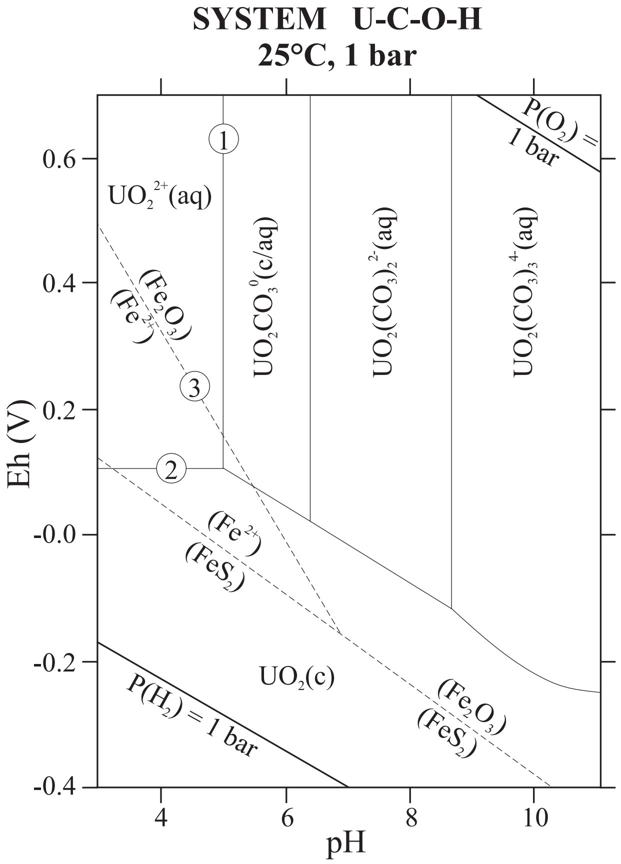

Fig. 1. Eh-pH diagram for part of the system U-C-O-H (solid lines) with part of the system Fe-S-O-H superimposed (dashed lines). Reactions related to boundaries (1), (2) and (3) are discussed in more detail in the text. The assumed activities (-) for dissolved species are : $a(U) = 10^{-10}$, $a(C) = 10^{-3}$, $a(Fe) = 10^{-6}$, $a(S) = 10^{-3}$. The physical state of uranium species are shown in parentheses: c = crystalline, aq = aqueous (modified from Brookings 1988).

The equilibrium between crystalline and aqueous UO_2CO_3 (c/aq) controls the concentration of UO_2CO_3(aq):

$$UO_2CO_3(aq) \leftrightarrow UO_2CO_3(c) \qquad (6)$$

which in turn affects the equilibrium between UO^{2+} and UO_2CO_3(aq) {cf. Eq (1)}. The presence of crystalline UO_2CO_3(c) means that aqueous uranium concentration under oxidising (Eh > 0.1 V) conditions in the U-C-O-H system temporally diminishes as pH values evolve from acid towards neutral.

There are several redox half-reactions in our system, e.g. sub-system (2) in Fig. 1:

$$UO_2 \leftrightarrow UO_2^{2+} + 2e^- \qquad (7)$$

If electron consuming counter reactions for these are defined, we can write equilibrium reactions to the whole U-C-O-H system, and give a mathematical formulation for the whole system. We may, for example, produce electrons for our sub-system (2) reactions via iron reduction, e.g. sub-system (3) in Fig. 1:

$$Fe_2O_3 + 6H^+ + 2e^- \leftrightarrow 2Fe^{2+} + 3H_2O \qquad (8)$$

Reduction of iron from hematite is a slow process (Bruno 1997) and it occurs step-wisely in nature, i.e. hematite alters first to less crystalline goethite which then may produce Fe^{2+} into aqueous solution.

There are, however, also fast naturally occurring oxidant flows which may affect the U-C-O-H system. For instance, oxygenous glacial melt water may possibly intrude into repository depth. Dissolved oxygen is eager to reduce and will thus dominate over the slow oxidants. On the other hand, if there is not any UO_2 available, i.e. UO_2 is isolated from the aqueous system, at the time of the oxygenous intrusion, then the question, how quickly we consume the dissolved oxygen in harmless mineral processes, becomes important. Guimera et al. (1998) have studied this question in respect of biotite alteration, which in turn is a slow kinetically controlled process.

To be accurate, there are only few aquatic systems where all chemical reaction equations can be formulated as equilibrium reactions (Steefel & MacQuarrie 1996), although, of the modelling approaches, equilibrium method has been applied longest (e.g. Thompson 1959) and it is in many cases possibly the “safest” way to model chemical reactions.

References

Brookings, D.G. 1988. Eh - pH diagrams for geochemistry. Springer-Verlag, Berlin.

Bruno, J. 1997. Trace element modelling. In: Grenthe, I. & Puigdomenech, I. (eds.) Modelling in aquatic chemistry. Paris: Organisation for Economic Co-operation and Development (OECD), Nuclear Energy Agency. P. 593 - 621.

Guimera, J., Duro, L., Jordana, S. & Bruno, J. 1998. Effects of ice melting and redox front migration in low permeability media. The 3rd Äspö International Seminar, Abstracts. Äspö Hard Rock Laboratory, Oskarshamn, Sweden. 10 - 12 June 1998. P. 31.

Kirkner, D.J. & Reeves, H. 1988. Multicomponent mass transport with homogenous and heterogeneous chemical reactions: Effect of chemistry on the choice of numerical algorithm. I. Theory. Water Resources Research, vol. 24, p. 1719 - 1729.

Steefel, C.I. & MacQuarrie, K.T.B. 1996. Approaches to modeling of reactive transport in porous media. In: Lichtner, P.C., Steefel, C.I. & Oelkers, E.H. (eds.) Reactive transport in porous media. Mineralogical Society of America, Reviews in Mineralogy, vol. 34, p. 83 - 129.

Thompson, J.B. 1959. Local equilibrium in metasomatic processes. In: Abelson, P.H. (ed.) Researches in geochemistry. New York, NY: John Wiley & Sons. P. 427 - 457.