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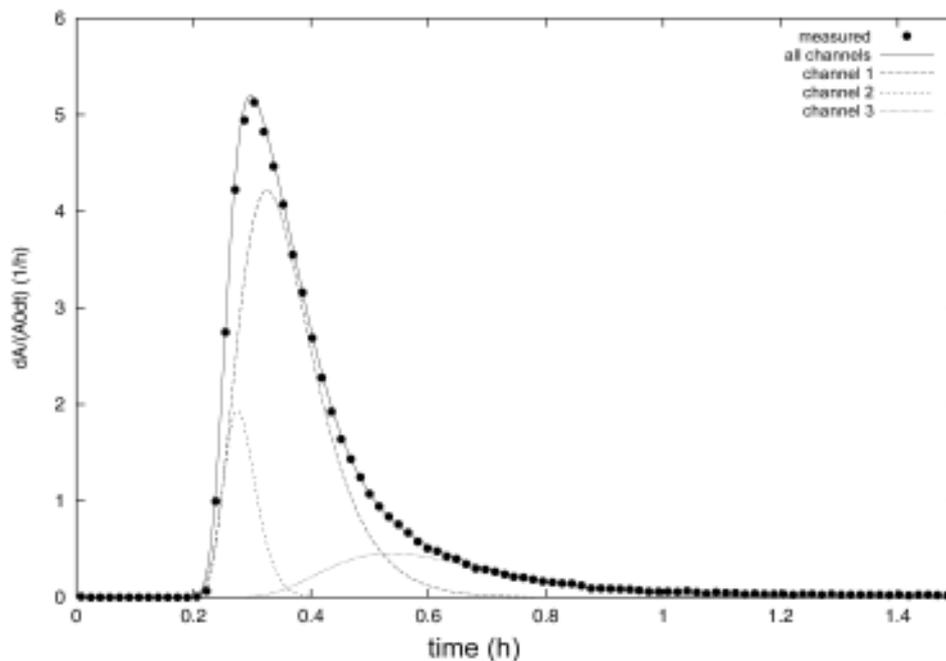
Retardation mechanism studies for performance assessments

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Abstract

Performance assessments of geological repositories for nuclear waste require information about how possibly escaping radionuclides will be transported through the bedrock. Retardation mechanism studies provide an important part of the database required. So far Finnish performance assessments have considered sorption and matrix diffusion as retardation mechanisms. In this report we discuss how the data supplied by experimental retardation mechanism studies meet those required by performance assessments in the Finnish case.

Experimental structural studies on small-scale pore network are discussed in detail. The C-14-PMMA method and helium-gas methods provide porosity, diffusivity and permeability data. The effort within the Palmottu natural analogue project that aimed to locate large-scale flow channels is described briefly. Specific retardation mechanism studies are discussed. The laboratory studies cover column experiments and anion exclusion studies. Column experiments provide data on sorption and matrix diffusion. The natural analogue studies cover work done in the Palmottu, the Hämeenlinna boulder, and the Hästholmen projects. Studies at Palmottu provide in situ data about sorption and matrix diffusion.

This review indicates that data required by current migration models in performance assessments can be met by existing experimental methods. But the situation changes if more detailed modelling is wanted. In that case, a strategic question must be answered: what is a reasonable level of detail and conceptual rigour in performance assessment modelling, considering the unavoidable overall uncertainties due to long time scales and heterogeneous bedrock? The results obtained so far in natural analogue studies indicate that there is room for improvements in sorption modelling. The current K_d based approach could be supported by parallel mechanistic sorption modelling. It is acknowledged, however, that mechanistic sorption modelling is possible for neither all nuclides, nor all minerals, nor all geochemical conditions. Notwithstanding this, it would nevertheless better utilise the current state-of-the-art understanding of sorption.

Preface

This study belongs to the Public Sector's Research Programme on Nuclear Waste Management (JYT 2001) in Finland. The programme is financed jointly by the Ministry of Trade and Industry (KTM), and the Radiation and Nuclear Safety Authority (STUK).

Nuclear waste disposal and performance assessment related topics are covered by Kari Rasilainen. The C-14-PMMA method is described by Marja Siitari-Kauppi. Helium gas methods are covered by Jussi Timonen. Large-scale flow channel issues are covered by Antero Lindberg and Nuria Marcos. Column experiments are discussed by Pirkko Hölttä. Anion exclusion studies are reviewed by Matti Valkiainen and Jarmo Lehikoinen. Natural analogue studies at Palmottu are discussed by Juhani Suksi and Kari Rasilainen. Boulder studies are described by Juhani Suksi, Nuria Marcos and Kari Rasilainen. Natural analogue studies at Hästholmen studies are discussed by Matti Valkiainen.

Contents

1. Introduction

Geological disposal is universally the most extensively studied option for nuclear waste management. Practically all countries producing nuclear energy have a national research programme aiming at the disposal of their respective wastes in a stable geological formation. The geological formations under consideration vary, of course, from country to country depending on the geological setting. Geological disposal can in principle be done near the surface or deep in the bedrock. Deep geological disposal has been studied particularly for highly radioactive spent nuclear fuel or reprocessing waste.

The Finnish approach to the disposal of all nuclear wastes generated in Finland is geological approach that disposes of the waste in the crystalline bedrock. For low and intermediate level wastes the disposal depth is about 60–90 m in Olkiluoto repository and 110–120 m in Loviisa repository, and both are already in operation. For low and intermediate level wastes the policy is to construct and operate separate disposal facilities at the nuclear power plant sites were the wastes are generated. The wastes from the decommission of the nuclear reactors are planned to be disposed of in extensions of the repositories for low and intermediate level wastes.

For the disposal of spent nuclear fuel, direct disposal is being planned. In other words, the reprocessing of spent fuel is, for the time being, ruled out in Finland. The planned disposal depth for the spent fuel repository is of the order of 500 m. A schematic presentation of the basic concept for spent fuel disposal is depicted in Figure 1.1.

In 1999 Posiva[1] submitted an application for a Decision in Principle to the Government proposing Olkiluoto in Eurajoki municipality as the final disposal site. This was preceded by an extensive environmental impact assessment (EIA) process. So far the Radiation and Nuclear Safety Authority (STUK) and the municipality of Eurajoki have given favourable statements about the proposal. The Government made the Decision in Principle in December 2000. The decision was favourable to Posiva's application. In order to remain in force the decision will still need to be ratified by the Parliament. According to current schedule, the repository should commence operation around year 2020.

Finnish nuclear waste disposal facilities will in all cases be excavated in the saturated bedrock under groundwater level, meaning that eventually they will be flooded. In Finland groundwater level follows closely the features of the terrain with mild rounding of the topographical gradients. Therefore, migration of radionuclides potentially

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[1] Posiva Oy is the company in charge of the safe disposal of spent nuclear fuel generated in Finland. It is owned by the Finnish nuclear energy producing companies Fortum and Teollisuuden Voima.

escaping from the repository will take place along water-carrying fractures with groundwater acting as the carrier.

While migrating away from the repository along the flowing groundwater, radionuclides are subject to geochemical reactions with the bedrock - groundwater system. As a result of these reactions, part of the radionuclides are attached to the mineral surfaces along the water-carrying fracture, and thus removed from the mobile inventory. In addition, part of the radionuclides will slowly diffuse from the flowing water into the stagnant pore water of the rock matrix surrounding the fracture. This diffusion is facilitated by the continuous pore network from the fracture surface further into the rock matrix. As a result of this diffusion, more radionuclides will be removed from the mobile inventory as it migrates with the flowing groundwater.
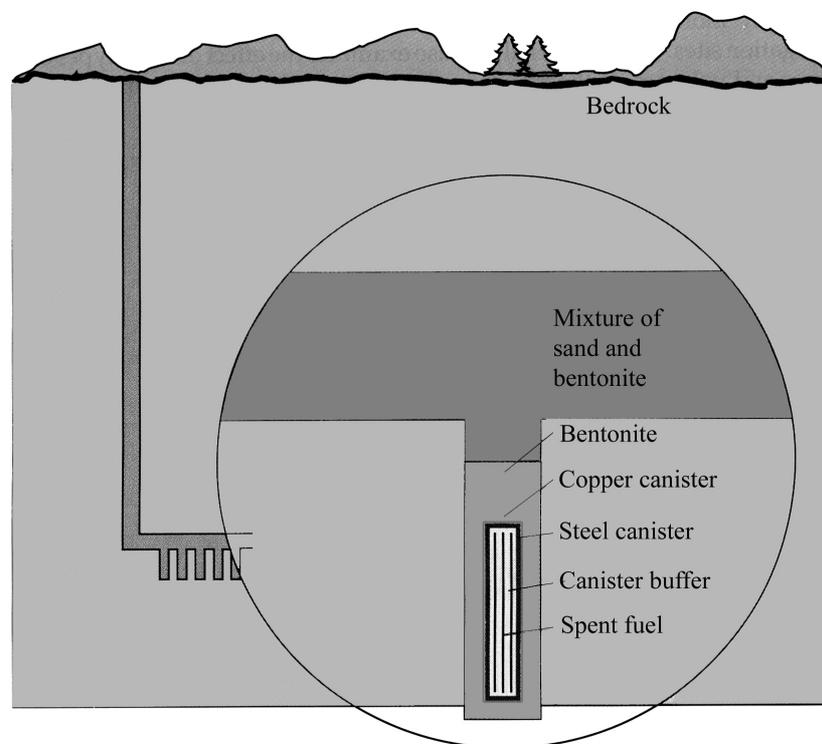
Figure 1.1 Spent fuel disposal concept: disposal depth is about 500 m (Teollisuuden Voima 1992). The current canister concept is copper canister with cast iron insert.

The net outcome of the above mentioned geochemical and physical reactions is a general retardation in the transport of the radionuclides. The geochemical reactions are collectively called sorption, and the physical diffusion is called matrix diffusion. In nature they, of course, occur simultaneously, while sorption reactions begin immediately when new mineral surfaces are exposed to radionuclides via matrix diffusion. Sorption at the same time, however, retards diffusion, as, according to classical matrix diffusion theory, the mobile inventory is the one dissolved in water.

Sorption and matrix diffusion are considered the most important retardation[2] mechanisms for migration in fractured crystalline bedrock.

The basic purpose of geological disposal of nuclear wastes is to isolate them from human environment for time periods long enough to allow the activity of the wastes to decrease to an acceptable level. How well the planned disposal concept fulfils this isolation function in the long term, is studied in performance assessments of the disposal facility. As bedrock is the ultimate natural barrier between man and the nuclear waste, modelling the migration of radionuclides in the bedrock is an important component in any quantitative performance assessment of the repository.

In order to contribute to a well founded migration modelling in performance assessment we compare modelling concepts applied in recent performance assessments with those used in interpreting experiments expressly planned to study in detail retardation mechanisms in the bedrock. It is acknowledged that the models and modelling concepts used in performance assessments are deliberately conservative simplifications of reality. In contrast, the main idea in models used in interpreting experiments is naturally to explain as well as possible what has really happened in the experiment.

The main aim of this report is to summarise the latest results of retardation mechanism studies, both experimental and theoretical, achieved in Finland. The summary is based mainly on the interpretation of laboratory tests and natural analogue studies. Field-scale migration experiments have been relatively few in number in Finland. Compilation of the conclusions serves the purpose of documenting current understanding of retardation phenomena in fractured crystalline bedrock. In this capacity, the review may be useful in assessing future research needs in relation to geological disposal of nuclear waste.

The structure of the report is as follows: first the data needs of a performance assessment of a nuclear waste repository are reviewed briefly, then structural studies both for small and large scale features are discussed. Experimental and theoretical retardation mechanism studies are presented in relatively great detail, while laboratory experiments and natural analogue studies are given special emphasis. Finally we discuss the balance of information (or understanding) between the needs of performance assessment and the supply of the retardation mechanism studies.

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[2] Besides retardation mechanisms there are also mechanisms potentially "accelerating" the migration of radionuclides in the bedrock. Colloids are small particles in the groundwater that could in principle carry an inventory attached on them unretarded, in other words with the groundwater velocity. The concentration of colloids in Finnish groundwater is, however, very small (see e.g. Laaksoharju et al. 1994, Blomqvist et al. 2000). Microbes are in principle capable of changing redox conditions in their living environment. Current understanding of the role of microbes is that they would turn the chemical conditions into more reducing which, in turn, would actually contribute to increased retardation for redox-sensitive elements, as sorption is much higher under reducing than under oxidising conditions.

2. Data needs in performance assessments

2.1 Overall uncertainties in migration modelling

There are two main factors that contribute to the uncertainties of migration modelling in performance assessments. The uncertainties affect the selection of scenarios, i.e. alternative outlinings of the evolution of the groundwater–bedrock system, conceptual models used in migration modelling, and the selection of input data for the models. Both uncertainties are inevitable in the sense that they cannot be fully avoided in practice. In other words, they belong to the nature of geological disposal.

The first uncertainty is based on the long time scales that a performance assessment must cover. It is clear that one cannot 'predict' the behaviour of the groundwater–bedrock system for hundreds of thousands of years as, for instance, in a weather forecast for tomorrow. Rather, one must apply a set of alternative scenarios that cover the feasible evolution possibilities of the groundwater–bedrock system. In order to be able to quantitatively compare the respective outcomes of different scenarios the same migration model is often used for all scenarios. Therefore, the model must by necessity be universal in nature so as to be applicable for a set of scenarios.

The second uncertainty stems from the fact that only a limited number of observations of the bedrock volume under consideration is available. A bedrock volume considered for spent fuel disposal is usually a block surrounded by major fracture zones (see e.g. Löfman 1999), and its size is of the order of km^3. It is, of course, pointless to drill a site full of characterisation holes if the site is afterwards to be used for nuclear waste disposal. This state of affairs leads to a situation in which one has a set of well characterised, but sparsely located observations as the starting point for a performance assessment. In particular, there are no direct observations of the heterogeneity of the bedrock between neighbouring drill holes. Also in this case, the migration models must be simple, universal, and applicable for varying material properties.

2.1.1 Glacial effects

Bedrock in the Fennoscandian Shield is currently very stable in geological terms, and very likely to continue to be so in the future, because there is no volcanism, major earthquakes, or mountain formation in the area. This in turn is because there are no colliding continental plates beneath the Fennoscandian Shield. In Finnish latitudes, repeated glaciations are actually the only mechanism that can create abrupt changes in the conditions of the bedrock. Therefore glaciations must be taken into account in performance assessments of nuclear waste repositories. Not all features of glaciations

are well understood currently and, therefore, glaciations generate uncertainties in the future behaviour of the bedrock–groundwater system.

The end of glaciation is considered to be the time of most rapid and violent changes in the bedrock and in the geochemical conditions within the bedrock. The mechanical changes are due to the rebound effect of the earth's crust. For instance, it has been assessed that during the last Weichselian Ice Age Finland, for a period of time, was covered with an ice sheet of a thickness of around 3 km. This load had compressed the earth's crust by about 700–900 m; this compression was released rapidly after the ice sheet melted (e.g. Eronen and Olander 1990). In this bedrock uplift process existing fractures and fracture zones opened, and some new fractures may also have formed.

It may be noted here that although the most rapid post-glacial rebound took place relatively quickly after the deglaciation, the slower mode of land uplift is still continuing. The mosaic-like block structure of Finnish bedrock may cause small-scale local earthquakes as all neighbouring bedrock blocks may not always rise equally smoothly. Currently land uplift is about 6 mm/a at Olkiluoto and somewhat more towards the Gulf of Bothnia where the glacial compression was highest.

The geochemical changes are due to the local high-pressure inflow of glacial melt waters into the bedrock. This inflow was very high as compared to that prevailing currently, due to the huge hydraulic gradients for a short period of time. This period covers the moment just before the margin of the ice sheet starts to melt and the weight of the ice still can generate a hydraulic pressure around the ice margin. The inflow of glacial meltwater changes geochemical conditions in the bedrock in mainly two ways.

On the one hand the oxic water changes redox conditions towards more oxidising: After the high-pressure inflow ends, redox conditions start to return towards the original more reducing. How fast this happens, depends on the respective flows of oxygen and reducing agents. Here it must be kept in mind that also after the end of glaciation infiltrating precipitation will still carry oxic water (perhaps with different oxygen concentration) into the bedrock, but without the high pressure. High-pressure inflow can also activate normally closed flow channels that will return to their isolation after the hydraulic high-pressure pulse has ended.

On the other hand the glacial meltwater causes effective mixing of different water types. In particular, it may shift the boundary between deep saline water and surficial fresh water. The Finnish glaciation cycle probably includes a long permafrost period during which the bedrock is frozen to maybe hundreds of metres, the actual depth depending on the average temperature, duration of the permafrost period, thermal conductivity of the bedrock, and on geothermal heat generation within the bedrock. During the freezing

of groundwater the salts dissolved in the water are forced out of the ice, thereby eventually forming a layer of saline water below the frozen topmost bedrock layer (see. e.g. Gascoyne 2000). After glaciation this water may also be mixed with the glacial meltwater.

Because of these uncertainties, the migration models used in performance assessments must be versatile enough to be applicable under varying conditions. It may be noted here that the uncertainties above do not prevent a performance assessment from being made, but they do affect the way in which it can be done if this is to be justified as fully as possible.

2.2 Description of heterogeneous medium

The groundwater flow route along water-carrying fractures is usually heterogeneous in at last two directions, and at the same time in two very different length scales. In the direction of the groundwater flow there may be considerable large-scale heterogeneities (of the order of 100 m), but as the flow route is deduced from hole to hole observations there is no direct data about this heterogeneity. Therefore, in flow direction bedrock properties are usually described as stepwise homogeneous subsections with the length of individual homogeneous subsections correlating with the distance between neighbouring drill holes.

Along fracture surfaces there is also a marked heterogeneity due to the channelling of groundwater flow. This is also very difficult to quantify, because, as mentioned above, the flow route is deduced from hole to hole observations. Estimating the distribution of groundwater flow in fractured bedrock is considered a major problem in performance assessments, and special approaches have been used to take the phenomenon into account, as well as technically possible (see next section).

In the direction perpendicular to the flow route, i.e. into the rock matrix there may also be small-scale (of the order of cm's) heterogeneities. Via matrix diffusion and coincident sorption these small-scale heterogeneities may, however, have a considerable retarding effect on the migrating radionuclides. As the drill holes intersect water-carrying fractures there is a good possibility to obtain direct observations of the local heterogeneity of the rock matrix in this direction.

Groundwater flow and migration models applied in performance assessments are usually numerical models based on finite difference or finite element method. With these models increasing the number of elements (unit cells) increases the possibility to describe more detailed features in the medium, see Figure 2.1.

330 elements
2654 elements
1043 elements
6439 elements
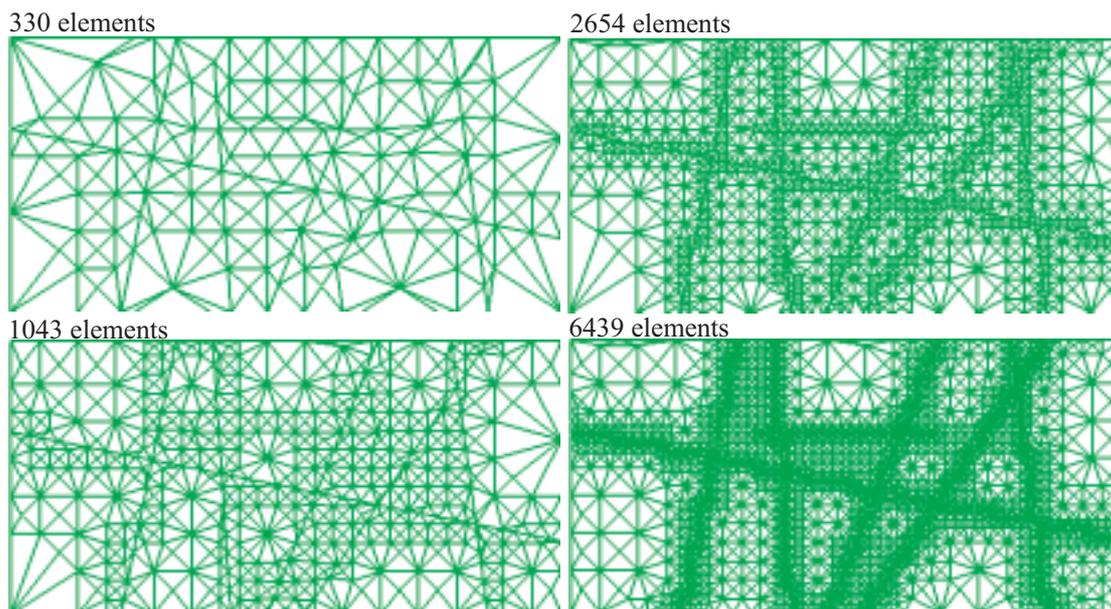
Figure 2.1 An example of how increasing the number of elements in a groundwater flow model increases the possibility of describing heterogeneities in greater detail (Vuori 2000). In this particular example, the increase in the number of elements is focused close to the areas of heterogeneity by applying the adaptive mesh generation package Quadtree (see Mészáros 1999 for details).

In principle, there is a clear correlation between the size of elements in the numerical model, and the heterogeneities or features that can be handled in modelling. From the computational point of view the size of the element is the mathematical limit. In practice, however, there is a technical limit that dictates how small features can in reality be taken into account in simulations. This technical limit is derived, on the one hand, from the small number of observation holes and, on the other hand, from the resolution of technical methods used to characterise the bedrock. The limiting factor in the size of the element is the ability to characterise all the parameters needed in the model for this particular element size.

It is important to understand that the experimental method with the poorest resolution actually defines the real level of resolution in modelling. In the sense of overall modelling it will not help if the rest of the methods have much higher resolution, because the parameter value obtained with the poorest method cannot be defined with any smaller scale.

2.3 Migration models used in performance assessments

So far migration modelling in Finnish performance assessments has been based on advection-dispersion-matrix diffusion approach. This simplified concept is actually used, with various adaptations in most countries considering fractured crystalline bedrock as the host medium for their nuclear waste repositories. In this concept, migration is assumed to take place along water-carrying fractures where advection and dispersion occur. Retardation mechanisms occur both in the fracture and within the rock matrix. In addition, radioactive chain decay is also taken into account as migration continues for long periods of time.

2.3.1 The classical advection dispersion matrix diffusion approach

While being carried along the fracture by flowing groundwater the nuclides interact instantaneously with the fracture surface and diffuse slowly into the rock matrix along a continuous pore network. The water flow as this occurs is assumed to be in x-direction and matrix diffusion in z-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 adsorption described by mass-based distribution coefficients, K_d, (in rock matrix) and area-based distribution coefficient K_a (on fracture surfaces). The transport of radionuclides in the fracture is described by Eq. (1), and within the rock matrix by Eq. (2). The coupling between the two transport equations is provided by the matrix diffusion term. Matrix diffusion is the mechanism that allows groundwater flowing in the fracture to communicate with the stagnant pore water in the rock matrix (cf. Jakob et al. 1989, SKI 1991):

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

$$R_{p,i}\frac{\partial c_{p,i}}{\partial t} = \frac{\partial}{\partial z}\left(D_p\frac{\partial c_{p,i}}{\partial z}\right) - \lambda_i R_{p,i}c_{p,i} + \lambda_{i-1}R_{p,i-1}c_{p,i-1} \tag{2}$$

where $c_{f,i}$ is the concentration of the dissolved migrating nuclide i in the flowing water (atoms/m^3), $c_{p,i}$ the concentration of the dissolved migrating nuclide i in the stagnant pore water (atoms/m^3), D the dispersion coefficient in the x-direction (m^2/s), $R_{f,i}$ the retardation coefficient of nuclide i in the fracture (-), v the groundwater velocity in the fracture (m/s), D_e the effective diffusivity in the rock matrix (m^2/s), λ_i the radioactive

decay constant of nuclide i (1/s), $R_{p,i}$ the retardation coefficient of nuclide i in the rock matrix (-), and D_p the 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):

$$D_p = \frac{\delta_D}{\tau^2} D_w \qquad (3)$$

$$D_e = \varepsilon_p D_p \qquad (4)$$

where δ_D is the constrictivity of the pore network (-), τ^2 the the tortuosity of the pore network (-), D_w the molecular diffusivity in free water (m^2/s), and ε_p the porosity of the rock matrix (-). The factor δ_D/τ^2 is called the geometric factor, and 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:

$$c_{p,i}(z = b,t)\big|_x = c_{f,i}(x,t) \qquad (5)$$

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.

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

$$R_{f,i} = 1 + \frac{2}{2b} K_{a,i} \qquad (6)$$

$$R_{p,i} = 1 + \frac{\rho_s(1-\varepsilon_p)K_{d,i}}{\varepsilon_p} \qquad (7)$$

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where 2b is the fracture aperture (m), $K_{a,i}$ the area-based distribution coefficient of nuclide i (m^3/m^2), $K_{d,i}$ the 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:

$$K_{d,i} = K_{a,i}a_f \tag{8}$$

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. (1) represent advection, dispersion and matrix diffusion, respectively. The coefficient 2/(2b) in the matrix diffusion term in Eq. (1) 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 (2) describes matrix diffusion together with chain decay. The two sets of equations are coupled via the matrix diffusion term and must be solved simultaneously. The total number of equations in both sets equals the number of radionuclides in the decay chain.

Advective transport of radionuclides 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):

$$D_l = \alpha_l v_l + D_w \tag{9}$$

where α_l is the dispersivity (m), v_l the mean groundwater velocity (m/s), and D_w the molecular diffusion coefficient (m^2/s).

WL/Q approach to describing the channelling of groundwater flow in fractured rock

Estimating the exact distribution of groundwater flow along a network of intersecting fractures in bedrock is an extremely demanding task. According to field observations, groundwater flow is clearly channelled, in other words concentrated into active flow channels within fractures charcterized as 'water-conducting'. From migration modelling point of view the problem is that in a typical scale of observation the number of active flow channels is relatively small, so that the Fickian dispersion model included in the classical Eq. (1) does not give a good representation of the dispersion process. If the number of flow channels would be very large, then the Fickian approach would work

better. Another problem is that it is beyond current experimental methods to characterize each active flow channel individually. Some kind of simplifying approximation is obviously needed.

Finnish performance assessments have taken the channelled groundwater flow into account by using the WL/Q approach coupling the flow wetted surface and groundwater flow rate (Vieno & Nordman 1999). This number can be shown to be related to fracture aperture and groundwater transit time:

$$\frac{W\,L}{Q} = \frac{W\,L}{v\,W\,2b_V} = \frac{t_w}{2\,b_V} \tag{10}$$

where W is the width of the flow channel (m), L the transport distance (m), Q the flow rate in the channel (m^3/a), v the advection velocity of the groundwater in the channel (m/a), t_W the groundwater transit time (a), and $2b_V$ the volume aperture (m) of the channel. WL represents the flow wetted surface, i.e. the fracture surface area in direct contact with flowing groundwater. The number WL/Q can be considered as transport resistance in the sense that the higher the value the more effective the bedrock is as a release barrier; see Vieno et al. (2001) for further details.

The channelling of groundwater flow has a profound effect on the overall retardation of radionuclides migrating along a fracture network. Because the whole fracture surface is not in contact with flowing water the retarding effect of matrix diffusion (and the related sorption) is markedly reduced.

The numerical analyses in Finnish performance assessments have been performed with the finite element code FTRANS, effectively incorporating Eq. (1)[3]. The code, however, employs the conventional parameters for advection along the fracture: length of the migration path, velocity of the water flowing in the fracture, and aperture of the fracture. Therfore, these input parameters are fixed in such a way that the chosen value for the primary input parameter WL/Q is obtained (by using the above equation). In TILA-99 the WL/Q was assumed to vary between $5 \cdot 10^3$ and $5 \cdot 10^4$ a/m for the reference scenarios (Vieno & Nordman 1999).

The WL/Q approach is related to similar approaches for instance in Sweden. WL represents the 'flow wetted surface' as used by Elert (1997). In SITE-94 (SKI 1996) the transport characteristics are represented by the so-called F-ratio, F =a_r/q = 2 WL/Q

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[3] In performance assessment analyses the Fickan dispersion was omitted for reference scenarios as groundwater flow channelling was described by the WL/Q approach. Sensitivity studies were performed, however, using Fickian dispersion (Vieno & Nordman 1999).

where q is the Darcy velocity (m/a) and a_r the wetted fracture surface area per volume of rock (m^2/m^3).

2.3.2 Variations to the classical approach

Anion exclusion

Pore surfaces generally carry some negative net 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).

These two mechanisms have different effects on migrating radionuclides. Anion exclusion enhances overall migration of anions due to decreased matrix diffusion and, therefore, decreased retardation. In contrast, surface diffusion retards overall migration due to enhanced diffusion of radionuclides into rock matrix. In Finnish performance assessments so far, anion exclusion has been considered in the migration modelling for the far field. The inclusion of anion exclusion and exclusion of surface diffusion has been motivated by the conservatism principle applied in the performance assessment (Vieno & Nordman 1999). In the case of surface diffusion it may also be noted that modelling surface diffusion would require a diffusion coefficient for the adsorbed inventory, the parameter which is very difficult to obtain in an independent manner (see details in e.g. Rasilainen 1997). In practice, anion exclusion has been taken into account by simply applying decreased porosity and diffusivity values for anions.

Heterogeneous rock matrix properties

The properties of rock matrix are often heterogeneous in terms of diffusion. Closest to the fracture there may be fracture coating material and beneath it an altered layer, Figure 2.2.

The altered layer has repeatedly been observed and linked to increased porosity and diffusivity. Table 2.1 shows the diffusion properties assumed in the TILA-99 performance assessments; in the table the fact that saline or non-saline groundwater affects anion exclusion has also been taken into account.
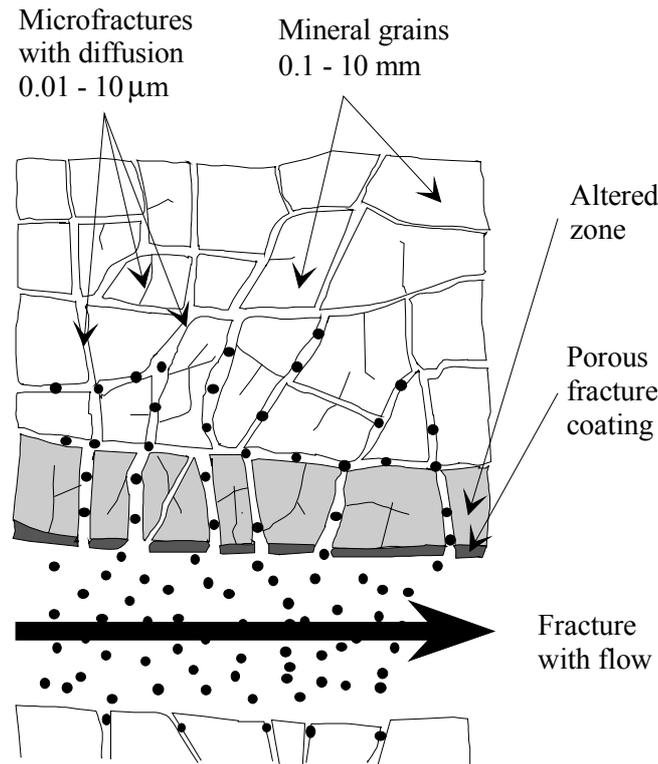
Figure 2.2 Heterogeneous structure of rock matrix (Rasilainen 1997).

Table 2.1 Porosity (ε_p) and effective matrix diffusion coefficient (D_e) in the rock matrix (Vieno & Nordman 1999). In TILA-99, the thickness of rock matrix was limited to 10 cm as, according to sensitivity studies, increasing matrix thickness did not effect dose rates in the cases studied.

	Distance from the fracture 0 - 1 cm	Distance from the fracture 1 - 10 cm
Non-anions Non-saline and saline groundwaters	$\varepsilon_p = 0.5\ \%$ $D_e = 1 \cdot 10^{-13}\ m^2/s$	$\varepsilon_p = 0.1\ \%$ $D_e = 1 \cdot 10^{-14}\ m^2/s$
Anions Non-saline groundwater	$\varepsilon_p = 0.1\ \%$ $D_e = 1 \cdot 10^{-14}\ m^2/s$	$\varepsilon_p = 0.02\ \%$ $D_e = 1 \cdot 10^{-15}\ m^2/s$
Anions Saline groundwater	$\varepsilon_p = 0.2\ \%$ $D_e = 5 \cdot 10^{-14}\ m^2/s$	$\varepsilon_p = 0.04\ \%$ $D_e = 5 \cdot 10^{-15}\ m^2/s$

In line with general observations, the porosity and diffusivity values applied in TILA-99 are higher closest to fracture and decrease clearly with distance into the rock matrix. For porosity the decrease is by a factor of five, and for diffusivity by a factor of ten. Furthermore, both porosity and diffusivity values are systematically smaller for anions than for non-anions, thus mimicking the effect of anion exclusion.

3. Structural studies

3.1 Small-scale pore network studies

3.1.1 PMMA method

PMMA-technique (Hellmuth et al. 1993, 1994; Siitari-Kauppi et al. 1998) measures diffusion porosity but it also gives the porosity distribution, e.g. 2D and 3D information of different porous minerals inside the centimetric scale rock sample. Combined with mineralogical-petrographic characterization of the water-filled pore space, it provides the porosity distribution along the water conducting fracture.

C-14-PMMA- and H-3-PMMA-methods involve impregnation of rock samples with respectively C-14 or H-3 labelled methylmethacrylate in vacuum, polymerisation by irradiation, and autoradiography and optical densitometry with digital image processing techniques. The low molecular weight and low-viscosity carrier monomer MMA, which can be fixed after impregnation by polymerisation, provides direct information about the accessible pore space in crystalline rock. This information cannot be obtained using water or gas phase methods.

Total porosity is calculated by using 2D autoradiographs of sawn rock surfaces. The geometry of porous regions is then visualized. The preconditions for applying this method are: (i) known local bulk density; (ii) presence of only two phases, namely mineral and PMMA; and (iii) homogeneous distribution of pores and minerals below the limit of lateral resolution of autoradiography.

Properties of the MMA tracer

Methylmethacrylate (MMA) is a monomer with very low viscosity, 0.00584 P (20°C), while the viscosity of water is 0.00895 P (25°C). An MMA molecule penetrates to pores of 2 nm, as tested with standard material. A water molecule, 0.2 nm, penetrates still smaller pores. Because MMA's contact angle on silicate surfaces is low, impregnation of bulk rock specimens is rapid, its exact rapidity depending on the existing pore apertures. The MMA molecule is small (molecular weight 100.1 g/mol). It has non-electrolytic properties and only low polarity, the polarity of the ester being considerably lower than that of water, and it behaves in the rock matrix like a non-sorbing tracer. The low β energies of the carbon-14 isotope, max 150 keV, and of the tritium isotope, max 18 keV, are convenient for autoradiographic measurements.

Drying, impregnation with C-14-MMA, and polymerisation of samples

Rock samples are vacuum dried in a chamber for several days at a maximum temperature of 110°C. After drying they are cooled to 18°C. For MMA impregnation, the tracer is put into a reservoir and transferred under vacuum to the impregnation chamber. The impregnation time changes from a few to several days. After impregnation, the samples are irradiated with gamma rays from a Co-60 source, in order to polymerise the monomer in the rock matrix; the required dose is 50 to 70 kGy. The samples are irradiated under water with MMA emulsion in polyethylene vials.

Autoradiography

Irradiation of rock samples with Co-60 causes strong luminescence of K-feldspar and other major rock-forming minerals, which exposes autoradiographic film. To avoid this, the luminescence is pre-released by heating samples to 120°C for 3 hours before sawing. Mylar foil with aluminium coating is placed on top of the film to shield it from the rest of the emissions.

The heated samples are sawn into pieces. The sawn rock surfaces are exposed on autoradiographic films. The film is high-performance autoradiographic film for C-14 and other low energy β-emitting nuclides. The resolution of the film is just a few μm. The final resolution depends on the roughness of the sawn surface and the range of the 150 keV or 18 keV beta particles in the rock matrix. As compared to the range of beta particles (100 μm), the rock samples used are infinite in thickness; the range of beta particles also has to be taken into account. The beta absorption correction is obtained from the ratio of the density of rock to the density of polymethylmethacrylate.

Calculation of porosity by digital image analysis of autoradiographs

Interpretation of the results is based on digital image analysis of autoradiographs. Digital image analysis starts from dividing the autoradiograph into area units called pixels. Basically all intensities in the sub domains are converted into corresponding optical densities, which in turn are converted into activities with calibration curves measured for each exposure. Finally, the activities are converted into respective porosities.

Intensity and optical density

Since the response of the image source and the amplifier of the digital image analysator are linear, the digitised grey levels of the film can be handled as intensities. Optical

densities, which according to Lambert & Beer's law are concentration proportional, are derived from the intensities:

$$D = \log\left(\frac{I_0}{I}\right)$$

(11)

where D is the optical density (-), I_0 the the intensity of the background (grey levels 0-256) and I the intensity of the sample (grey levels 0-256).

Activity and optical density

A conversion function is needed to relate the optical densities (grey levels) measured to corresponding activities. PMMA standards (tracer diluted with inactive MMA) having specific activities have been used to establish the calibration function. The following calibration curve was used:

$$D = D_{max}\left(1 - e^{-kA}\right)$$

(12)

where D_{max} is the maximum optical density (-), k a fitting parameter, and A the specific activity (-). Solving A from the Eq. (12) gives:

$$A = -k^{-1}\ln(1 - D / D_{max})$$

(13)

Porosity

The local porosity ε of the sample is obtained simply from the abundance of the tracer (assuming constant tracer concentration in the PMMA): the higher the abundance of the tracer, the higher the local porosity:

$$\varepsilon = \beta(A / A_0)$$

(14)

where A_0 is the specific activity of the tracer used to impregnate the rock matrix (Bq/ml), and β is the β-absorption correction factor (-). The absorption of β radiation in a substance depends roughly linearly on the density of the substance. Therefore factor β can be approximated from:

$$\beta = \rho_s / \rho_0$$

(15)

where ρ_s is the density of the sample (g/cm^3) and ρ_0 is the density of pure PMMA (1.18 g/cm^3). In the interpretation, the sample is assumed to consist of rock material and pores (containing PMMA), and therefore ρ_s can be expressed as:

$$\rho_s = \varepsilon\rho_0 + (1-\varepsilon)\rho_r \qquad (16)$$

where ρ_r is the density of mineral grains (g/cm^3). In bulk measurements the average density of the rock sample (2.70 g/cm^3) is used. Substituting Eqs. (15) and (16) into Eq. (14), the porosity and the activity relationship can be solved:

$$\varepsilon = \frac{\dfrac{\rho_r}{\rho_0}\dfrac{A}{A_0}}{1+\left(\dfrac{\rho_r}{\rho_0}-1\right)\dfrac{A}{A_0}} \qquad (17)$$

where A is the specific activity of individual pixel (Bq/ml) and A_0 is the specific activity of the tracer (Bq/ml). The porosity of each individual pixel n from the autoradiogram is calculated according to Eqs. (13) and (17). The porosity histogram gives the relative frequency of regions of individual porosities. The total porosity is obtained from the porosity distribution by taking the weighted average:

$$\varepsilon_{tot} = \frac{\sum_n Area_n \varepsilon_n}{\sum_n Area_n} \qquad (18)$$

where $Area_n$ is the area of pixel n and ε_n the local porosity of pixel n. An example of porosity determination by the C-14-PMMA method is given in Figure 3.1
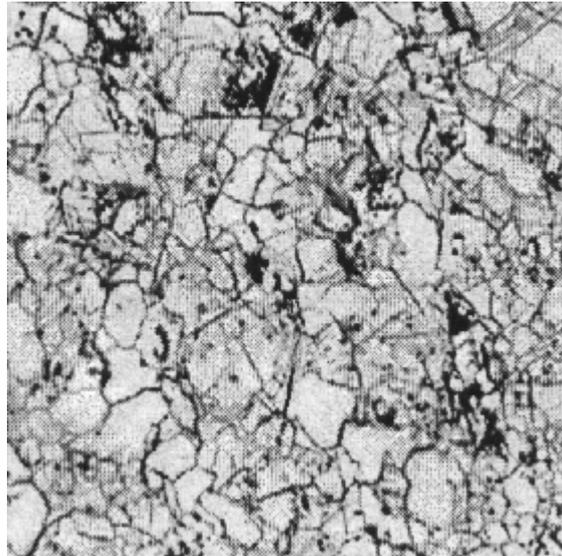
Figure 3.1 Example of spatial porosities obtained by the C-14-PMMA method, darker areas indicate higher local porosity (Simbierowicz & Olin 1997).

Multigrid based interpretation of autoradiographs

An autoradiograph can be scanned to obtain a two-dimensional porosity map of the section in bitmap form (see Figure 3.1). The method of Gáspár and co-workers (see references in Simbierowicz & Olin 1997) was used to build a quadtree grid based on the intensity data. In this method a square 'root cell' is chosen to contain a typical area of the bitmap and then all the bitmap pixels within the root cell are scanned for maximum and minimum intensity value. If the difference between the maximal and minimal intensity exceeds some prescribed limit, then the root cell is divided into four congruent child cells. Each of the child cells is then scanned separately and those still exceeding the prescribed limit become subdivided further. This recursive subdivision process continues until all originating grid cells contain sufficiently uniform intensity values, or until the prescribed maximal number of successive divisions in a cell is reached. The overall number of grid cells is often substantially smaller than in an equidistant grid of the same resolution (Figure 3.2).
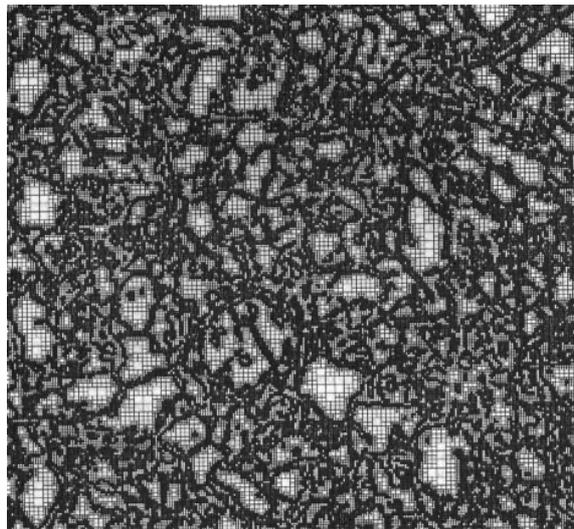
Figure 3.2 Ten level quadtree generated from the bitmap shown in Figure 3.1
(Simbierowicz & Olin 1997).

After generating the grid structure, bitmap intensities are converted to porosity values with the aid of a conversion table.

To study diffusion phenomena numerically in heterogeneous vs. homogeneous systems two otherwise comparable bitmaps were generated for the two systems. The heterogeneous bitmap had conductive (permeable) and non-conductive (impermeable) cells, while the homogeneous one had the weighed average of the two permeabilities. Theoretical (i.e. numerical) leaching experiments for both models were performed. A clear difference was found between the respective model calculations using

homogeneous and heterogeneous (scanned bitmap) grid. Also a better agreement was found qualitatively with experimental leaching results performed with tracers using the heterogeneous bitmap.

While being numerically sound and convenient, the full potential of the multigrid approach could not be tested for real samples. The reason is that the theoretical exercise described above was loaded with assumptions (see Simbierowicz & Olin 1997 for details). It would be worthwhile to try to verify the approach against corresponding analytical solutions, if available.

In general, the C-14-PMMA method provides detailed information about the distribution of porosity in rock matrix. In some cases it may go down to the scale of μm's. Concerning practical matrix diffusion modelling, this information cannot be utilised to its full potential because porosity data alone is not sufficient. Diffusivity data is needed also. For the time being, however, there is no defendable method to derive D_e (or D_p) values from the ε_p distributions.

A practical drawback of the C-14-PMMA method is that after measurements the rock samples are impregnated with PMMA and, therefore, no longer available for other physical studies. Chemical analyses, for instance USD studies, are possible, however, because after sub-sampling the impregnated rock sample, rock sub-samples can be technically analysed so that the small PMMA amount involved (at most of the order of per cent) does not affect the results. Another practical drawback is that the amount of sample material required for the C-14-PMMA technique is more than negligible.

3.1.2 Helium gas method

Helium gas techniques of measurement offer versatile possibilities for rapid studies of migration phenomena in fractured and porous media. Porosity, permeability and effective diffusion coefficients are important factors in migration studies, and they have traditionally been determined by liquid phase experiments. In the gas phase it is possible to make these measurements in a much shorter time scale. An in situ version of the method and specially designed in situ equipment have also been developed and tested both in laboratory and in the research tunnel at Olkiluoto.

Through–diffusion measuring techniques

In the through-diffusion technique, the helium injection cell at one end of the sample was initially filled with helium, and the flow of helium at the other end of the sample was measured continuously (Figure 3.3). The whole set of breakthrough curves for helium were measured and modelled. Porosities and effective diffusion coefficients

were determined as results from these model fits. For an accurate characterization of the samples, a thorough drying treatment turned out to be necessary.
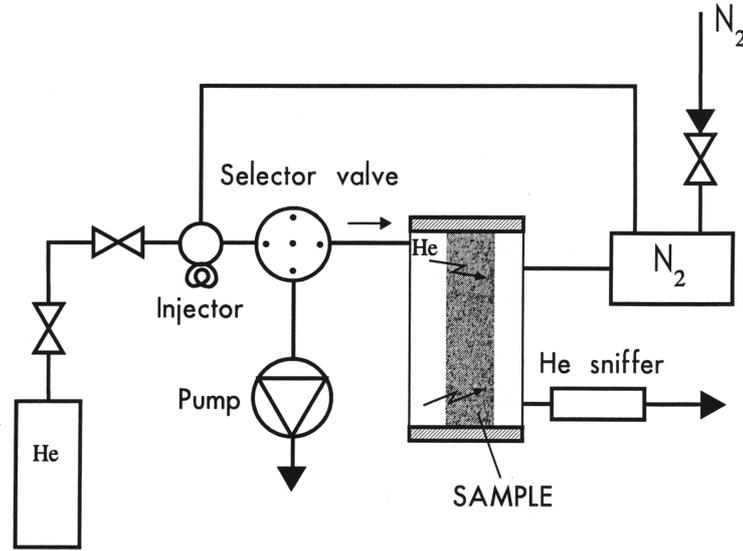
Figure 3.3 Schematic picture of the helium through-diffusion measurement set-up.

Modelling

The modelling of the through-diffusion measurements is based on the solution of an appropriate diffusion equation. Because of the planar geometry of the samples and reflective boundary conditions in the transverse directions, one can use a one-dimensional approximation, and the diffusion equation to be applied for the concentration of helium $C(x,t)$ (kg/m^3) is simply:

$$\frac{\partial C}{\partial t} = \frac{D_e}{\varepsilon_p} \frac{\partial^2 C}{\partial x^2} \tag{19}$$

where t (s) is time, D_e (m^2/s) the effective diffusion coefficient, ε_p the porosity and x the position inside the sample.

Boundary conditions in the direction of helium transport are such that the concentration of helium in the injection chamber is assumed to decrease according to the diffused amount. It is also assumed that there is no sorption and that helium concentration at the outer surface of the sample is zero due to continuous flushing with nitrogen.

Porosity ε_p and the effective diffusion coefficient D_e (m^2/s) can both be determined from the breakthrough curves of helium by fitting the curves with the solution of Eq. (19). In

this one-dimensional approximation it is in fact possible to derive an analytical expression for the mass flow of helium through the sample:

$$\dot{m} = -D_e A \frac{\partial C}{\partial x}\bigg|_{x=1} \quad [kg/s] \tag{20}$$

in the form:

$$\frac{\dot{m}}{m_0} = D_a h \sum_{n=1}^{\infty} \frac{2h\alpha_n e^{-D_a \alpha_n^2 t}}{\sin(\alpha_n l)\left[l\left(\alpha_n^2 + h^2\right) + h\right]} \tag{21}$$

where $A(m^2)$ is the cross-sectional area of the sample, m_o (kg) the mass of the injected helium, $D_a = D_e/\varepsilon_p$ (m^2/s) the apparent diffusion coefficient, $h = \varepsilon_p/s$, s (m) being the average length of the injection cell, α_n, $n = 1, 2, ...,$ are the roots of $\alpha \tan(\alpha l) = h$, and 1 (m) is the average length of the sample (Väätäinen et al. 1993, Carslaw & Jaeger 1959). The average length of the injection cell (s) and the length of the sample (l) are both needed as input parameters.

Once the above-mentioned parameters have been fixed, the theoretical model is fitted to the breakthrough curves by varying the effective diffusion coefficient D_e and the porosity ε_p. Another possibility is to derive the value of porosity from independent measurements, in this case the effective diffusion coefficient is the only parameter to be fitted.

Although measurements are carried out in the gas phase, the corresponding diffusion coefficients for the water-saturated case can be derived. This is based on the fact that, in both cases, the diffusion equation is the same, apart from the actual values of the diffusion coefficients. Significant changes in the pore space are not expected to occur upon drying the samples.

For helium diffusing in free nitrogen gas at 22°C, the diffusion coefficient $D_e(N_2)$ is $6.75 \cdot 10^{-5}$ m^2/s, and for helium diffusing in free water at 22°C the diffusion coefficient $D_e(H_2O)$ is $5.8 \cdot 10^{-9}$ m^2/s. The ratio $D_e(H_2O) / D_e(N_2)$ is therefore 1/11 600. Scaling of the measured diffusion coefficients by this factor provides a good estimate of the corresponding coefficients for helium atoms diffusing in rock samples saturated with water. If other inert molecules are considered, their mass and size should also be taken into account. For typical molecules consisting of only a few atoms, the diffusion coefficient in free water is close to $2 \cdot 10^{-9}$ m^2/s. Measurements can therefore be scaled to the diffusion coefficients of these heavier molecules in water-saturated samples by using an approximate scaling factor of 1/35 000 (Hartikainen et al. 1996, Rasilainen et al. 1996). An example break-through curve is shown in Figure 3.4.
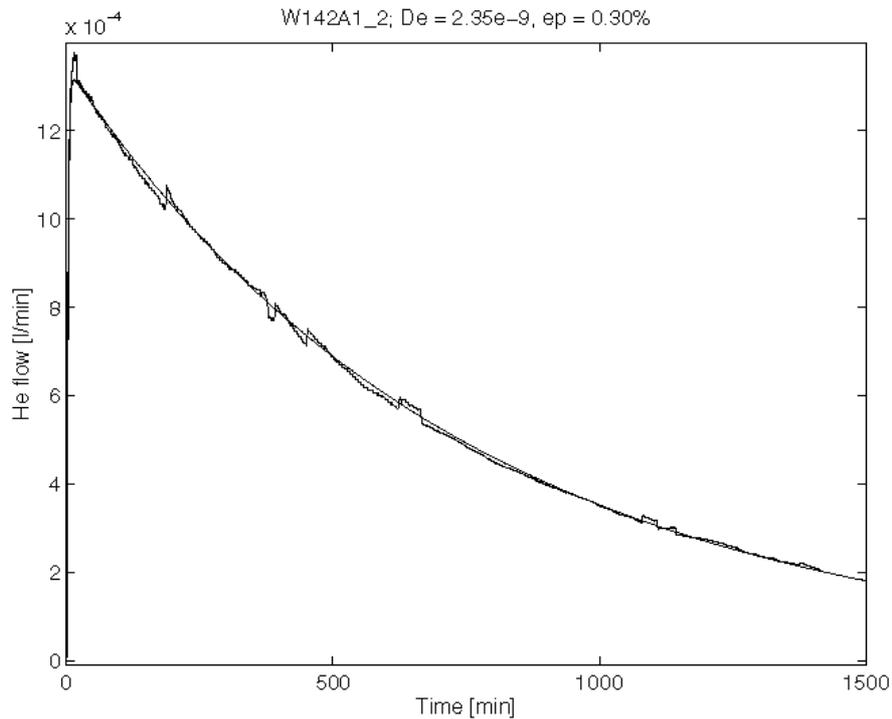
Figure 3.4 Typical measured and fitted curve for through-diffusion.

Permeability measurements

The experimental set-up of permeability measurements is similar to that of the through-diffusion measurements (Figure 3.5). A pressure difference p_2-p_1 is introduced over the measured sample.

The surface of the sample in the injection cell is exposed to an elevated pressure of helium. This is the inner surface of the central hole in the case of the ring samples and one of the rectangular faces in the case of the cubic samples. A constant pressure difference is maintained between the opposite surfaces. The outer surface of the sample is flushed with nitrogen, and the concentration of helium in the nitrogen is measured. The flow rate of helium through the sample is measured for several pressure differences. For each pressure difference, the flow rate is allowed to stabilize before reading its value.
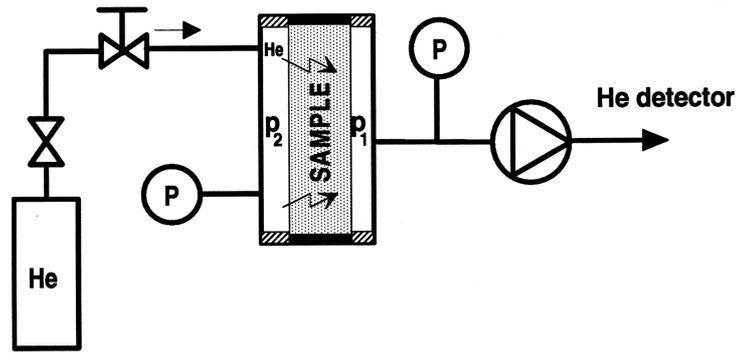
Figure 3.5 Schematic picture of the permeability measurement set-up.

Modelling

When a pressure difference exists across the sample, helium transport through the sample is mediated by diffusion, and also by flow induced by the pressure gradient. According to Fick's and d'Arcy's laws for a compressible fluid, the volume flow of helium through the sample is then given by (Dullien 1979):

$$Q = Q_{diff} + \frac{KA}{\mu l} \frac{\left(p_2^2 - p_1^2\right)}{2 p_1} \tag{22}$$

where Q (m^3/s) is the flow rate through the sample, Q_{diff} (m^3/s) the flow rate due to diffusion only, K (m^2) the permeability coefficient, A (m^2) the cross-sectional area of the sample, μ (Pa s) the dynamic viscosity of helium gas, l (m) the length of the sample, p_2 (Pa) the pressure of helium in the injection cell, and p_1 (Pa) the pressure of helium at the outlet. The total flow rate through the sample is measured for several pressure differences, and the permeability coefficient is determined from a fit to the measured points by Eq. (22) (Figure 3.6).
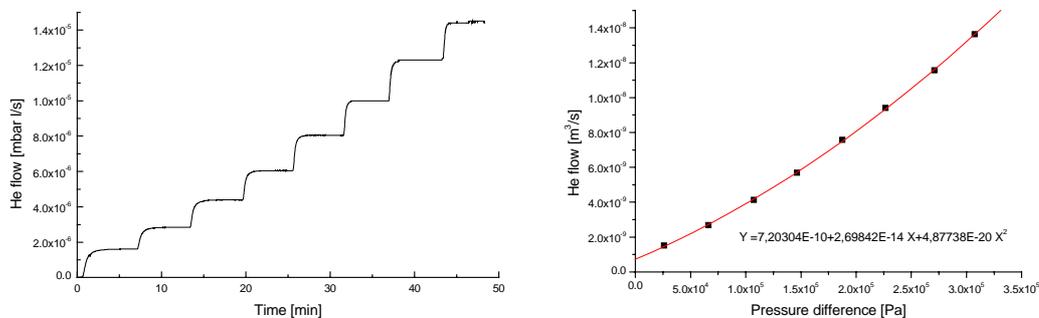
Figure 3.6 Permeability measurement and the related fit.

The measured permeabilities, K (m^2), can be used to determine the hydraulic conductivities, K$_H$ (m/s), of the samples. These are given by (Dullien 1979):

$$K_H = \frac{\rho g}{\mu} K \tag{23}$$

where ρ is the density of water (kg/m^3), g the acceleration of gravity (m/s^2), and μ the dynamic viscosity of water.

Porosity measurements with helium pycnometer

The experimental arrangement of the pycnometer used in the porosity measurements is shown in Figure 3.7. According to the equation of the state of an ideal gas, the porosity of the sample can be determined when the pressures and the temperatures of the cells, and the bulk volume of the sample V$_b$ (m^3), are all known. The bulk volume of the sample is determined by the water immersion method. The porosity ε$_p$ (%) can then be expressed in the form:

$$\varepsilon_p = \frac{V_b - V_g}{V_b} \cdot 100 \tag{24}$$

where V$_g$ is the grain volume determined in the pycnometer measurement (m^3). The pycnometer arrangement can be used to measure the porosity of irregularly shaped rock samples, whereas in the previously presented techniques a regular geometry was assumed.
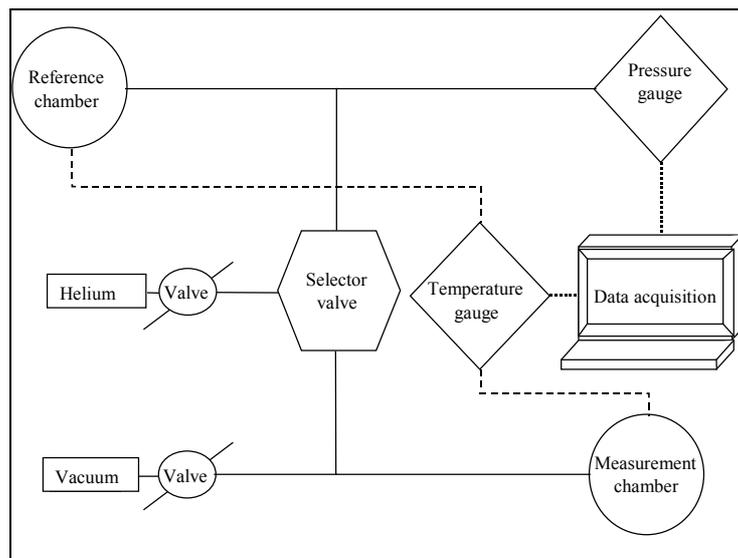
Figure 3.7 Experimental set-up of the He-pycnometer.

Channel flow measuring techniques

The channel flow technique is designed for ordinary drill cores. This technique takes into account the effect of matrix diffusion on the break-through curve, and it is suitable for scanning a relatively large volume of rock in a rather short time. In this method a cylindrical drill core sample is placed into a cylindrical measuring chamber of slightly larger dimensions. Matrix diffusion takes place from the annular flow channel between the sample and the wall of the chamber.

The flow channel in this method is formed between the sample surface and the inner surface of the tightly fitted metal tube. The experimental set-up for this measuring geometry is shown in Figure 3.8.

1) Pressure valves
2) Flow rate gauge
3) He injector/valve

4) Sample
5) Flow resistance valve
6) He sniffer
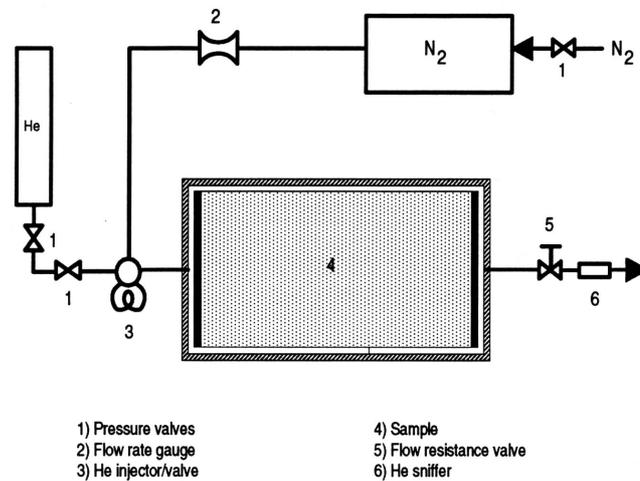
Figure 3.8 Schematic picture of the channel flow measurement set-up.

Modelling

The break-through curve is measured for several different flow rates that are of the order of 1–100 ml/min. It is possible to model hydrodynamic dispersion, molecular diffusion in the channel, and matrix diffusion, if the aperture of the channel and the flow rate are known. In this model the channel is divided into small compartments. The mass transport of the tracer between the neighbouring compartments is covered with longitudinal molecular diffusion and Taylor dispersion:

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial x} - D\frac{\partial^2 C}{\partial x^2} = 0 \qquad (25)$$

where $C(x,t)$ is the concentration of the tracer (kg/m^3), v the velocity of the flow (m/s) and D a combination of molecular diffusion coefficient and Taylor dispersion coefficient (m^2/s).

Because of the strong molecular diffusion, the concentration of helium is effectively homogenised across the annular flow channel. Therefore the break-through curve, as determined by molecular diffusion and Taylor dispersion, can be treated as independent sharp pulses of helium. The effect of matrix diffusion can now be calculated for each of these pulses separately, and the appropriate equations include only advection with velocity v_n and matrix diffusion. These equations can be expressed in the form:

$$\frac{\partial C_n}{\partial t} + v_n \frac{\partial C_n}{\partial x} = \frac{D_e}{2b} \frac{\partial C_p}{\partial z}\Big|_{z=0}$$
$$\frac{\partial C_p}{\partial t} = \frac{D_e}{\varepsilon_p} \frac{\partial^2 C_p}{\partial z^2}$$

(26)

where $C_p(x,z,t)$ is the concentration of helium inside the rock matrix (kg/m^3), z the distance from the surface of the sample (m), 2b the aperture of the flow channel (m), and ε_p and D_e the porosity and effective diffusion coefficients of the rock matrix. Now that each C_n corresponds to a very sharp pulse of helium, Eqs. (26) can be solved in the limit of a delta function pulse. Within this limit the solution can be found in analytic form, and the corresponding results for the break-through curve $\tilde{C}_n$ can be expressed in the form:

$$\tilde{C}_n = \frac{Y_n C_n}{\pi^{1/2}(t - 1/v_n)} e^{-Y_n^2}$$
$$Y_n = \frac{l\sqrt{\varepsilon_p D_e}}{2bv_n(t - 1/v_n)^{1/2}}$$

(27)

which is valid for all $t > 1/v_n$. The total break-through curve C is the sum of separate contributions:

$$\tilde{C}(t) = \sum_{n=1}^{N} \tilde{C}_n$$

(28)

In this model the porosity and the diffusion coefficient cannot uniquely be separated from each other. The product of these coefficients is the main factor affecting the calculated break-through curve. The channel flow measurement results are therefore given as a product $D_e \cdot \varepsilon_p$.

In situ -version of the channel flow measurements

Laboratory measurements alone may not be sufficient for characterizing the migration properties of bedrock. Therefore an in situ -version of the channel flow method was developed (Autio 1996, Hartikainen et al. 1997, Autio et al. 1999). The method was tested both in laboratory and in in situ -conditions. The in situ -equipment is designed for measuring diffusion properties near the rock surface, at present less than three meters away from the surface.

The in situ -method is based on the channel flow measurements described in the previous section. In the in situ -method the flow channel is formed between the outer surface of the metal tube and the inside wall of the drill hole (Figure 3.9).
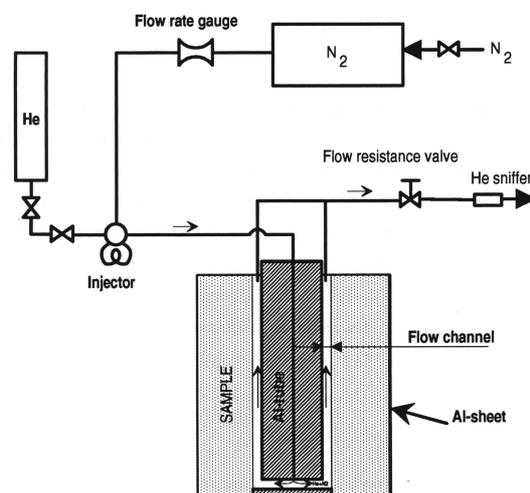
Figure 3.9 The experimental set-up for testing the in situ -measurements in laboratory conditions.

One important benefit of the helium gas method in the laboratory as well as in the field is that it is non-destructive. This means that the rock samples or rock volumes used in helium gas measurements are still available undisturbed for other measurements afterwards.

3.2 Large-scale flow channels

Large-scale flow channels have been looked for at the Palmottu natural analogue project. The incentive was to characterise a flow route for migration related studies. In the following we briefly present the methods used for locating the Eastern Flow System that was finally selected as the reference flow system, Figure 3.10.
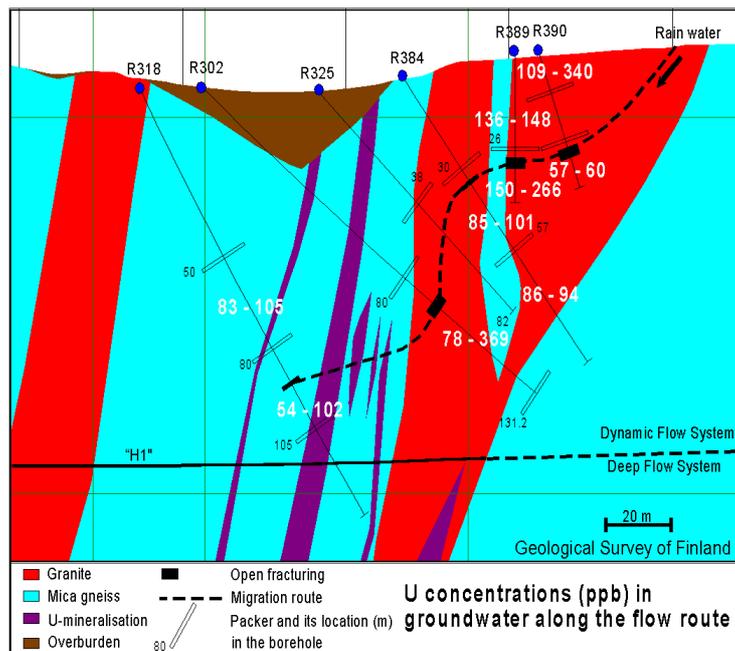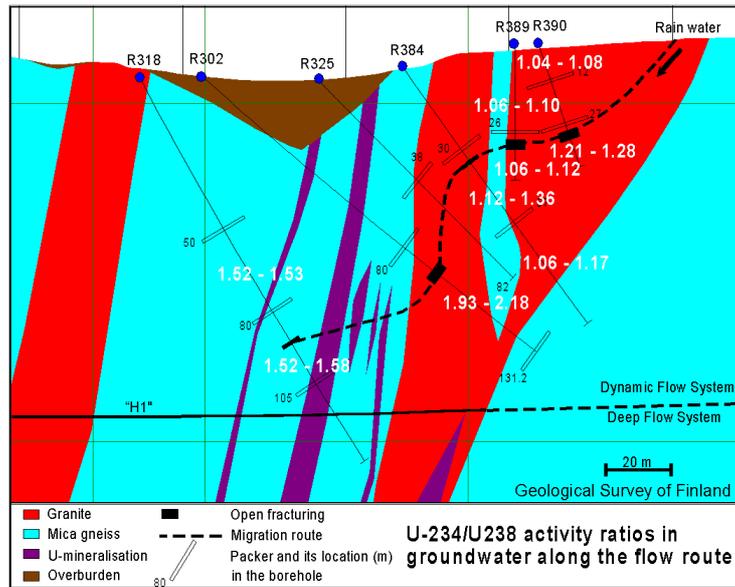
Figure 3.10 The Eastern Flow System at Palmottu. The drill holes were sampling holes for groundwater and rock material. Activity ratios (U-234/U-238) and uranium concentrations are shown along the flow route. The packer intervals applied in groundwater sampling are shown as distance (m) from the top of the respective borehole (Blomqvist et al. 2000).

The first stage in the hydrological site characterisation programme was to test hydraulic connections between the numerous boreholes at the site. Several different measurements

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were performed. All studies were aimed at 1) locating flow paths in bedrock, 2) measuring their respective hydraulic properties and 3) estimating natural groundwater flow conditions. The interesting structures (zones) were first located by geological drillcore logging and geophysical studies made in the boreholes.

The first hydrologic studies in Palmottu area concentrated on the study of hydraulic heads in 3D space in the local borehole area (Hakkarainen et al. 1991). A preliminary 2D numerical study of deep natural groundwater flow was also conducted in order to describe the natural deep groundwater conditions in local fracture zones and their immediate vicinity (Lampinen et al. 1996). The final groundwater flow interpretation was done in 3D (Korkealaakso & Pitkänen 1997, and Koskinen & Kattilakoski 1997).

Hydraulic head measurements

The hydraulic head data were collected from the packed-off borehole sections at the study site. The main aim of these concentrated towards the Eastern Granite and its surroundings to the depth of 200 meters.

The 3D block of bedrock consisted 23 packed-off boreholes. The head data were interpolated to a 3D element mesh with some 10 m x 10 m x 10 m elements. The depth of the block was 200 metres. The number of packers in individual boreholes varied from one to three, meaning that two to four measurement-intervals are present in these boreholes.

Cross-hole testing disturbed the natural field for a while, but it was possible to monitor the hydraulic response caused by pumping in the specified borehole section.

RESULTS

Hydraulic head levels were observed to fluctuate widely when the system is disturbed by outside effects, for example by rain or by waters due to melting of snow in the spring. The variations in head values can be seen in all of the measured packed-off sections, but the magnitude varies in different sections. This could be due to the nature of the overburden, the thickness of the overburden, ground frost, the existence of flow routes in the bedrock and the hydraulic parameters of the water bearing structures.

At Palmottu hydraulic head tests have indicated which structures are water-conducting, and what the flow directions in large scale are. They have also located water divides. Seasonal variations have an effect on head distribution and, hence, on possible flow directions in the zone (Lampinen 1997). These directions can be considered to indicate the more conducting fractures or fracture systems. Usually these directions coincided

with the general schistosity. A nearly horizontal boundary could be found, which restricts flow to the upper part of the rock mass, and, therefore, only small amounts of water move between these upper and lower parts of bedrock.

Spinner test and cross-hole tests

The spinner method gives the exact locations of the hydraulically most conductive structures, while simultaneous monitoring of surrounding boreholes gives information on the geometry and hydraulic properties of the conductors (Lampinen et al. 1996).

During the spinner test (Jönsson et al. 1995a, b) water is pumped from the borehole using an airlift pump and out coming flow from the borehole is recorded by a flow meter. A spinner probe placed in the borehole detects fractures where groundwater flows into the borehole.

Eleven boreholes were tested using spinner equipment. Simultaneously during the spinner measurements, changes in the groundwater levels in the surrounding boreholes were recorded. Three boreholes were packed-off using one to three packers. Hydraulic connections were usually seen in the nearby boreholes and discharges (m^3/s) were measured. The maximal drawdowns varied from 0 to more than 2 metres.

A short cross-hole measurement campaign was carried out in order to test equipment and working methods (Lampinen et al. 1996). In a cross-hole test, water is pumped from one borehole and the groundwater drawdowns observed in several surrounding boreholes. Both pumping and observation takes place in packed-off borehole sections. Water is pumped out from the packed-off section using an airlift pump, the discharge pumped from the borehole is measured with a flow meter and the drawdown in the packed-off section is observed during pumping.

Spinner and cross-hole testing methods complement each other. Using the downhole spinner method, water conductive sections can be located, and the wideness and the transmissivities of these zones can be effectively defined. This method records cumulative flow information. In many cases the most conductive sections are situated in the upper parts of the bedrock; the less pronounced hydraulic conductors deeper in the bedrock may not be detected. Using cross-hole tests, the hydraulic properties of fractures and fracture zones located between two boreholes can be evaluated.

Geophysical methods

Geophysics provides a wide range of methods for identification of hydraulically conductive fractures/fracture zones in boreholes. These methods are based on the fact

that physical properties of an open, water-bearing fracture differ from its surroundings. Typically an open fracture or fracture zone is electrically more conductive than intact bedrock, and its density and seismic velocity are lower. The methods used for site characterization at Palmottu are classified in Table 3.1.

Table 3.1 Summary of Geophysical methods used at Palmottu.

Geophysical method	Examples
Electrical (DC) methods	short normal, long normal, Wenner and single point configurations; self-potential; dipmeter
Electromagnetic methods	borehole radar
Seismic/acoustic methods	P- and S-wave velocity; tube waves, acoustic televiewer
Radiometric methods	density, back scattering of neutron radiation.

Tracer test

A tracer test was performed in Palmottu to verify the hydraulic connections indicated by the methods described previously (Gustafsson et al. 1998). It was done at shallow depth (25–85 m) between inclined boreholes (R302, R335 and R384) interpreted to intersect known structures (V6 and/or E1). The general idea of the tracer test was to pump water out of the deepest borehole section (R302, 88–98 m) in the Eastern Granite. Thus, a converging flow field was created. The tracers were injected in Eastern Granite (R384, 30–57 m, R335 54–81.5 m) and in the mica gneiss (R335, 30–45 m) about ten metres from the granite contact. The tracers were injected with the forced pulse technique. Distances between tracer injection and collection were 28–46 metres.

Three different non-sorbing fluorescent dye tracers were injected, one in each borehole sections. Transport of tracer labelled groundwater was then determined by analysing water samples taken in the pumped-out water. Complementary sampling was done in the pumping and injection boreholes after pump stop, in order to check any tracer by-pass. At pump stop (336 hours) the recovery from R384 was about 44 % of injected mass and 54 % from R335/45–81.5 m. There was no recovery from R335/30–45 m.

From the tracer test the hydraulic conductivity of the fracture flow paths was calculated to $1.4 \cdot 10^{-4}$ m/s in route R384–R302 and $1.6 \cdot 10^{-4}$ m/s in route R335–R302.

The tracer test verified earlier concluded hydraulic connections in the Eastern Granite. The evaluation of tracer breakthrough curves indicated that transport in the granite rock between boreholes (R384–R302 and R335–R302) took place in many low conductive, interconnected fracture flow paths. The proposed features (V6 and E1) can thus not be seen as a set of only a few continuous, highly conductive fractures.

Geochemical and isotope technique studies performed in the selected Eastern Flow System have shed further light on the more detailed characteristics of the flow system. For instance, USD studies could identify practically isolated channels of the flow system as well as mixing points in the active flow channels (Suksi et al. 2000).

In general the experience obtained at Palmottu in characterising the Eastern Flow System is quite important for a repository performance assessment, although the site-specific data as such is not transferable to another site. One reason is that state-of-the-art methods were used (Blomqvist et al. 2000). But the more important reason is that at Palmottu the network of observation holes is much denser than would be possible at a repository site. Therefore, the observations represent something that is beyond reach at a repository site, from a level of detail point of view.

Mineralogical considerations

The hydrological considerations presented above are a necessary pre-requisite to locating water-conducting structures. They are, however not sufficient alone, as groundwater is known to flow along distinct flow channels within a 'water-conducting structure'. Therefore, mineralogical studies along the hydrologically located structure can further specify the channelling of groundwater flow. From a migration point of view, mineralogical characteristics have direct input to sorption of radionuclides.

The Eastern Flow System, located and characterized above, is the site of origin for most samples to be discussed in connection with natural analogue studies at Palmottu later in section 4.3.1.

4. Retardation mechanism studies

4.1 Experimental approach

The experimental retardation mechanism studies described here are performed either in the laboratory or as part of natural analogue research. These experiment types differ in many ways from each other. Obviously, laboratory experiments are short term, while natural analogues have evolved for geological periods of time. A laboratory experiment is relatively well controlled, while natural analogues have evolved under uncontrolled and maybe even unknown conditions. Laboratory experiments are inevitably facing the question of realistic experimental conditions and representativity, while natural analogues have undoubtedly evolved under in situ conditions. For these reasons the quantitative interpretation of laboratory experiments is considerably easier, but, nevertheless, seldom self-evident and unambiguous.

In a normal laboratory experiment, the sample is first taken, the experiment done, and, finally, the result is interpreted. In the case of a natural analogue the "experiment " has been done by nature before sampling and subsequent interpretations. This means that laboratory experiments appear to be more sensitive to the disturbances induced by the sampling process, because the sample has already been disturbed before the experiment.

A common feature in both types of experiment is, maybe surprisingly, that both are ultimately extremely complicated systems. This means that in both cases the actual systems will have to be simplified considerably in order to be able to study the phenomena at all. In laboratory studies it may mean technically excluding certain processes in order to see the ones we are interested in. In natural analogue studies a certain "screening" must be done in order to be able to concentrate on the dominating features, because, by definition, a natural analogue sample contains its whole evolution history with a respective set of responses.

4.2 Laboratory studies

4.2.1 Column experiments

The underlying assumptions in migration models used in performance assessments (cf. section 2.3) are being tested in dynamic[4] column experiments. The main processes

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[4] In this report the term 'dynamic' is used to indicate that there is flowing water in the system, the term 'static' means that the water used is non-flowing.

being tested are sorption, hydrodynamic dispersion and matrix diffusion. Static batch experiments and standard diffusion tests are done to support the column experiments, and to provide independently obtained input data. Two types of column experiments have been done, namely fracture columns and crushed rock columns.

The experimental set-up of column systems consists of a water container, pump, tracer injector, flow column and tracer collector, and thin tubes connecting the different components, see Figure 4.1. The pump is used to create a steady water flow through the system, upon which the tracers are injected as short pulses. So far, the columns applied have been either artificial fracture columns or crushed rock columns. Fracture columns are made by first cutting a cylindrical drill core sample into halves along the axis, then polishing the cutting surfaces, and finally setting the polished surfaces against each other. Inlet and outlet tubes are connected directly to the fracture. To prevent leaks the whole column is finally sealed from outside (Hölttä et al. 1992, 1996).
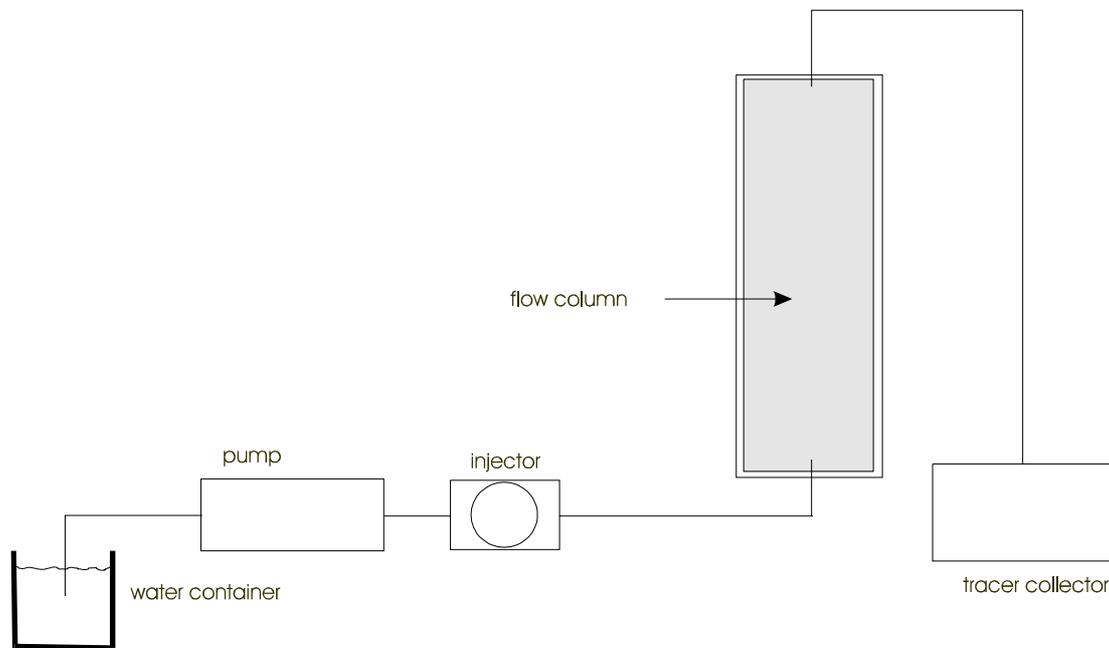
Figure 4.1 The principle and equipment of column experiments (modified from Tukiainen 2000).

Transport of non-sorbing radionuclides was studied using different volumetric flow rates of groundwater in order to distinguish matrix diffusion from hydrodynamic dispersion. Relatively long and narrow rock columns and an experimental set-up enabling very low water flow rates were introduced for the purpose (Hölttä et al. 1996). To begin with, a high porosity ceramic column having a narrow fracture width was introduced in order to demonstrate the effects of matrix diffusion in a break-through of non-sorbing solutes (Hölttä et al. 1992). The rock columns are made of drill cores from

hole SY-KR7 drilled in the Syyry area in Sievi in western Finland, and consist of mica gneiss, unaltered, moderately altered, and strongly altered tonalite.

The volumetric flow rate was determined before each experiment by collecting water over known time periods and weighing the collected water. The experiments were performed using tritiated water and chloride (HTO, Cl-36) as non-sorbing tracers and sodium (Na-22), calcium (Ca-45) and strontium (Sr-85) as sorbing tracers. Sorption of sodium, calcium and strontium was studied also using crushed rock columns made of the same rock material. Static batch experiments were done in order to compare sorption parameters from static and dynamic experiments (Hölttä et al. 1997, 1998).

The possibility of measuring the retardation factor directly in column experiments is a valuable test of the K_d concept. In the case of fracture columns, this test is relevant because, in performance assessments also migration is assumed take place along water-conducting fractures. Here the problem is that the K_d has been measured in a static batch experiment for crushed rock with an obviously different specific surface area from intact rock. In the case of the crushed rock column, the same crushed rock as that used in batch experiments can also be used in the column experiment, which makes the measured K_d value more directly transferable. Of course, the time constants may be different between respective batch and crushed rock column experiments. In order to facilitate easier comparison between fracture and crushed rock column tests, crushed rock columns have been physically made of fracture columns in some cases.

Modelling of batch experiments

A new model has been developed for a more detailed interpretation of static batch experiments. In the model, crushed rock grains are tentatively assumed to be spheres of equal radius. The new idea (i.e. the idea so far untested in these experiments) is that matrix diffusion from water into the rock grains is taken into account (Tukiainen 2000):

$$\frac{\partial C}{\partial t} = -AD_e \frac{\partial C'}{\partial r}\bigg|_{r=a} \tag{29}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 D_e \frac{\partial C'}{\partial r}) = \frac{\partial}{\partial t}(\varepsilon' R' C') \tag{30}$$

where C is tracer concentration in the solution surrounding the crushed rock (mol/m^3), C' the tracer concentration in the pore water inside the rock grains (mol/m^3), D_e the effective diffusion coefficient (m^2/s), ε' the porosity of crushed rock grains, R' the retardation coefficient in matrix, r the distance from the centre of the sphere (m), a the

radius of the sphere (m), and *A* the surface area of the spheres divided by the volume of the surrounding water (1/m). The retardation factor R' has been defined in section 2.3.

The model can explain the recurrent observation in batch experiments that after an initial rapid decrease in tracer concentration in solution there usually is also a slower trend of decrease. An example of a model fit is shown in Figure 4.2.
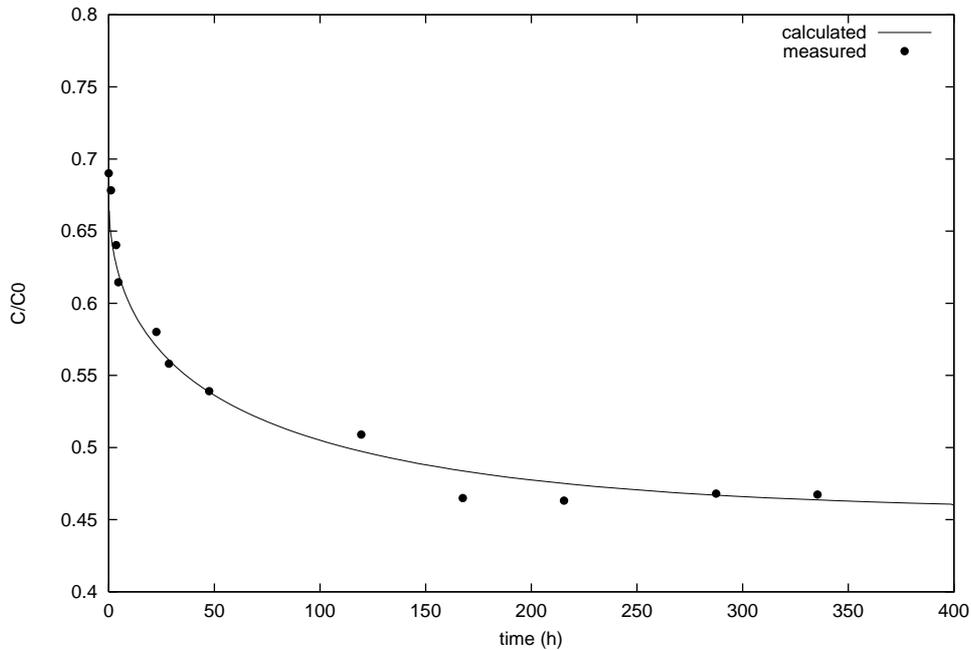
Figure 4.2 Matrix diffusion–sorption model fit to an experiment for crushed rock, grain size 300–500 μm (modified from Tukiainen 2000).

Modelling of column experiments

The possibility of directly observing the effect of matrix diffusion on the breakthrough curve under different well-controlled flow conditions is a valuable test of the classical advection-dispersion-matrix diffusion modelling concept (e.g. Hölttä et al. 2001). It is well known in the literature that the response of matrix diffusion may be very difficult to distinguish in practice from that of dispersion, or from diffusion into stagnant pools in a channelled flow system. According to our experience the response of matrix diffusion can be distinguished when water flow is slow enough so that dispersion can be controlled technically (Hölttä et al. 1996).

The model for crushed rock column includes 1-dimensional advection, dispersion, and diffusion from the flowing water into the crushed rock grains. Due to the brief duration of the experiments radioactive decay and chain decay have been omitted. The rock

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grains are tentatively assumed to be spheres of equal radius. Tracer transport in flowing water is described by (Tukiainen 2000):

$$\frac{\partial C}{\partial t} = \frac{\alpha_L v}{\varepsilon} \frac{\partial^2 C}{\partial x^2} - \frac{v}{\varepsilon} \frac{\partial C}{\partial x} + \Gamma \tag{31}$$

and in the pore water inside crushed rock grains by:

$$\frac{D_e}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial C'}{\partial r}) = \frac{\partial}{\partial t} (\varepsilon' R' C') \tag{32}$$

A reflecting boundary condition is set at the centre of the sphere:

$$\left. \frac{\partial C'}{\partial r} \right|_{r=0} = 0 \tag{33}$$

Tracer flux from water to matrix (or vice versa) is given by:

$$\Gamma = -AD_e \left. \frac{\partial C'}{\partial r} \right|_{r=a} \tag{34}$$

A is the specific surface area of the crushed rock:

$$A = \frac{(1-\varepsilon)}{\varepsilon} \frac{3}{a} \tag{35}$$

where a is the radius of the spheres.

The basic model for fracture columns has already been introduced in section 2.3. As a conceptual variation to studying sorption in more detail a model without matrix diffusion, but with kinetic sorption on fracture surfaces, was developed (Tukiainen 2000):

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + \alpha_L v \frac{\partial^2 C}{\partial x^2} - \frac{1}{b} k^f K_a C + \frac{1}{b} k^f C_a \tag{36}$$

$$\frac{\partial C_a}{\partial t} = -k^f (C_a - K_a C) \tag{37}$$

Multichannel models

As column experiments integrate many phenomena, many different conceptual models have been tested (Tukiainen 2000). It is quite usual to observe that no single conceptual model can be calibrated to fit the measured breakthrough curve perfectly. Although "blind" model calibration as such does not guarantee that the modelling concept is correct, the impossibility if calibrating it probably means that the concept needs improving.

A common, and as such reasonable, technique to improve model fit is to postulate more than one flow channels in the system, because channelling of groundwater flow has been observed at all scales of observation. The different postulated flow channels may have different properties; in this case the final breakthrough curve is obtained by superposing the individual channel-specific breakthroughs. Here, however, there is a genuine interpretation problem, because one can obtain seemingly as good model fits with different sets of channels, Figure 4.3.

From the interpretation point of view, the situation shown in Figure 4.3 is problematic. On the one hand, one can obviously improve the model fit by introducing separate flow channels. Flow channels are most probably involved in water flow at all scales. But on the other hand, just how to determine the number of individual flow channels and their properties in a technically independent and unambiguous manner has remained unsolved. It appears that with the current experimental set up of column experiments there are no direct technical methods to extract the data needed for a more detailed flow channel description.
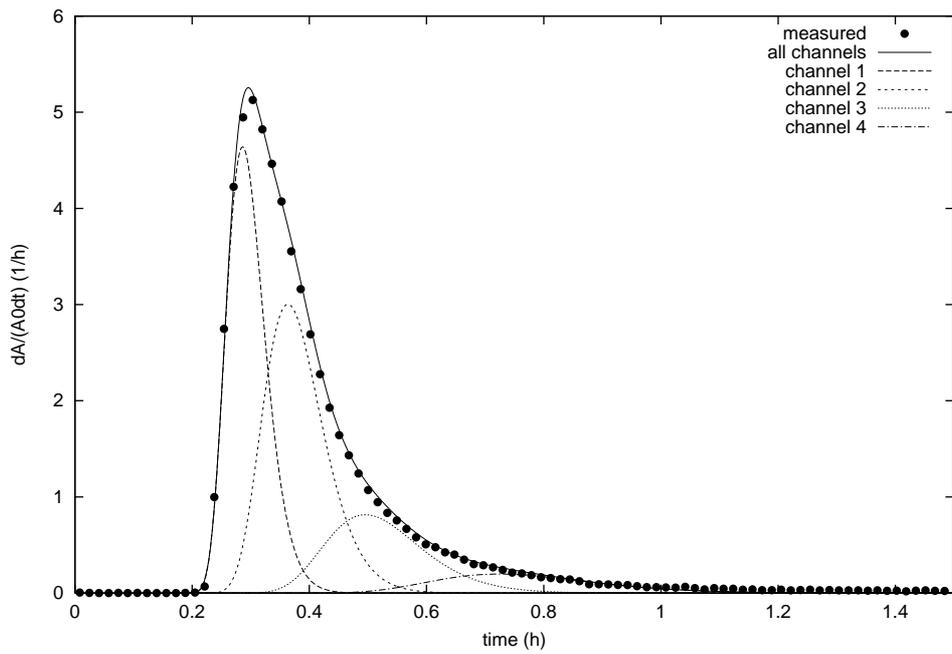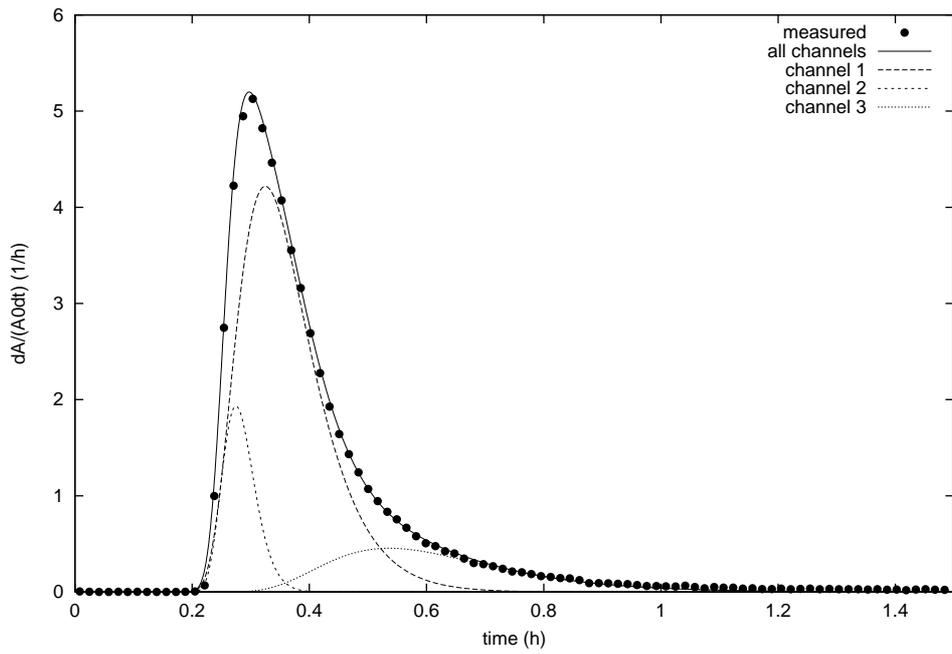
*Figure 4.3 Measured and calculated breakthrough curves. Calculated curves have
been obtained using three (upper picture) or four (lower picture) independent flow
channels (modified from Tukiainen 2000).*

4.2.2 Anion exclusion studies

Anion-exclusion tendency has been observed when comparing the rock-capacity factors for Cl⁻ (Cl-36) to corresponding values for H-3 [e.g. Valkiainen et al. (1995), Olin et al. (1997)]. The effective porosity for anions was found to be an order of magnitude less than the porosity accessible to a water-equivalent tracer (tritium).

Diffusion phenomena in porous media are affected by the connectivity of the pore network. Electrically neutral species "see" the pore structure only as a tortuous geometric hindrance, whereas charged species are either attracted to, or repelled from, the electrically charged pore walls. Attraction leads to an increase in concentration near the pore wall, which may result in an increased mass transfer in the direction of the macroscopic concentration gradient. Repulsion leads to a reduction of the available pore space and, consequently, to co-ion exclusion effects.

To study anion exclusion in a systematic way, simple water compositions and tracers in an uncomplexed ionic[5] state were used. Two sets of studies were carried out:

- Six natural rock types were included in the first stage: three unaltered and three altered ones. The ionic strength of the aqueous solution was varied. The radioactive isotopes, H-3, S-35 (sulphate) and Cl-36 (chloride), were selected as tracers. Diffusion coefficients and rock capacity factors were determined. This stage was part of the TVO/Posiva research programme.

- To simplify the surface chemistry of the pore walls, a group of artificial reference materials was studied. The capacity factors of the samples were measured using beta-active tracers. This stage belonged to the Public Sector's Research Programme, JYT.

Studies with natural rock samples

The material for the study was selected from the drill-core of the drill-hole OL-KR5 from the Olkiluoto investigation site. Six rock types were included in the study: three unaltered and three altered ones. The samples for the diffusion study were disc-shaped, 20 mm in thickness, and cut vertically to the 42 mm drill-core axis. The water types selected could be divided into two groups according to whether the ionic strength or the ionic type was varied. The diffusion measurements were carried out partly by the non-stationary equilibration-leaching method and partly by the stationary through-diffusion method. The measurements by the equilibration-leaching method were performed in an

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[5] H-3 was in the form of tritiated water, however.

anaerobic glove box and the through-diffusion measurement in laboratory conditions. The radioactive isotopes, H-3, S-35, Cl-36 and Na-22, were selected as tracers. These isotopes do not change the chemical properties of the liquids used.

The results are reported in Valkiainen et al. (1999). In general, the rock capacity factor[6] for chloride was found to be a decreasing function of the liquid phase molarity (Figure 4.4). The measurements were complemented by specific-surface-area measurements, which were utilised to estimate the pore apertures. The application of the surface complexation model to rock samples suffered, however, from the lack of specific data for the pore-size distribution and detailed knowledge of the surface chemical properties.
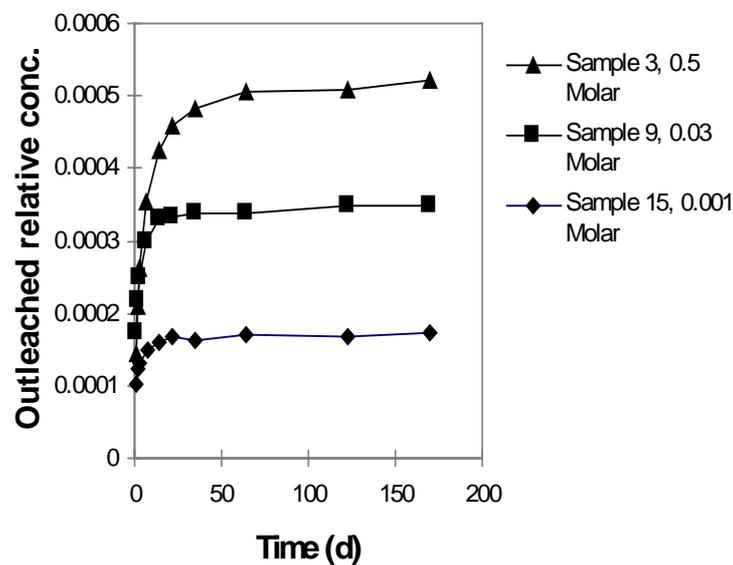
Figure 4.4 Equilibration-leaching experiment on tonalite samples. The cumulative leaching phase of Cl-36 is presented. The long-time asymptotes of the cumulative curves give in each case the rock-capacity factor, which was around 0.0025 for H-3. A decrease in the chloride exclusion can be seen with increasing liquid salinity. Quantitative modelling of the exclusion was limited due to the lack of pore-specific data.

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[6] The capacity factor α is the ratio of the concentration inside the specimen and that of the equilibrating solution. It can be measured for a tracer by the equilibration-outleaching technique, when equilibration takes place in a tracer-containing solution and outleaching takes place in a tracer-free solution. The outleached relative concentration is $(Q_{out(tracer)}/V_{sample})/C_{liquid(tracer)}$, which gives asymptotically for $t \to \infty$, $C_{sample(tracrer)}/C_{liquid(tracer)} = \alpha$. Using standard retardation parameters the capacity factor of rock matrix is defined as: $\alpha = \varepsilon_p + (1 - \varepsilon_p)K_d\rho_s$ (e.g. Valkiainen 1992).

Studies with reference materials

Because the surface properties of the pore walls in the natural rocks studied were partially unknown, it was decided to simplify the system and to consider certain artificial porous materials as reference materials for these rocks. When simplified the parameters needed by models will be known more precisely. This also makes it possible to use fewer assumptions while testing the models. Aluminium oxide, sillimanite and silica were used as reference materials. In these materials, the porosity and the diffusion coefficient are larger than in rocks, thus shortening the experimental time scale.

Among the reference materials available for the study, synthesized mesoporous silica was found to be the most suitable because of its variety of pore sizes within the nanometer range where surface-induced effects are most clearly visible. The pore diameters of the silica samples, obtained from Geltech, Inc. (AMIX-060-020-K), were 2.5, 5, 7.5 and 20 nm. These samples were discs with a diameter of 6 mm and a thickness of 2 mm. Table 4.1 gives selected pore-specific data of the samples, as provided by the manufacturer.

Table 4.1 Pore diameters and specific surface areas of the silica samples as specified by the manufacturer, Geltech, Inc.

Sample type	A025	A050	A075	A200
Pore diameter (nm)	2.5	5	7.5	20
BET-surface area (m^2/g)	610	580	525	220

The discs were equilibrated in NaCl solutions of 0.00255, 0.01 and 0.1 mol/l containing H-3 and Cl-36 as tracers. After an equilibration period, each sample was rinsed to remove the outer surface layer of equilibration solution and then moved to a chemically equivalent, unspiked solution. The liquids were air-saturated. The outleached amount of the tracer was converted to the concentration inside the sample at the end of the equilibration period (Figure 4.5). The concentration was then compared to the concentration in the equilibrating solution to obtain the capacity factor, α. The ratio α_{Cl}/α_{H-3} gives the anion exclusion for each solution-pore diameter combination (Figure 4.6).
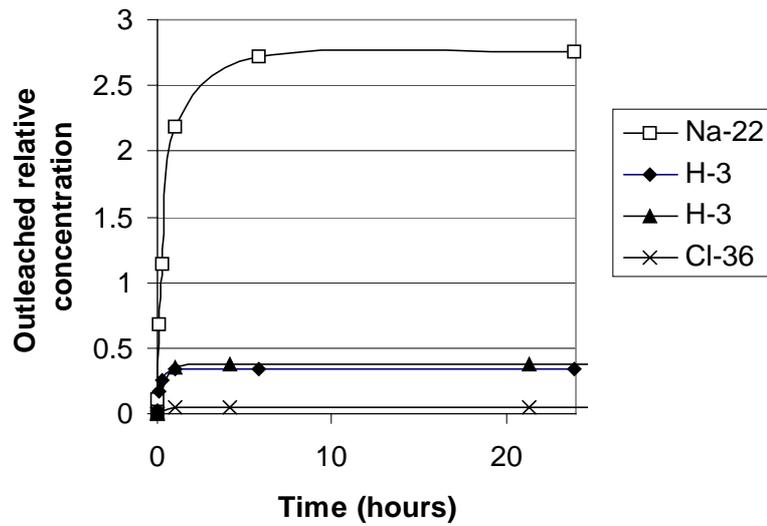
Figure 4.5 Leaching phase results of the sample with the smallest pore diameter, 2.5 nm, and the most dilute solution used in the study, 0.00255 mol/l. The capacity factors, α, were obtained from the asymptotic part of the graph. The overall level in outleched relative concentration differs considerably from that shown in Figure 4.4 due to strongly differing capacity factors.
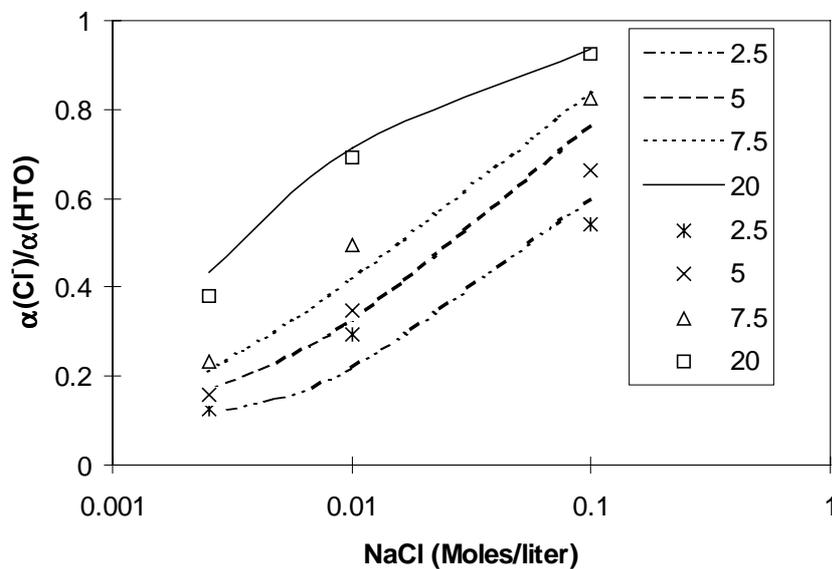
Figure 4.6 The ratio of the capacity factor for Cl^- (Cl-36) ion and the neutral H-3 as a function of the liquid molarity. The pore diameter is taken as a parameter. Calculated values are designated with lines and experimental values with symbols.

What do the results mean?

A model, based on certain simplifying assumptions and the use of a surface complexation approach was developed for anion exclusion. The surface complexation model was used to quantify the surface charging of pore surfaces. In surface-complexation systems, some of the surface protons are released to the adjacent solution phase to give rise to a negative surface charge. In the present case, the modelling was based on the assumption that silica surface acts as a proton donor according to:

$$SiOH \rightleftharpoons SiO^- + H^+ \qquad \log K_{a2} \qquad (38)$$

where K_{a2} is the second acidity constant of the surface (mol/l). The net effect is such that some of the anions, accompanied by an equal number of protons, move to the free solution, while some of the cations move into the pores to balance the negative surface charge. This is termed 'anion exclusion'.

By assuming the porous medium to consist of slit-like diffusion channels with a very small aperture in comparison to the channel width (2δ), the calculations are greatly simplified. If the monovalent ion concentration in the bulk solution is c_r (mol/l), then the Poisson-Boltzmann equation is written as:

$$\frac{d^2\psi}{dx^2} = \frac{F}{\varepsilon} c_r \sinh\left(\frac{F\psi}{RT}\right) \qquad (39)$$

where $\psi = \psi(x)$ is the electrostatic potential (V), ε the dielectric permittivity of bulk water (F/m), T the absolute temperature (K), F Faraday's constant (96485.3 C/mol) and R the universal gas constant (8.31451 J/mol/K). The boundary conditions at the surface and at the mid-plane of the pore are, respectively:

$$\left.\frac{d\psi}{dx}\right|_{x=0} = \frac{FN_s}{\varepsilon} \frac{1}{1 + 10^{-pH} K_{a2}^{-1} \exp\left(-\frac{F\psi_0}{RT}\right)} \qquad (40)$$

and:

$$\left.\frac{d\psi}{dx}\right|_{x=\delta} = 0 \qquad (41)$$

where N_s is the surface site density (mol/m^2) and ψ_0 the electrostatic potential at the surface (V). The extent of deviation from the bulk concentration is calculable from Eq. (42) for a monovalent ion:

$$\frac{\langle c \rangle}{c_{\mathrm{r}}} = \frac{1}{\delta} \int_0^{\delta} \exp\left(\mp \frac{F\psi}{RT} \right) dx \tag{42}$$

where $\langle \; \rangle$ denotes spatial averaging. The minus sign applies to sorption and the plus sign to exclusion. Strictly speaking, the boundary condition in Eq. (41) should be relaxed to some extent (in favour of $\psi(\delta) = 0$) with the higher ionic strength or/and the largest δ used in the study.

An obvious way to define the distribution coefficient, K_d, for a tracer solute within the electric double layer is (Lehikoinen 1999):

$$K_{\mathrm{d}} = \frac{\phi \Gamma}{(1-\phi)\rho}, \tag{43}$$

where ϕ is the porosity, ρ the specific density of the solid phase, and Γ the reduced surface-excess (here, $\Gamma = \langle c \rangle / c_{\mathrm{r}} - 1$) in full compliance with the IUPAC's (International Union of Pure and Applied Chemistry) definition of adsorption (Everett 1972). This definition is quite general in that it assumes no particular adsorption mechanism. Rather, adsorption merely implies a change in concentration relative to a reference concentration, c_{r}. In the case of pure electrostatic adsorption, this gives rise to positive Γ-values for cations (the cross-hatched area subtended by $c_+(x)$ and c_{r} in Figure 4.7), negative Γ-values for anions [the cross-hatched area between $c_-(x)$ and c_{r} in Figure 4.7] and $\Gamma = 0$ for electroneutral molecules (e.g., Sposito 1984). In other words, $\langle c_+(x) \rangle > c_{\mathrm{r}}$, $\langle c_-(x) \rangle < c_{\mathrm{r}}$ and $c_0(x) = c_{\mathrm{r}}$, where c_0 is the concentration of the electroneutral solute. A negative Γ is a manifestation of a local deficit of co-ions in the vicinity of the charged pore wall in comparison with the equilibrium solution. This deficit has been termed negative adsorption (or co-ion exclusion), which can occur only for species in the diffuse-ion swarm.
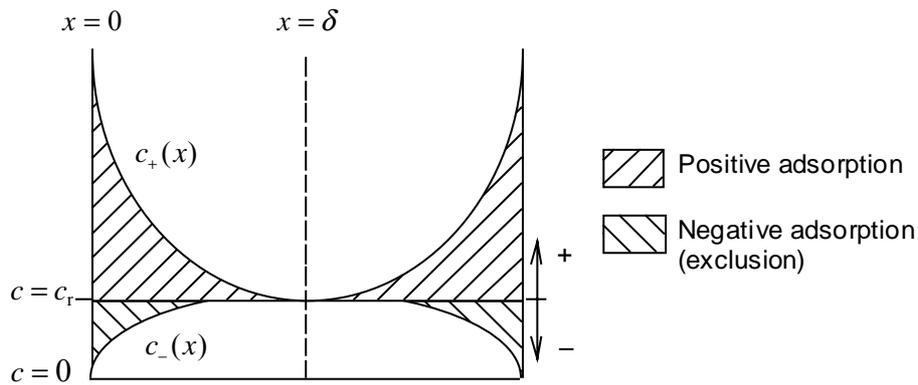
Figure 4.7 Electrostatic adsorption and exclusion of cations and anions, respectively, between two negatively charged surfaces. $c_+(x)$ and $c_-(x)$ are the cation and anion concentration profiles, respectively. The arrows indicate the sign of adsorption.

Implications for diffusion

If electrostatic adsorption by coulombic forces is the dominating contribution to Γ, the bulk of this surface-excess may have normal mobility in the direction of the macroscopic concentration gradient. It is, therefore, paramount to distinguish ion mobility from mass transfer: while the former may be greater in interstitial pore water, the latter may be dominant on pore surfaces, under the influence of local equilibrium adsorption (Cole et al. 2000). This is to be looked upon as the true cause of surface (more properly termed "surface-excess") diffusion of counter-ions that are not in immediate contact with the pore wall, but translate along an equipotential surface parallel to it and, therefore, encounter no electrical energy barriers. Despite this physically sound background for the concept of surface diffusion, which is strictly a macroscopic notion [Brenner & Ganesan (2000) and references therein], it has remained a highly controversial issue in the open literature. For direct evidence in favour of surface diffusion, consult Aalto et al. (2000).

Discussion

It was found that by utilising a model stemming from micro-level considerations, the observed anion exclusion could be explained semi-quantitatively in natural rocks. In many cases, the observations could be explained quantitatively for reference materials. In the applied surface complexation model of adsorption, the dimension perpendicular to the direction of the macroscopic concentration gradient is relevant to the formation of a surface potential and, consequently, to the accompanying concentration effects. In the presence of a negatively charged surface, the concentration of cations (anions) increases (decreases) within the diffuse double layer on approaching the surface. The

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characteristic thickness (Debye length) of the double layer at 25 °C is given by $0.3/\sqrt{I}$ (nm), where I is the ionic strength of the 1:1 electrolyte (mol/l). Assuming the bulk of the tracer ions in the diffuse layer to have normal mobility, the concepts of anion exclusion and surface diffusion can be explained with the same unified macroscopic model (e.g. Lehikoinen et al. 1999).

Our results suggest that surface complexation in combination with matrix diffusion can provide valuable insight into the observed exclusion phenomena in natural rocks too, despite the fact that the parameters needed for successful application of any model are more difficult to obtain for natural rocks. This state of affairs poses challenges for the future, because it is the natural rocks that ultimately will have to be studied in performance assessments.

4.3 Natural analogue studies

4.3.1 Palmottu uranium deposit

The natural analogue site at Palmottu in southwestern Finland comprises a uranium-thorium ore deposit located in the granitic bedrock. The mineralisation extends from ground surface to at least the currently drilled depth of 300 m in an irregular and discontinuous geometry, see Figure 3.10. The deposit contains about one million tonnes of uranium ore with the average grade being 0.1 %. The age of the deposit is approximately 1.7–1.8 Ga (Blomqvist et al. 1995). Being located at various depths in various geochemical conditions within the fractured bedrock, the deposit covers structurally, mineralogically and geochemically a spectrum of physicochemical conditions which is the same as that expected at disposal depth, and above, for a spent nuclear fuel repository in a crystalline bedrock.

The important feature about the ore deposit at Palmottu is that it has survived all glaciations that have occurred at Finnish latitudes. Thus, in principle, the effect of repeated cycles of permafrost – glaciation – melting of ice – interglacial period can be studied. This fact makes the site particularly relevant for performance assessments that have to cover glacial scenarios in northern countries like Finland, Sweden and Canada.

The mineralisation is intersected by a regular mesh of parallel drill holes that were drilled for ore prospecting purposes in the late 1970's and early 1980's. For this reason they are of varying length. Natural analogue studies have been pursued at Palmottu since 1988, and between 1996 and 1999 the site was studied as an international EU project (Blomqvist et al. 1998, 2000). The studies within the EU project provide the general background for the retardation mechanism results discussed here.

The studies related to retardation mechanisms at Palmottu were mainly focused on sorption and matrix diffusion of uranium. In this context the term 'sorption' refers to fast reversible adsorption, in line with the K_d concept used in performance assessment modelling. Chemical extractions were used as the technical method to obtain information about uranium fixed to mineral surfaces. Because the extracted inventories so obtained do not automatically represent any single fixation mechanism, great care had to be taken to extract only the adsorbed inventories. In other words, one had to be sure that the adsorbed inventory could be technically separated from a whole spectrum of other inventories also fixed in situ. Two broad types of processes that can both cause uranium fixation on mineral surfaces can be distinguished (Suksi et. al. 2000), see Table 4.2.

Table 4.2 Classification and definition of sorption and co precipitation processes of trace elements according to Curti (1997).

PROCESS	SUBDIVISION	EXPLANATION
SORPTION The reversible uptake of ions, atoms or molecules on a mineral surface	SPECIFIC ADSORPTION (= SURFACE COMPLEXATION)	The uptake of dissolved species on a mineral surface through formation of covalent bonds.
	ION EXHCANGE	The uptake of ions on a mineral surface with the simultaneous displacement of previously adsorbed ions.
	PHYSICAL ADSORPTION	The uptake of molecules to a mineral surface through Van der Waals forces.
COPRECIPI-TATION The trapping of foreign chemical components in a solid of stoichiometric composition	ISOMORPHOUS REPLACEMENT (= SOLID SOLUTION)	The incorporation of foreign ions in crystal lattice sites usually occupied by a major ion of the solid.
	INCORPORATION IN CRYSTAL DEFECTS	Incorporation of foreign ions, atoms or molecules outside the crystal lattice positions (e.g. in vacancies or dislocations). For an amorphous compound, any incorporation at atomic scale.
	NON-UNIFORM INCORPORATION	The trapping of discrete particles (e.g. colloids) in a growing solid.

Both fracture surfaces and rock matrix were studied in sorption investigations, see Figure 4.8. In general, good agreement was obtained between standard laboratory K_d derived from batch experiments, and in situ K_d derived from careful extractions. It was

found that reversible adsorption covers approximately one per cent of the total uranium inventory in rock.
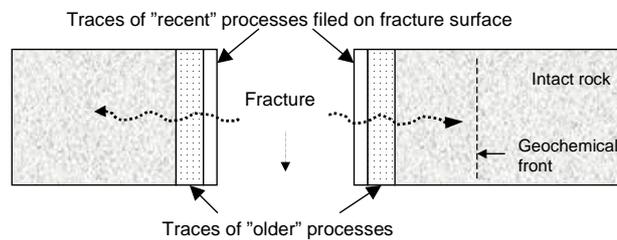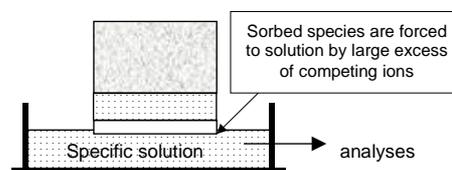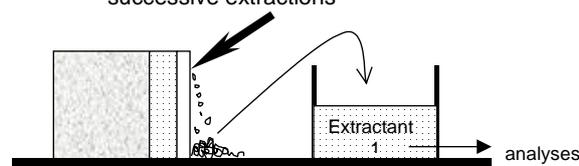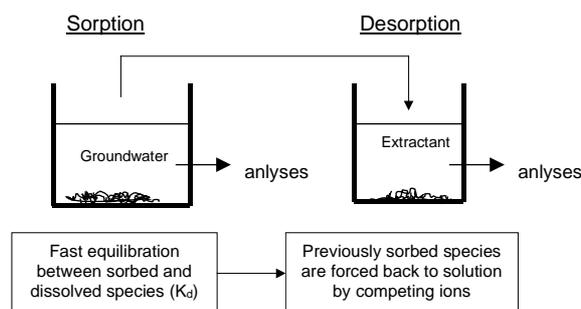
Figure 4.8 Experimental approaches in studying uranium fixation and matrix diffusion. In order to obtain a concentration distribution as a function of distance from fracture surface for in situ matrix diffusion, the drill core sample was cut into slabs, the slabs were crushed, and the crushed sub samples were extracted (Suksi et al. 1999).

Matrix diffusion studies used measured uranium concentration and activity ratio distributions as experimental reference against which modelled results were compared (e.g. Rasilainen 1997, Blomqvist et al. 2000). The standard matrix diffusion model

could not reproduce the measured concentrations well enough, which led us to suggest a slowly moving redox front within the rock matrix. The movement of the redox front is postulated to be controlled by oxygen flow from the fracture and by the oxygen consuming redox reactions within the rock matrix. An example of measured uranium distributions is given in Figure 4.9.
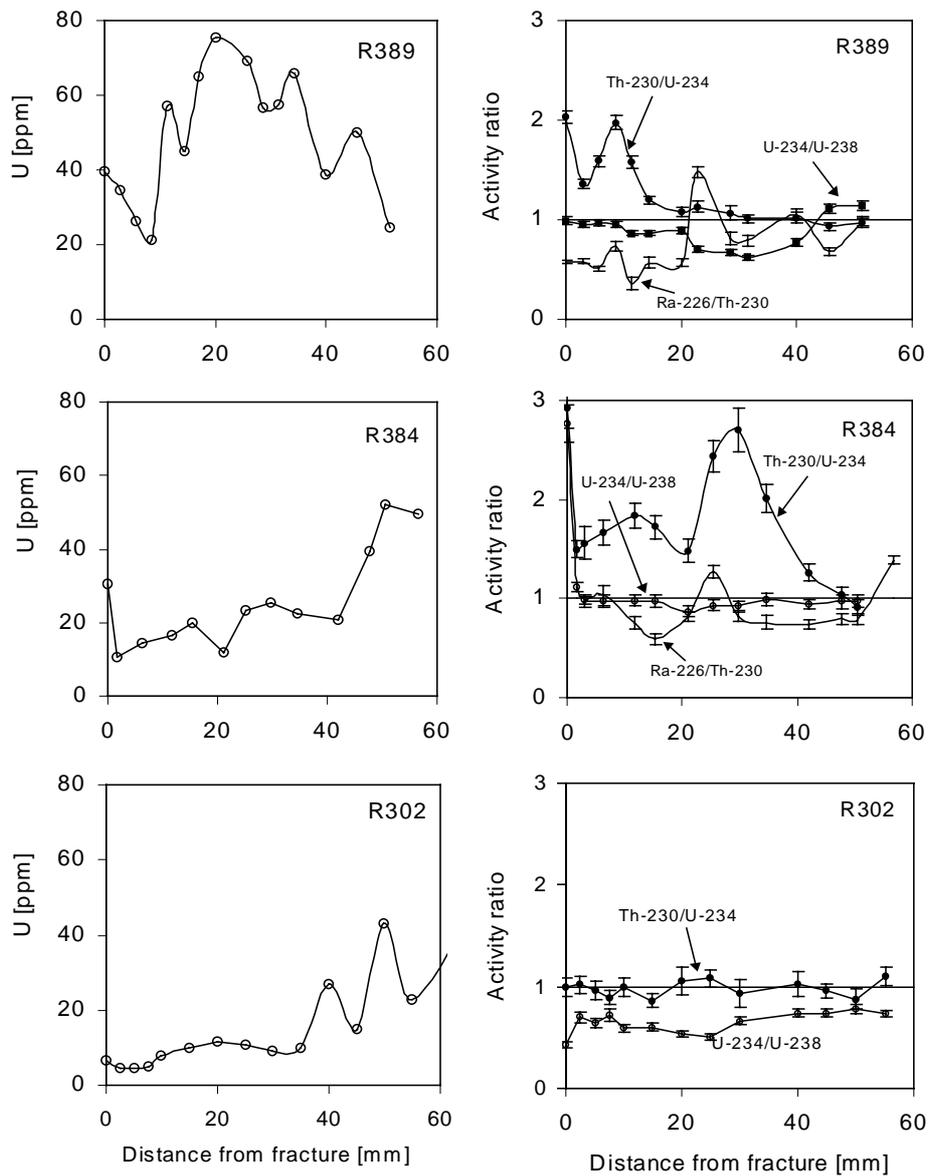
Figure 4.9 Uranium concentrations and activity ratios U-234/U-238, Th-230/U-234 and Ra-226/Th-230 (not measured for R302) for drill core samples taken from hydraulically active flow channels in the Eastern Flow System (cf. Fig. 3.10). Samples R389/31.56 m and R384/34.50 m represent the upper part of the route, while R302/90 m is taken from the lower end of the route (Blomqvist et al. 2000).

In general, matrix diffusion in the scale of cm's was indicated both by the measured reference and model simulations. However, the modelled uranium out-diffusion from rock matrix assuming oxidising conditions extended too deep into the rock matrix, which suggested that the rock matrix could be reducing inside, although the groundwater in the fracture may be clearly oxidising. The hypothesis of an oxidation front generated by the intrusion of oxidising waters progressing slowly from the fracture towards a reducing rock matrix was investigated. The results demonstrated that the model formulated for diffusive transport of oxygen and uranium in the rock matrix was basically feasible and realistic.

The important implication for performance assessment is that the redox front in the rock matrix may act as a chemical barrier that moderates matrix diffusion. In performance assessments the basic concept of diffusion is from groundwater flowing in a fracture into the surrounding rock matrix. This diffusion may be retarded by the redox front. The front is not impermeable, but, beyond it, diffusion proceeds with decreased rate, according to reducing conditions. The net effect of the redox front can be decreased matrix diffusion and, therefore, decreased overall retardation of the migrating radionuclides.

The effective diffusivity and the porosity of the rock matrix were measured in the laboratory using the He-gas method. The values obtained are $7.4 \cdot 10^{-15} - 5.0 \cdot 10^{-13}$ m^2/s for the effective diffusivity and 0.07−0.45 % for the porosity (Blomqvist et al. 2000). These data are generally consistent with previous studies in Finland and Sweden.

4.3.2 Boulder samples

The boulder, containing a considerable uranium accumulation inside, was found on top of a morainic hill in the Kolkanmäki area close to the town of Hämeenlinna in southern Finland. The study area is covered with glacial till and more sorted sediments, see Figure 4.9. In contrast to the multi-targeted natural analogue studies at Palmottu, where retardation mechanisms were only one research area among others, the granitic boulder sample is studied specifically as a matrix diffusion (and sorption) analogue. Another difference is that uranium accumulation within the boulder is apparently recent (postglacial) as compared to the very old ore deposit at Palmottu.

The mineralogy of the boulder was used in an effort to locate the parent rock and, taking into account the known direction of ice flow at the site, 312–316° (NW–SE), the only reasonable granite outcrop with the same mineralogical composition (microcline granite) was found in Hirsimäki, see Figure 4.10. This notwithstanding, areal gamma radiation mapping shows a local maximum at the Kolkanmäki site, but, interestingly, not at the

outcrop. It appears probable, therefore, that the parent rock of the boulder is located in the soil-covered area between Hirsimäki and Kolkanmäki.
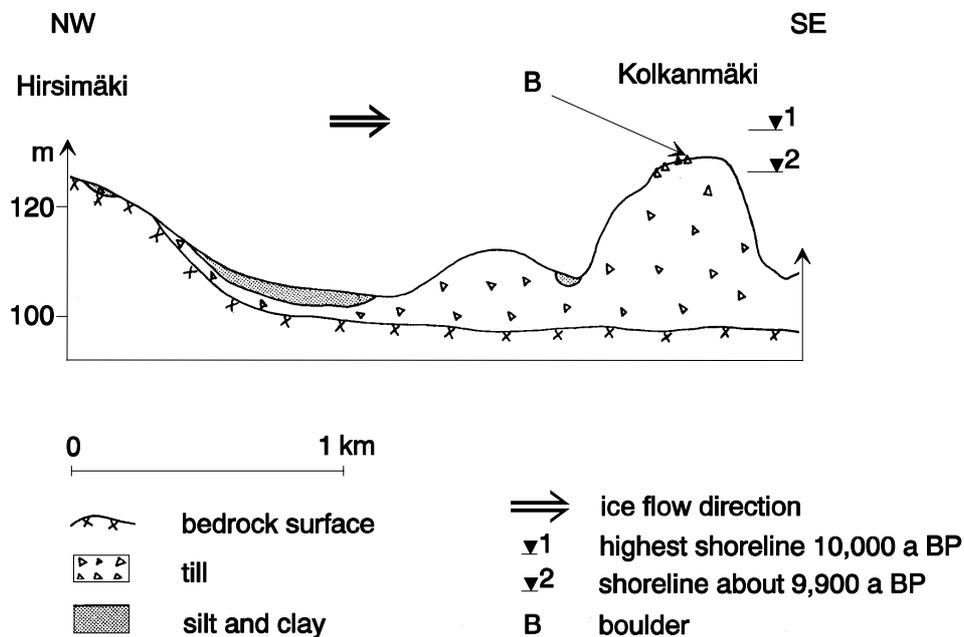
Figure 4.10 Cross-section of the geological surroundings of the boulder sample. The boulder (B) is assumed to have been transported by the ice to its current location (Rasilainen 1997).

So far, three boulders from the area have been studied, and several drill core samples have been analysed across the boulders. The boulder studied most intensively has a weathered zone on top of it while the lower part appears fresh, i.e. unaltered. The lower part refers to the side of the boulder on which it was lying when found. A U(VI) enrichment up to nearly 300 ppm (compared to about 10 ppm background concentration) mostly as uranophane was observed in the zone between the weathered and fresh rock, see Figure 4.11. U-series disequilibrium studies indicated unambiguously that most of the U has accumulated recently, about 10 000 years ago (Rasilainen et. al. 1996, Rasilainen & Suksi 1997).
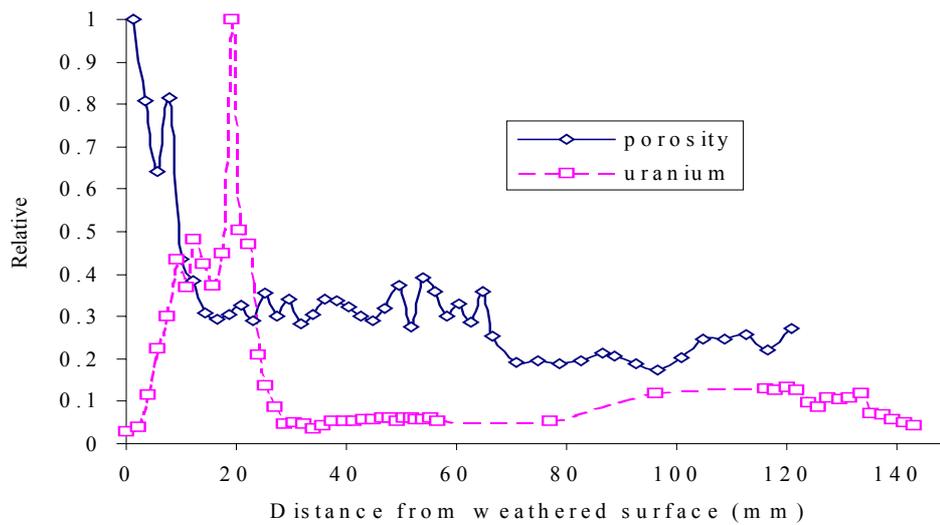
Figure 4.11 Normalised uranium concentration and porosity profiles across the boulder (Marcos et al. 2000).

High interconnected porosity (total porosity of > 1% and up to about 5.5% in altered minerals) characterises the weathered zone (upper part), whereas the maximum porosity values in the fresh zone (and lower part) of the rock are about 0.4–0.6%. Stable isotope studies $\delta^{18}O$ and δ^2H confirm that the mineralogical changes observed in the weathered upper part are due to old hydrothermal events. That is, the alteration is much older than uranium accumulation. Mössbauer spectroscopy showed that the Fe(III) content of the biotites from the upper to the lower part decreases from 30% in the weathered zone to 17% in the fresh rock, thus indicating possible redox control for the observed U precipitation. Fission track studies showed that secondary U(VI) also occurs within minerals grains (especially plagioclase) in the upper part.

Deglaciation took place in the Hämeenlinna region about 10 000 years ago. The highest shoreline of the subsequent Yoldia sea stage at Hämeenlinna was 133 m above the current sea level. As the location of the boulder is only 2–3 m lower, it can be approximated that the boulder was below the Yoldia sea level for 50–100 years. Estimates of ice velocities towards the margin vary from a few to tens of m/year. This rate means a travel time of 50–500 years for the boulder over the estimated distance of 1–2 km. For at least part of this time, the boulder was in wet conditions near the basal layers of the ice.

The asymmetrical uranium concentration profile shown in Figure 4.11 indicates a partly different history for the two sides of the boulder. Apparently, the beginning of the uranium accumulation must have been identical. The currently postulated accumulation history includes a rapid in-diffusion period (100 years) from uranium rich waters that discharged onto the boulder, or into which it was submerged at the end stage of glaciation.

The in-diffusion process included simultaneous precipitation of uranophane (Marcos et. al. 2000). This was followed by rapid out-diffusion period (50 years) due to the Yoldia Sea stage during which the boulder was submerged in the sea. After out-diffusion, the histories of the two sides of the boulder differed.

The upper part is on dry land and there is no diffusion, only radioactive chain decay for the post-glacial period 10 000 years. In contrast, the lower side experiences out-leaching due to the fact that capillary forces "soak" the lower part at a depth of cm's. Finnish soil is moist practically all summer. The northern climate ensures that for approximately half of the year the soil and the boulders are frozen, but during summer time out-leaching is possible. Thus the lower part is postulated to have radioactive chain decay for the whole 10 000 years and repeated out-leaching for the same period 6 months a year, in other words, the effective out-leaching period is 5 000 years.

Mathematical simulations applying the classical matrix diffusion model have roughly reconstructed the observation that U levels are clearly higher in the upper part of the boulder than in the lower part. However, they also indicate that matrix diffusion combined with adsorption is not enough to reconstruct the past U accumulation alone. The simulated concentrations that were derived from U concentration in pore water by multiplying by measured K_d are clearly too small. This is in line with the overall conceptual model which includes precipitation of uranophane, a phenomena not included in the classical matrix diffusion model applied so far. The next step in modelling is obviously to combine the matrix diffusion model with a geochemically sound interaction model including adsorption and precipitation.

4.3.3 Hästholmen

The island of Hästholmen started to rise from the Baltic Sea due to postglacial land uplift some 5000 years ago. Land uplift is currently some 3 mm per year on the coast of the Gulf of Finland. Rainwater infiltrating into the ground has formed a layer of fresh groundwater floating on top of the originally saline groundwater. Land uplift has moved the boundary between upper fresh and lower saline water continuously downwards. The bedrock of Hästholmen consisting of coarse-grained granite has been studied by drilling for an underground repository for reactor wastes. Currently, the repository is in operation at the site.

The purpose of the retardation mechanism study at Hästholmen was to investigate the porosity available for matrix diffusion in the bedrock. This was done by investigating the communication between stagnant porewater in the rock matrix and flowing groundwater in the surrounding fractures. Theoretically one should see the gradual change of salinity in porewater long after the salinity has changed in the flowing

groundwater. The reason is that matrix diffusion is the only migration mechanism in rock matrix, and is a very slow process. As a result, rock matrix can "preserve" past conditions for a considerable time.

The study was carried out by studying the amount of porewater in the drill-core samples and its chemical composition. Various drill cores were sampled and the porewater or soluble salts from the dried pores were leached into pure water. The amount of leached salts was analysed by ion chromatography. The method can give information of the interaction between porewater and groundwater of surrounding conducting fractures. The amount of porewater must be sufficient to leave measurable concentration in the leachant: the open porosity must be sufficiently large. Those fluid inclusions, which were broken in the sampling procedure, form a background concentration in the leachant.

In the case of rapakivi granite it was found that the groundwater - porewater communication indeed exists, and that it can be studied with the leaching method. When the rock-sample is leached in pure water, minerals are dissolved in addition to the leaching out of the porewater. It turned out that chloride has shown favourable properties in the case of rapakivi granite. Sulphate, Na^+ and K^+ in the leachant were also related to the salinity of the groundwater, but the results were more scattered.

In terms of in situ matrix diffusion it was found (Olin & Valkiainen 1990, Lehikoinen et al. 1992) that the salinity in the groundwater of Hästholmen is reflected in the anion concentration of the pore water as expected, see Figure 4.12. Regions could be found at Hästholmen, where the salinity inside the rock matrix is still gradually decreasing, indicating in situ matrix diffusion in the scale of meters.
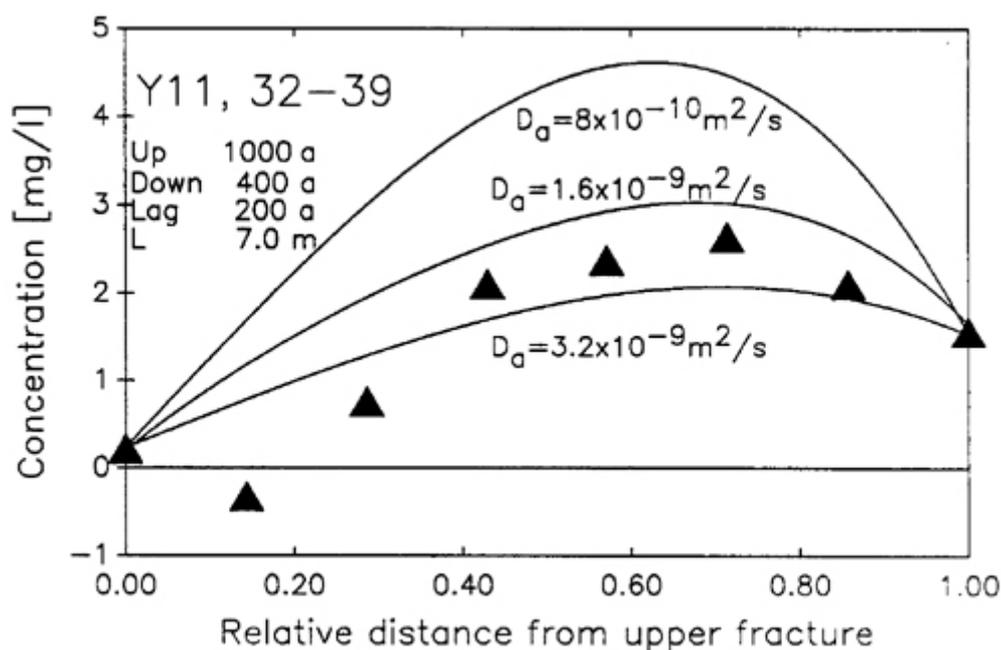
Figure 4.12 Concentrations of chloride in the originally pure water equilibrated for three months with crushed samples of granite from different depths. Samples are from drill hole Y11. Sampling interval 32–39 m. Calculated profiles are based on the assumption that the salinity had started to drop to the background value 2500 years ago in the upper fracture, and 1000 years later in the lower fracture. The apparent diffusion coefficient giving a reasonable fit to the profiles is $2 \cdot 10^{-9}$ m^2/s, which corresponds to an effective diffusion coefficient $1 \cdot 10^{-12}$ m^2/s (Valkiainen 1992).

4.4 Main findings

Column experiments provide a valuable tool with which to study the basic phenomena of the migration model used in performance assessments. Experimental conditions can be controlled relatively well. The respective roles of matrix diffusion, sorption and dispersion have been studied, and the lesson learned is that dispersion must be well under control before there is any hope of seeing the response of matrix diffusion. Very low volumetric flows are required for the control of dispersion. Multichannel models consisting of parallel flow channels in the flow column appear to be the only models capable of obtaining a good model fit for the breakthrough curve for all parts of the curve. Unfortunately, the current experimental set-up does not yield any direct information to help in constructing the required set of differing flow channels.

Anion exclusion studies have been performed applying natural rock samples and artificial reference materials. Reference materials were chosen to avoid the very large

heterogeneity in natural rock samples. It was found that by applying reference materials and the surface complexation model, a quantitative explanation could be given to experimental observations in many cases. While model testing was admittedly much simpler using reference materials, the fact remains that natural rocks are heterogeneous by definition, and it is these rocks that one must ultimately study in performance assessments.

Natural analogue studies provide a method with which to study retardation phenomena in situ. Furthermore, the geologic time scales involved are often of interest for performance assessments. The interpretation of natural analogues is, however, quite demanding, because every sample can in principle have the responses of all the physico-chemical processes it has experienced. Therefore, one must be careful not to over-interpret the information provided by natural analogues. In general, we have seen the obvious trend that the younger the event (e.g. diffusion incident) the easier it is to detect its response (e.g. in rock matrix).

The studies at Palmottu have shown that sorption and matrix diffusion occur in situ. Laboratory derived K_d and in situ K_d give a relatively coherent picture of adsorption. Fast reversible adsorption appears to cover only one percent of the fixed uranium inventory in rock. The inside of rock matrix appears reducing even though the flowing water around it would show a strong oxidising signal. This indicates very high redox buffering potential of rock matrix.

Boulder studies also indicate that matrix diffusion has occurred in situ and that the classical modelling concept is not enough to explain all observations. A more rigorous geochemical sub model is required to account for adsorption and precipitation: the K_d model is obviously not enough.

The studies done at Hästholmen indicate that in this particular type of rapakivi granite, continuous pore network open for matrix diffusion, extends at least meters from the fracture.

5. Do performance assessments and experimental studies meet?

5.1 Are performance assessment data needs covered?

The classical advection-dispersion-matrix diffusion approach used so far in migration models for performance assessments has relatively limited and straightforward data needs. In principle, all data needs can be covered with the established experimental studies described above. Porosity and diffusivity data for rock matrix can be obtained from the structural studies described in section 3.1. Distribution coefficient (K_d) for the description of sorpion can be obtained from batch experiments as described in section 4.2, and also from natural analogue studies as described in section 4.3.

The question is somewhat different for the conceptually more detailed and more rigorous "non-classical" approaches, because there are not necessarily established experimental methods to obtain all the necessary input data (cf. section 4.2.2). As long as this is the case, their use as standard modelling tools will be very limited. Notwithstanding this, these models still can serve as valuable research tools. Therefore, the actual usefulness of these more rigorous methods in practical performance assessment modelling is also more difficult to assess, and requires a detailed analysis of the availability of input data.

Paradoxically, in some cases the experimental methods yield information so detailed that it cannot be fully utilised by migration models. One good example is the very detailed structural and porosity information of the rock matrix samples obtained with the C-14-PMMA method in which structures of an order as small as μm can be identified. The reason for the models being unable to utilise this data is that the other input data cannot be measured with an equal level of detail.

Based on many structural studies of rock matrix it can be generally stated that diffusivity cannot be reliably deduced from porosity, although different versions of Archie's law have been suggested in the literature (e.g. Parkhomenko 1967). Therefore, diffusivity data must be measured independently for every rock sample in order to have a truly sample-specific diffusion database. Based on numerous diffusivity measurements it has been observed that, for average grain sized rock sample, when sample thickness is less that 1 cm there tends to be artificial connections between the two ends of the sample, and the experimental results become "contaminated" with artefacts (see e.g. Hartikainen et al. 1996). Generally, the probability of artificial connection increases with decreasing sample thickness.

This state of affairs, however, does not diminish the value of the structural information obtained for other purposes. One particularly interesting area is natural analogue research where it is quite important to know exactly where, for example, uranium accumulation is actually located. Another area of use for the detailed structural information is when something unexpected is observed in diffusion experiments. The structural data can be of assistance in interpreting the observation.

5.2 Is matrix diffusion described reasonably?

The classical matrix diffusion model has so far been applied in Finnish performance assessments. A number of variations of the classical model are, however, being tested against laboratory experiments (cf. section 4). One fundamental assumption in all these versions is that there is a continuous pore network along which diffusion can take place.

5.2.1 Continuity of pore network

Diffusion studies are useful in testing whether there is continuous pore network within the rock sample under consideration. Diffusion is sensitive to the geometry of the pore network in the sense that it is the narrowest of the "bottlenecks" that control the diffusivity value. So far diffusion studies have been conducted in the laboratory, in field studies, and in connection with natural analogue studies. With few exceptions all studies have indicated continuous pore network in all rock samples studied.

In laboratory studies, diffusion has been observed through altered, unaltered and partly altered rock samples. Usually the values of measured porosity and diffusivity tend to increase with increasing alteration. Diffusion has also been observed in samples with and without mechanical stress (simulated in situ stress conditions). Laboratory experiments have been done using tracers in water phase, gas phase, and, e.g., mercury, indicating that pore network is a real physical entity, and not an entity just connected with one particular method. Reviews of laboratory experiments performed can be found, for example, in Skagius (1986), Valkiainen (1992), Ohlsson & Neretnieks (1995).

In the International Stripa Project diffusion experiments were conducted under in situ stress conditions at a depth of about 360 m (Birgersson & Neretnieks 1987, 1988). Although in this experiment the interpretation of the precise migration mechanism was difficult because advection within the rock matrix could not be ruled out (due to the very disturbed hydraulic conditions prevailing in the old iron mine) the conclusion about the continuity of pore network was unambiguous. The existence of pore network is the prerequisite for both mechanisms, and migration of tracers was undeniably observed in surroundings that did not have water-conducting fractures. In this

experiment it was concluded that all three tracers used had migrated from the zone disturbed by the drilling of the injection hole into the "undisturbed" rock matrix.

In the natural analogue literature numerous studies on drill core samples have been reported (see e.g. Miller et al. 1994, Rasilainen 1997, Miller et al. 2000, and references therein). In many of these studies, naturally occurring radioactive decay chains have been observed as tracers, for instance U-238 – U-234 – Th-230 – Ra-226. In most of the studies absolute concentration distributions of the chain members and/or daughter-parent activity ratios have been measured as a function of distance from the fracture surface. If there is a clear increase or decrease in absolute concentration distributions as a function of distance there must be a continuous pore network route to the fracture surface, otherwise the trend could not have formed. Similarly, if there is radioactive disequilibrium along the drill core sample, there must be a route along which the preferentially released isotopes have been able to migrate away. Otherwise, the disequilibrium could not have formed and we would have radioactive equilibrium, because decay chain members, in spite of their different mobility, would have had to stay in the location where they were born.

Some natural analogue researchers have concluded that matrix diffusion is physically limited to the altered zone around water-conducting fractures that is usually characterised by enhanced porosity. Usually the conclusion has been motivated by an observed U concentration profile of limited penetration into rock matrix without much consideration of the possible time scale involved. In most of these cases there is simultaneously clear radioactive disequilibrium within the drill core sample also beyond the concentration profile. The supporters of limited matrix diffusion theory have not given much credit or consideration to this observation (see Rasilainen 1997 and references therein).

In Finnish natural analogue research samples from Palmottu U-Th deposit, Hämeenlinna boulders, and Hästholmen have been analysed in connection with retardation mechanism studies. All studies so far have indicated the existence of continuous pore network. Of course, porosity and diffusivity values are often increased in the altered zone, but there seem to be no grounds to assume that matrix diffusion would be physically limited to this zone.

5.2.2 How do different laboratory techniques see diffusion porosity?

When comparing results obtained by different experimental methods one must take into account that the methods may not actually observe the same entity. As a result they may "see" different pores in the sense that below a certain method-specific threshold the method no longer indicates open porosity. Concerning the migration of dissolved

species in saturated rock matrix, the penetration ability of water into small radius pores is obviously the criterion. The optimum method would be the one yielding the same resolution as water molecules, no higher, no lower.

Methylmetacrylate has been observed to penetrate into pores down to 2.5 nm of diameter. This has been tested with a purpose-constructed standard matrix. The size of a water molecule is 0.19 nm, but electrical charges make the minimum size of pores detected somewhat higher. Thus water penetrates pores smaller than methylmetacrylate; however, the pores are of the same order of magnitude. Most often mineral surfaces are negatively charged.

The helium gas method is based on monitoring the helium flow within nitrogen carrier flow. Therefore the penetration ability of both gases is of importance here. From the penetration point of view it is noteworthy that both the gas molecules used are neutral in terms of electrical charge. The size[7] of helium molecules is (0.3 nm) and that of nitrogen is (0.1 nm). Thus, one can see that the molecular sizes are relatively close to the pores that can be detected by water.

In performance assessments, diffusion porosity, i.e. porosity that is accessible for diffusion, has been considered as a purely geometrical quantity of the rock matrix that is the same for all nuclides. Although this is roughly true different molecules obviously have different molecule sizes (cf. Frick 1993) and thus behave differently in terms of matrix diffusion when it comes to the smaller pores. Likewise, ions having different charges while having the same sign, obviously behave differently in small pores. Furthermore, anions and cations have been observed to behave differently (cf. anion exclusion). In order to take into account anion exclusion smaller values of porosity and diffusivity were used for anions than for cations (see, for example, Vieno & Nordman 1999).

5.3 Is sorption described reasonably?

In geochemistry the term 'sorption' covers, in principle, all mechanisms that remove dissolved material from groundwater. However, for performance assessments of nuclear waste disposal in bedrock a much narrower definition is used; essentially it includes only fast reversible adsorption. For the purpose of discussion, this report adopts the narrower definition of sorption. Thus the variability within the 'sorption' concept here deals with different fast (ad)sorption mechanisms, e.g. ion exchange and a range of

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[7] In this context, 'size' means the inter-nuclear distance between atoms in the element (Webelements. 15.12.2000.)

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.

5.3.1 Approaches to sorption modelling

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) and EPA 1999, is defined as:

$$K_d = \frac{adsorbed\ inventory\ /\ mass\ of\ solid}{inventory\ in\ water\ /\ water\ volume} \qquad (44)$$

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

$$K_a = \frac{adsorbed\ inventory\ /\ surface\ area\ of\ solid}{inventory\ in\ water\ /\ water\ volume} \qquad (45)$$

The K_d model can be described as a "linear isotherm" model, because the adsorbed inventory depends linearly on the tracer concentration in water. The fundamental assumption behind this is that radionuclide concentrations are of "trace level", and so the distribution coefficient is independent of radionuclide concentration. For higher concentrations there may be saturation of sorption sites; non-linear sorption isotherms are used to take this into account.

In line with the general conservativity principle, K_d 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. K_d is further assumed to represent solely reversible adsorption.

The advantage of K_d values is that the concept is simple and the experimental method is well established, thus offering a feasible way of characterising sorption for a large number of elements, species and geochemical conditions. The K_d value describes the net partitioning of the tracer even if all the sorption mechanisms involved are not understood. A K_d value, 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. It 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. However, if the experimental conditions do not replicate those encountered in the field, then the approach will not provide a meaningful description of sorption.

The conceptual drawback of 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 according to the timescale of the experiment.

Mechanistic sorption modelling

The above sorption model, like many performance assessment models, is a considerably simplified representation of reality. In contrast, mechanistic sorption modelling is an effort to describe sorption in a more detailed and conceptually more rigorous manner. Concerning mechanistic sorption modelling, our ambition here is limited to briefly discussing its overall applicability in practical performance assessment type modelling. In a brief review like this it is not possible to discuss any topic in great depth. The interested reader is well advised to consult good textbooks and review articles about the technical details (e.g. Dzombak & Morel 1990, Davis & Kent 1990, and Stumm 1992).

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). Fine-grained minerals having a large specific surface area, such as montmorillonite clays and micas, are especially efficient cation exchangers (Appelo & Postma 1993).

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. Owing to the complexity of natural systems, empirical approaches have been used widely in geochemical applications (Davis & Kent 1990). Adsorption isotherms are an example of a simple empirical concentration relationship between an aqueous species and the same species adsorbed on a surface, see, e.g., NEA (1983) and McKinley & Hadermann (1985).

The advantage of mechanistic models is that they utilise the current thermodynamic understanding of sorption. Furthermore, the models take into account changes in aqueous systems. 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.

Currently 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).

Comments on sorption modelling

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 (cf. Table 4.2). Distribution coefficients or sorption isotherm fittings do not provide any direct information as to the sorption mechanisms involved, even if they describe the net partition between solid and water correctly (cf. discussion in Rasilainen et al. 1999).

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.

If the geochemical conditions of the site under consideration are not known, then all approaches to model sorption are equally meaningless.

5.3.2 Implications from natural analogue studies

Natural analogue studies concerning sorption at Palmottu have given clear indications that there are many in situ fixation mechanisms other than rapid reversible adsorption. In fact the type of sorption represented in a K_d value appears to cover only around one percent of the total fixed uranium in rock samples. This data was obtained by careful sequential extractions. This evidence indicates that the K_d concept when used in migration modelling over-estimates the mobility of uranium. In reality uranium fixation to mineral surfaces appears to be only partly reversible.

An effort was made to study the relationship between laboratory derived "standard" K_d value and in situ K_d value obtained by careful extractions. This exercise was based on a parallel standard batch experiment for laboratory K_d and subsequent desorption. In the process a tracer (U-236) was allowed to equilibrate with the rock material already containing in situ sorbed natural uranium. After two weeks equilibration the adsorbed uranium (both the tracer and natural uranium) was desorbed and distribution coefficients were calculated. For the tracer uranium the standard batch experiment gave the highest K_d value (around $2 \cdot 10^{-3}$ m^3/kg), desorption of the tracer uranium gave around $1 \cdot 10^{-3}$ m^3/kg and desorption of natural uranium around $8 \cdot 10^{-4}$ m^3/kg (Blomqvist et al. 2000). The results are within a factor of three, which can be regarded as a good agreement between standard and in situ K_d values.

An extraction with $CaCl_2$ solution was used in an attempt to desorb *in situ* adsorbed uranium from fracture surfaces (Blomqvist et al. 2000). Fracture surface samples were taken from boreholes R302, R373 and R384. The idea was that if the extracted uranium represents the adsorbed component then its U-234/U-238 activity ratio should match that of the corresponding groundwater. The extraction results were variable; identical activity ratios were obtained[8] only in one case. In addition to different scales in water and fracture surface samples, it is possible that some mineral phases were undergoing dissolution, masking the signal of adsorbed uranium. Despite the uncertainty related to the origin of extracted uranium, estimates of loosely bound uranium inventories on fracture surfaces for evaluating site-scale uranium inventories were obtained.

5.4 Prospects for development

In interpreting column experiments, there is a degree of freedom not utilised so far in modelling. The theoretical tests performed (Tukiainen 2000) indicate considerable sensitivity of the system for kinetic sorption. This means that the actual sorption rate plays an important part in the migration of tracers in the column. To some extent, this sensitivity may be limited to short term and small-scale laboratory experiments, but in any case the topic appears worth studying in more detail. An example of the effect of kinetic sorption on the breakthrough curve in a column with an artificial fracture in the axial direction is shown in Figure 5.1. It is noteworthy that the entire shape of the breakthrough curve can change by just adjusting one parameter. For slow kinetics a part

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[8] Here one must keep in mind that the U-234/U-238 activity ratio in a groundwater sample represents a weighted average over the whole packed-off section of the drill hole which "dilutes" individual signals from fractures with less groundwater flow. In addition, the dominating flow channels that discharge into the packed-off section may derive their composition from a further location. In contrast, the U-234/U-238 activity ratio of the fracture coating sample is always strictly site-specific. In addition, many uranium-rich fracture coating samples have been found only in closed fractures off the main flow channels.

of the tracer migrates unretarded, and for fast kinetics the breakthrough curve is identical to that of corresponding K_d concept. Another important point about kinetic sorption is that the parameter describing the kinetics can be readily obtained from careful batch experiments (Tukiainen 2000).

In general it is clear that there is a continuous need in performance assessments for models that describe the physico-chemical reality as truly as possible. It is also equally clear that no matter how detailed and rigorous models are used in performance assessments, there will always be uncertainties, for two basic reasons. First, the performance assessment will have to cover long time scales and therefore there will be inevitable uncertainties related to the future development of the repository–bedrock-system. Second, the repository site will by necessity be characterised by a limited number of drilling holes that introduces inevitable uncertainties in the characterisation of the bedrock volume. Thus the following strategic question remains: what is the value of modelling parts of the system rigorously in conceptual terms and in great detail, when the overall performance assessment will inevitably be facing considerable uncertainties.

In the above situation, the role of migration modelling is quite important. In this sense, the discussions above have attempted to highlight the true potential of more developed modelling concepts in a performance assessment type of modelling case.
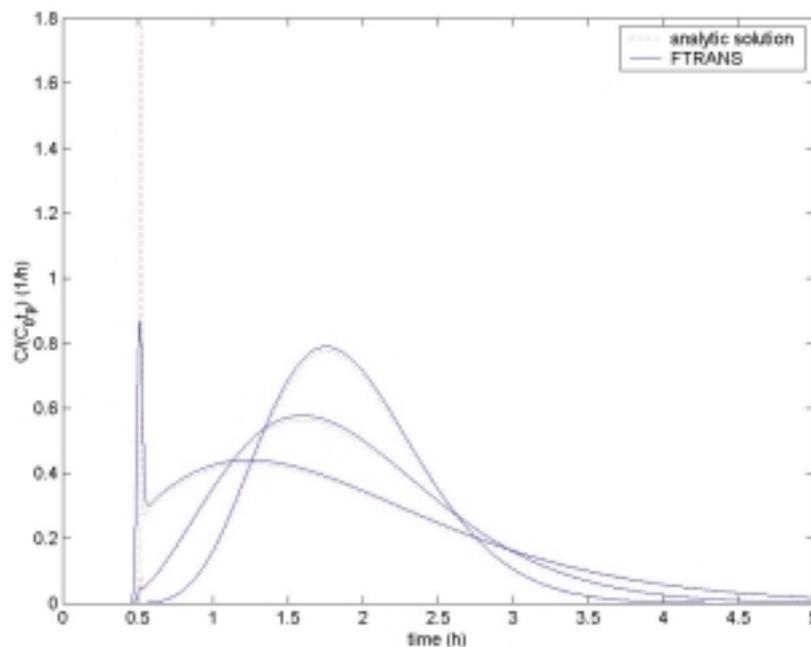
Figure 5.1 The effect of kinetic sorption on the breakthrough curve (modified from Tukiainen 2000).

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Strategy for the development of a conceptual migration model

It appears possible to develop further the conceptual model in the migration models used in performance assessments. Based on available experience a stepwise iterative process is suggested as the strategy. This means that we start with existing codes, test them against laboratory or natural analogue observations, and make the necessary adjustments to the conceptual model. This new model will subsequently be tested against new experimental observations and so on.

Concerning future performance assessments it appears worthwhile to consider the possibility of attempting more detailed reactive migration modelling in parallel with the traditional advection-dispersion-matrix diffusion approach. This attempt would serve the purpose of utilising the existing geochemical knowledge to a fuller extent, and also of repeatedly testing the real applicability of this modelling approach. It is acknowledged that while being the conceptually more rigorous of the two approaches, for data availability reasons, reactive modelling probably can only be done for few elements or species and for few mineral and groundwater settings.

Recommendations for future work

Laboratory experiments are usually relatively straightforward to interpret because they are well controlled. At the same time, however, there is uncertainty related to the representativeness of the experimental conditions vis-a-vis the natural in situ conditions. On the other hand natural analogue studies are much more difficult to interpret, because there is little direct information of the past events. The conditions under which the natural analogue has been developing have by definition been strictly in situ. The long-term evolution cannot be reproduced in short term laboratory experiments. Thus it appears that closer integration of the two fields of research is beneficial. The co-operation could be of the form that specific hypotheses presented in natural analogue research would be rigorously tested in suitable well-controlled laboratory experiments. The experiments could for instance be diffusion or column experiments.

6. Conclusions

Geological disposal of nuclear wastes is a widely studied option for ultimate nuclear waste management in many nuclear energy producing countries. Performance assessments of geological repositories require information about how escaping radionuclides will be transported in the bedrock. While being transported away by flowing groundwater along water-carrying fractures the escaped radionuclides will be retarded and spread out by various physico-chemical mechanisms. Therefore, retardation mechanism studies provide an important part of the database required by performance assessments. In this report we have discussed how the data demanded by performance assessments and data supplied by experimental retardation mechanism studies meet in the Finnish example.

Performance assessments will have to cope with two fundamental and unavoidable sources of uncertainty. The first is the long time-scale that will have to be covered and which brings about the fact that the future of the repository-bedrock system is, strictly speaking, impossible to know in advance. The scenario technique has been used to take this uncertainty into account. The second source of uncertainty is the heterogeneity of geological formations. The practical problem is due to the fact that the site for the repository can only be characterised from a limited number of observation holes. A partly homogeneous medium has been used in performance assessments to describe natural heterogeneities.

This state of affairs leads to a picture of the geologic medium in which primary samples are located quite sparsely, but, in contrast, they are analysed in great detail. There appears to be a point at which the results of detailed modelling still out-weigh the overall uncertainties, but, beyond which, the added value starts decreasing. Thus, the strategic question rises: what is the practical value of extremely detailed modelling of some specific mechanism when some other parts of the performance assessment will always contain considerable uncertainties? Or, what is a reasonable level of detail and rigour in performance assessment modelling, considering the overall uncertainties?

Concerning retardation mechanisms, Finnish performance assessments have so far applied sorption and classical matrix diffusion. Sorption has been described by K_d values (different sets for different groundwater type scenarios) and rock matrix as heterogeneous material with enhanced porosity and diffusivity closest to fracture. Anion exclusion has been taken into account by using smaller values for porosity and diffusivity. In order to be conservative, no other retardation mechanisms have been applied.

Laboratory scale structural studies of rock matrix fulfil the current need for porosity and diffusivity data in performance assessments. In the case of C-14-PMMA the porosity data obtained is so detailed that it cannot be used to its full potential in current matrix diffusion modelling. The reason is that diffusivity data must be measured independently. With current techniques, the measurements of samples with a thickness of less than cm have been observed to be disturbed by artificial connections. For the time being there is no defensible alternative to direct measuring to provide the diffusivity data.

Helium gas techniques provide a valuable tool because the slow diffusion process can be accelerated by a factor of 10 000 by applying gas instead of water as the carrier of tracer. Another advantage is that the method is non-destructive, and after helium gas methods the same samples are available for other studies. An in situ version has been constructed to study the structural disturbances caused by drilling.

The surface complexation model has appeared feasible in explaining anion exclusion observations in natural rocks and structurally simpler artificial reference rocks. Heterogeneity of the samples, in particular natural rock samples, has been observed to be a major hindrance to detailed model testing in the case of anion exclusion.

Column experiments have been useful in providing well-controlled tests for the classical advection-dispersion-matrix diffusion modelling concept. True matrix diffusion has been observed by using extremely small water flows through the column. In some cases, however, it appears difficult to match a modelled breakthrough curve with a measured one equally well for all parts of the curve. The reason appears to be channelled water flow through the column. For the current experimental set-up there is, unfortunately, no direct technical method to obtain independent data for channelled water flow. In other words, there is no support available for the flow channels one selects. This means that the improvement obtained by using a multichannel model is partly illusory.

Natural analogue studies have shown that both sorption and matrix diffusion actually take place in situ. The results obtained for uranium at Palmottu indicate that sorption in situ is to a large part irreversible. This means that the assumption of fast reversible adsorption used in performance assessments over-estimates the mobility of radionuclides. Sorption has been observed to be only one interaction mechanism between dissolved radionuclide and the water-rock system. A set of mechanisms has been observed; many mechanisms (e.g. precipitation) are actually more important than sorption. This is demonstrated in that on average K_d based sorption covers about 1 % of the attached radionuclide inventory on fracture surfaces.

It has been observed at Palmottu that within the topmost 100 metres of the bedrock, rock matrix appears to be reducing inside although the flowing groundwater along fractures that bound the matrix block is strongly oxidising. This indicates strong redox buffering capacity in the rock matrix within this most oxidising zone of the bedrock. It may be noted here that deeper down in the bedrock the flowing groundwater is reducing at Palmottu.

All Finnish natural analogue studies (i.e. Palmottu, the boulder, and Hästholmen) have indicated continuous open pore network in the rock matrix with, however, natural heterogeneity. This is in line with basic assumptions applied in Finnish performance assessments. Continuous pore network has previously been observed in the Stripa mine in undisturbed rock as well as in rock disturbed by excavations and drill holes.

Despite the unavoidable uncertainties in performance assessments there appears to be room for improvements in retardation mechanism modelling. In particular, sorption modelling in performance assessments is quite simplified. In some simple cases, the K_d based approach could be supported by parallel mechanistic sorption modelling. It is acknowledged, however, that mechanistic sorption modelling is not possible for all nuclides, all minerals, or all geochemical conditions. Notwithstanding this, it would utilise the current state-of-the-art understanding of sorption.

References

Aalto, H., Lehikoinen, J., Muurinen, A. & Valkiainen, M. 2000. Diffusion and adsorption in porous silica considered as a reference material for crystalline rock. Presented at the 24th International Symposium on the Scientific Basis for Nuclear Waste Management, Sydney 28–31 Aug. 2000.

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

Autio, J. 1996. Characterization of the excavation disturbance caused by boring of the experimental full scale deposition holes in the Research Tunnel at Olkiluoto. Helsinki: Posiva Oy. 118 p. (Report Posiva 96-09.)

Autio, J., Timonen, J., Aaltonen, T., Laajalahti, M., Kuoppamäki, K. & Maaranen, J. 1999. Determination of the porosity, permeability and diffusivity of rock in the excavation-disturbed zone around full-scale deposition holes using the He-gas method. In: Wronkiewicz, D. & Lee, J. (eds). Scientific Basis for Nuclear Waste Management XIX. Pittsburgh: Materials Research Society. Pp. 759–766 (Mat. Res. Soc. Symp. Proc. Vol. 556.)

Birgersson, L. & Neretnieks, I. 1987. Diffusion in the matrix of granitic rock. Field test in the Stripa mine. In: Apted, M.J. & Westerman, R.E. (eds). Scientific Basis for Nuclear Waste Management XI. Pittsburgh, PA: Materials Research Society. Pp. 189–198. (Mat. Res. Soc. Symp. Proc., vol. 112.)

Birgersson, L. & Neretnieks, I. 1988. Diffusion in the matrix of granitic rock. Field test in the Stripa mine. Final report. Stockholm: Swedish Nuclear Fuel and Waste Management Co. 76 p. + 5 app. (SKB Technical Report 88-08.)

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 1: Hydrogeological evaluation of the site. Brussels: European Commission. 98 p. (Report EUR 18202 EN.)

Blomqvist, R., Ruskeeniemi, T., Kaija, J., Ahonen, L., Paananen, M., Smellie, J., Grundfelt, B., Pedersen, K., Bruno, J., Pérez del Villar, L., Cera, E., Rasilainen, K., Pitkänen, P., Suksi, J., Casanova, J., Read, D. & Frape, S. 2000. The Palmottu natural analogue project − Phase II: Transport of radionuclides in a natural flow system at

Palmottu. Luxembourg: European Commission. 192 p. (Nuclear Science and Technology Series EUR 19611 EN.)

Blomqvist, R., Suksi, J., Ruskeeniemi, T., Ahonen, L., Niini, H., Vuorinen, U. & Jakobsson, K. 1995. The Palmottu natural analogue project. Summary report 1992–1994. Espoo: Geological Survey of Finland. 82 p. (Report YST-88.)

Brenner, H. & Ganesan, V. 2000. Molecular wall effects: Are conditions at a boundary "boundary conditions"? Phys. Rev. E, vol. 61, pp. 6879–6897.

Carslaw, H.S. & Jaeger, J.C. 1959. Conduction of heat in solids. 2nd edition. Oxford: Clarendon Press. 510 p.

Cole, T., Bidoglio, G., Soupioni, M., O'Gorman, M. & Gibson, N. 2000. Diffusion mechanisms of multiple strontium species in clay. Geochim. Cosmochim. Acta, vol. 64, pp. 385–396.

Curti, E. 1997. Coprecipitation of radionuclides: basic concepts, literature review and first applications. 107 p. (PSI Bericht Nr. 97-10.)

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. Pp. 177–260. (Reviews in Mineralogy, vol. 23.)

Dullien, F.A.L. 1979. Porous media fluid transport and pore structure. San Diego (CA): Academic Press Inc.

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

Elert, M. 1997. Retention mechanisms and the flow wetted surface – implications for safety analysis. (SKB Technical Report 97-01.)

EPA. 1999. Understanding variation in partition coefficient, K_d, values. Volume I: The K_d model, methods of measurement, and application of chemical reaction codes, United States Environment Protection Agency. 171 p. + 3 app. (EPA 402-R-99-004A.)

Eronen, M. & Olander, H. 1990. On the world's ice ages and changing environments. Helsinki: Nuclear Waste Commission of Finnish Power Companies. 72 p. (Report YJT-90-13.)

Everett, D.H. 1972. Manual of symbols and terminology for physicochemical quantities and units: Appendix II: Definitions, terminology and symbols in colloid and surface chemistry - part 1: Colloid and surface chemistry. Pure Appl. Chem., vol. 31, pp. 577–638.

Frick, U. 1993. An evaluation of diffusion in the groundwater of crystalline rocks, Wettingen: Nationale Genosseschaft für die Lagerung radioaktiver Abfälle (NAGRA). 96 p. + 5 app. (NAGRA Interner Bericht 92-92E.)

Gascoyne, M. 2000. A review of published literature on the effects of permafrost on the hydrogeochemistry of bedrock. Helsinki: Posiva Oy. 53 p. (Report Posiva 2000-09.)

Grisak, G.E. & Pickens, J.F. 1980. Solute transport through fractured media. 1. The effect of matrix diffusion. Water Resources Research, vol. 16, no. 4, pp. 719–730.

Gustafsson, E., Carlsson, A.-C., Wass, E. and Ahonen, L. 1998. Tracer test in the Eastern Granite, between boreholes R302, R335 and R384, Palmottu natural analogue study site. 29 p. + 15 p. The Palmottu Natural Analogue Project, Technical Report 98-02

Hakkarainen, V., Kurimo, M. & Niini, H. 1991. Surficial geology. In: Blomqvist, R., Jaakkola, T., Niini, H. & Ahonen, L. (eds). The Palmottu Analogue Project, Progress Report 1990. Espoo: Geological Survey of Finland, Nuclear Waste Disposal Research. Pp. 58–74. (Report YST-73.)

Hartikainen, K., Hartikainen, J. & Timonen, J. 1997. Through-diffusion, permeability, channel-flow and *in situ* results for porosity and migration properties of rock samples by He-gas methods. Helsinki: Posiva Oy. 43 p. (Report Posiva 97-13.)

Hartikainen, K., Pietarila, H., Rasilainen, K., Nordman, H., Ruskeeniemi, T., Hölttä, P., Siitari-Kauppi, M. & Timonen, J. 1996. Characterization of the altered zone around a fracture in Palmottu natural analogue. In: Murphy, W.M. & Knecht, D.A. (eds). Scientific Basis for Nuclear Waste Management XIX. Pittsburgh, PA: Materials Research Society. Pp. 839–846. (Mat. Res. Soc. Symp. Proc., vol. 412.)

Hellmuth, K.-H., Lukkarinen, S. & Siitari-Kauppi, M. 1994. Rock matrix studies with carbon-14-polymethylmethacrylate (PMMA): method development and applications. Isotopenpraxis. Isotopes in Environmental and Health Studies 30, pp. 47–60.

Hellmuth, K.-H., Siitari-Kauppi, M. & Lindberg, A. 1993. Study of porosity and migration pathways in crystalline rock by impregnation with ^{14}C-polymethylmethacrylate. Journal of Contaminant Hydrology 13, pp. 403–418.

Hölttä, P., Hakanen, M. & Hautojärvi, A. 1992. Transport and retardation of non-sorbing radionuclides in crystalline rock fractures. Radiochim. Acta 58/59, pp. 285–290.

Hölttä, P., Hakanen, M., Hautojärvi, A., Timonen, J. & Väätäinen, K. 1996. The effects of matrix diffusion on radionuclide migration in rock column experiments. J. Contam. Hydrol. 21, pp. 165–173.

Hölttä, P., Siitari-Kauppi, M., Hakanen, M., Huitti, T., Hautojärvi, A. & Lindberg, A. 1997. Radionuclide transport and retardation in rock fracture and crushed rock column experiments. J. Contam. Hydrol. 26, pp. 135–145.

Hölttä, P., Siitari-Kauppi, M., Lindberg, A. & Hautojärvi, A. 1998. Na, Ca and Sr retardation on crushed crystalline rock. Radiochim. Acta 82, pp. 279–285.

Hölttä, P., Siitari-Kauppi, M., Hakanen, M. & Tukiainen, V. 2001. Attempt to model laboratory scale diffusion and retardation data. J. Contam. Hydrol. (in print)

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.)

Jönsson, S., Jansson, F. & Ludvigsson, J.-E. 1995a. Flow meter logging in Palmottu test site. Boreholes R318, R343, R345, R347 and R357. Geosigma AB, Uppsala. 9 p. + 1 app.

Jönsson, S., Jansson, F. & Ludvigsson, J.-E. 1995b. Flow meter logging in Palmottu test site. Boreholes R302, R324, R332, R335, R373 and R384. Geosigma AB, Uppsala. 9 p. + 1 app.

Korkealaakso, J. & Pitkänen, P. 1997. Integration of hydrological and hydrochemical information at Palmottu. (The Palmottu Analogue Project. Technical Report. In prep.)

Koskinen, L. & Kattilakoski, E. 1997. Modelling of deep deep groundwater flow under natural conditions at the Palmottu site. 31 p. + app. 22 p. (The Palmottu Analogue Project. Technical Report 97-03.)

Laaksoharju, M., Vuorinen, U., Snellman, M., Allard, B., Pettersson, C., Helenius, J. & Hinkkanen, H. 1994. Colloids or artefacts A TVO/SKB co-operation project in Olkiluoto, Finland. Helsinki: Nuclear Waste Commission of Finnish Power Companies. 52 p. + 4 app. (Report YJT-94-01.)

Lampinen, P. 1997. Interpretation of hydraulic head measurements at Palmottu. 21 p., 7 fig., 5 app. The Palmottu Analogue Project. Technical Report 97-13.

Lampinen, P., Ahonen, L. & Blomqvist, R. 1996. Hydraulic connections at Palmottu. Evaluation based on down-hole spinner test and drawdown observations. 30 p. + 4 app. The Palmottu Analogue Project. Technical Report 96-02.

Lehikoinen, J. 1999. Ion diffusion in compacted bentonite. Helsinki: Posiva Oy. 37 p. (Posiva-99-21.)

Lehikoinen, J., Muurinen, A. & Valkiainen, M. 1999. A consistent steady-state model for anion exclusion and surface diffusion. In: Wronkiewicz, D.J. & Lee, J.H. (eds). Scientific Basis for Nuclear Waste Management XXII. Pittsburgh: Materials Research Society. Pp. 663–670. (Mat. Res. Soc. Symp. Proc. vol. 556.)

Lehikoinen, J., Muurinen, A., Olin, M., Uusheimo, K. & Valkiainen, M. 1992. Diffusivity and porosity studies in rock matrix. The effect of salinity. Espoo: Technical Research Centre of Finland. 28 p. (VTT Research Notes 1394.)

Löfman, J. 1999. Site scale groundwater flow in Olkiluoto. Helsinki: Posiva Oy. 121 p. (Report Posiva 99-03.)

Marcos, N., Siitari-Kauppi, M., Suksi, J., Rasilainen, K., Finch, R. & Hellmuth, K.-H. 2000. Discussion on the use of matrix diffusion model after a multidisciplinary study of a granitic boulder sample. Submitted to MRS'2000 conference.

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.)

Mészáros, F. 1999. Testing and QA of the quadtree package. Helsinki: VTT Energy. 29 p. (Technical report VIKU-1/99.)

Miller, W., Alexander, R., Chapman, N., McKinley, I. & Smellie, J. 1994. Natural analogue studies in the geological disposal of radioactive wastes. Amsterdam: Elsevier Science B.V. 395 p.

Miller, W., Alexander, R., Chapman, N., McKinley, I. & Smellie, J. 2000. Geological disposal of radioactive wastes & natural analogues. Amsterdam: Elsevier Science Ltd. 316 p.

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.

Ohlsson, Y. & Neretnieks, I. 1995. Literature survey of matrix diffusion theory and of experiments and data including natural analogues. Stockholm: Swedish Nuclear Fuel and Waste Management. 89 p. (SKB Technical Report 95-12.)

Olin, M. & Valkiainen, M. 1990. Concentration profiles of anions in granite bedrock caused by postglacial landuplift and matrix diffusion (IVO Technical Report 90-1.)

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

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

Parkhomenko, E.I. 1967. Electrical properties of rocks, New York: Plenum Press. P. 277.

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.)

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.)

Rasilainen, K., Hellmuth, K.-H., Kivekäs, L., Melamed, A., Ruskeeniemi, T., Siitari-Kauppi, M., Timonen, J. & Valkiainen, M. 1996. An interlaboratory comparison of methods for measuring rock matrix porosity. Espoo: Technical Research Centre of Finland. 16 p. + app. 26 p. (VTT Research Notes 1776.)

Rasilainen, K., Luukkonen, A., Niemi, A., Olin, M. & Pöllä, J. 1999. The feasibility of modelling coupled processes in safety analysis of spent nuclear fuel disposal. Espoo: Technical Research Centre of Finland. 83 p. + app. 4 p. (VTT Research Notes 1973.)

Rasilainen, K., Suksi, J., Hellmuth, K.-H., Lindberg, A. & Kulmala, S. 1996. Postglacial matrix diffusion in a boulder sample. In: Murphy, W.M. & Knecht, D.A. (eds). Scientific Basis for Nuclear Waste Management XIX. Pittsburgh, PA: Materials Research Society. Pp. 855–862. (Mat. Res. Soc. Symp. Proc., vol. 412). ISBN 1-55899-315-0

Rasilainen. K. & Suksi, J. 1997. On the accuracy of uranium-series dating: A comparison with a known matrix diffusion case. In: Gray, W.J. & Triay, I.R. (eds). Scientific Basis for Nuclear Waste Management XX. Pittsburgh, PA: Materials Research Society. Pp. 1177–1184. (Mat. Res. Soc. Symp. Proc., vol. 465). ISBN 1-55899-369-X

Siitari-Kauppi, M., Flitsiyan, E.S., Klobes, P., Meyer, K. & Hellmuth, K.-H. 1998. Progress in physical rock matrix characterization: structure of the pore space. In: McKinley, I.G. & McCombie, C. (eds). Scientific Basis for Nuclear Waste Management XXI, Pittsburgh: Materials Research Society. Pp. 671–678. (Mat. Res. Soc. Symp. Proc. vol. 506.)

Simbierowicz, P. & Olin, M. 1997. Investigation of the influence of heterogeneous porosity on matrix diffusion: a novel approach using adaptive tree multigrid technique and real porosity data. In: Gray, W.J. & Triay, I.R. (eds). Scientific Basis for Nuclear Waste Management XX. Pittsburgh, PA: Materials Research Society. Pp. 847–854. (Mat. Res. Soc. Symp. Proc., vol. 465.)

Skagius. A.-C.K. 1986. Diffusion of dissolved species in the matrix of some Swedish crystalline rocks. Stockholm: Royal Institute of Technology. 46 p. + app. 149 p. (PhD Thesis).

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

SKI. 1996. SKI SITE-94 Deep repository performance assessment project. (SKI Technical Report 96:36.)

Sposito, G. 1984. The surface chemistry of soils. New York, Oxford University Press. 234 p.

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

Suksi, J., Juntunen, P. & Ervanne, H. 1999. Study of natural uranium sorption and fixation. Espoo: Geological Survey of Finland. 22 p. (Palmottu Natural Analogue Project Technical Report 99-25.)

Suksi, J., Rasilainen, K., Casanova, J., Ruskeeniemi, T., Blomqvist, R. & Smellie, J.A.T. 2000. U-series disequilibria in a groundwater flow route as an indicator of uranium migration processes. J. Contam. Hydrol. 47, pp. 187–196.

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.)

Tukiainen, V. 2000. Interpretation of tracer experiments with a computational model (in Finnish). Espoo: VTT Energy. 125 p. (VTT Energian raportteja 17/2000.)

Valkiainen, M. 1992. Diffusion in the rock matrix − A review of laboratory tests and field studies. Helsinki: Nuclear Waste Commission of Finnish Power Companies. 52 p. (Report YJT-92-04.)

Valkiainen, M., Aalto, H., Lehikoinen, J. & Olin, M. 1999. Study of ion-exclusion using artificial reference samples for rocks. In: Wronkiewicz, D.J. & Lee, J.H. (eds). Scientific Basis for Nuclear Waste Management XXII. Pittsburgh: Materials Research Society. Pp. 641–646. (Mat. Res. Soc. Symp. Proc. vol. 556.)

Valkiainen, M., Aalto, H., Lindberg, A., Olin, M. & Siitari-Kauppi, M. 1995. Diffusion in the matrix of rocks from Olkiluoto − The effect of anion exclusion. 38 p. + app. (Report YJT-95-20.)

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. Pp. 81–120. ISBN 92-64-03700-4

Webelements. 15.12.2000. http://www.webelements.com/webelements/index.html

Vieno, T. & Nordman, H. 1999. Safety assessment of spent fuel disposal in Hästholmen, Kivetty, Olkiluoto and Romuvaara TILA-99. Helsinki: Posiva Oy. 253 p. (Report Posiva 99-07.)

Vieno, T., Nordman, H., Poteri, A., Hautojärvi, A. & Vira, J. 2001. The Posiva/VTT approach to simplification of geosphere-transport models, and the role and assessment of conservatism. In: Confidence in models of radionuclide transport for site-specific assessment. Workshop Proceedings Carlsbad, New Mexico, USA 14–17 June 1999. Paris: OECD Nuclear Energy Agency. Pp. 119–128.

Vuori, S. (ed). 2000. Public sector's research programme on nuclear waste management (JYT 2001) 1997–2001. Midterm report (in Finnish). Helsinki: Ministry of Trade and Industry. 159 p. (Ministry of Trade and Industry Studies and Reports 11/2000.)

Väätäinen, K., Timonen, J.& Hautojärvi, A. 1993. Development of a gas method for migration studies in fractured and porous media. In: Interrante, C. & Pabalan, R. (eds). Scientific Basis for Nuclear Waste Management XVI. Pittsburgh: Materials Research Society. Pp. 851–856 (Mat. Res. Soc. Symp. Proc. vol. 294.)

Appendix A: Statistics of rock matrix studies done with helium gas methods

Because of the variety of measuring techniques and places of origin of the samples, these statistics are divided into three paragraphs: diffusivity and porosity results, permeability results, and channel flow results. The results are divided further by rock type and by the regions where the samples were taken in Finland. Although the measuring accuracy of the He-gas method is fairly good, the average results over different rock types and origin of the samples are only advisory. The results in the following tables are averages over N measurements (column N). All D_e and channel flow results are given as helium molecule in nitrogen (He / N_2). To convert the coefficients to match diffusion in water, see section 3.1.2 in the main text.

Diffusivity and porosity results

The total number of measured samples in through-diffusion measurements is 214. The single measured diffusion coefficients varied in the range of $1.8 \cdot 10^{-11} - 9.2 \cdot 10^{-8}$ (m^2/s) (He/N_2). However, the data distribution not being normal, a reasonable order of magnitude of diffusion coefficient for a typical Finnish deep bedrock is between 10^{-9} and 10^{-8} m^2/s (He/N_2). The data set containing all measured through-diffusion coefficients was analysed as a Weibullian distribution (Figure 1).
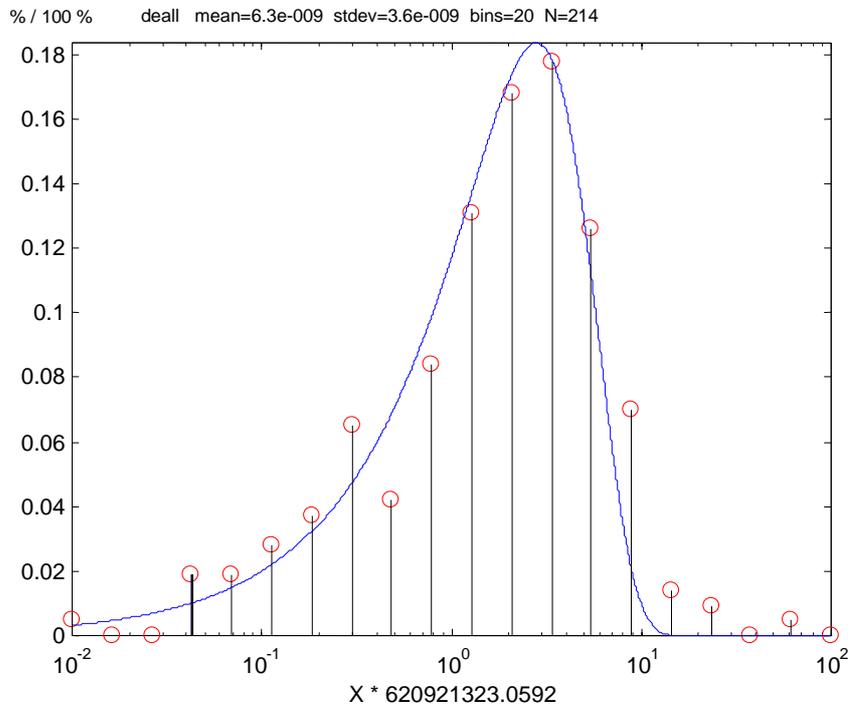
Figure 1. Scaled D_e -data (all measurements) and Weibullian distribution.

The porosity (ε_p) results were treated as logaritmico-normal distributed. As a conclusion it can be said that the porosity of Finnish deep bedrock is typically less than 1%. (Figure 2).
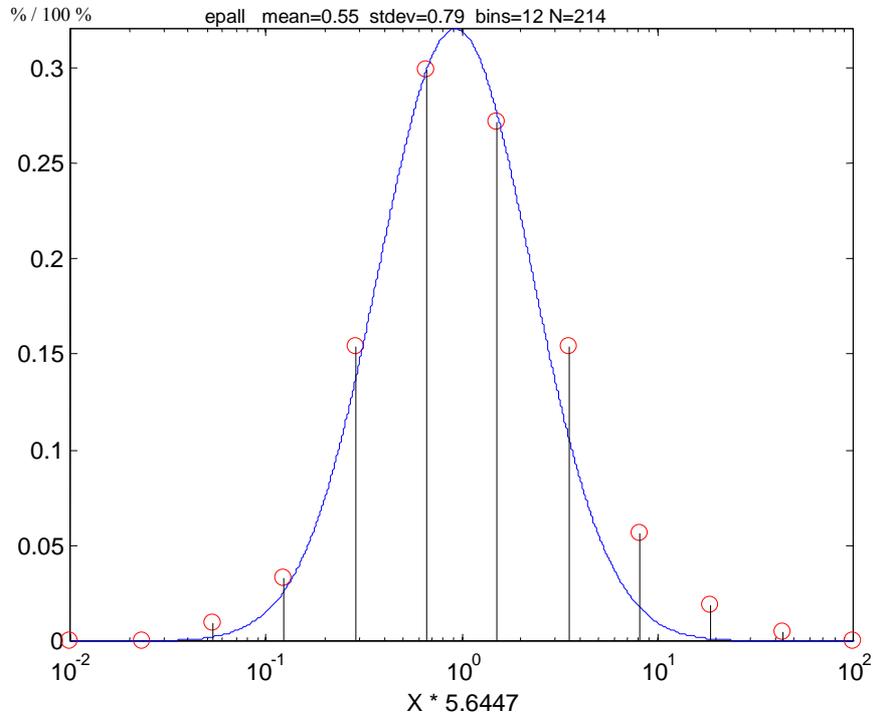
Figure 2. Scaled data and logaritmico-normal distribution.

Although the number of independent measurements done is relatively high, only rough predictions for diffusion characteristics for a non-measured single rock sample can be made (Tables 1 and 2). The variation of measurements results for the adjoining samples from the same drill hole is considerably higher than might be expected because of the significant natural inhomogenity of the rock matrix.

Table 1. D_e and ε_p results by rock type.

Rock type	D_e (avg) (m²/s)	ε_p (avg) (%)	N
Amfibolite	$1 \cdot 10^{-9}$	0.1	2
Diorite	$2 \cdot 10^{-9}$	0.3	7
Gneiss	$6 \cdot 10^{-9}$	0.2	29
Granite	$4 \cdot 10^{-9}$	0.2	67
Granodiorite	$3 \cdot 10^{-9}$	0.1	15
Tonalite	$6 \cdot 10^{-9}$	0.2	21

Table 2. D_e and ε_p results by regions.

Region	D_e (avg) (m²/s)	ε_p (avg) (%)	N
Hästholmen	$3 \cdot 10^{-9}$	0.1	19
Kivetty	$5 \cdot 10^{-9}$	0.6	52
Olkiluoto	$5 \cdot 10^{-9}$	0.5	59
Palmottu	$4 \cdot 10^{-9}$	0.7	21
Romuvaara	$6 \cdot 10^{-9}$	0.2	52
Äspö *	$5 \cdot 10^{-9}$	0.4	17

* Samples are from Sweden

For some of these samples, rock type was not defined. This is the reason for greater N for regional results vs. rock type results.

Permeability results

The permeability measurement data distribution also shows an approximation to Weibullian behaviour (Tables 3 and 4). Data including all measurements has its mean in $K_{(mean)} \approx 4 \cdot 10^{-19} \, m^2$. The variation of the data is large than might be supposed because of the appreciable sensitivity in permeabilities vis-a-vis inhomogenities in the sample.

Table 3. Permeability results by rock type.

Rock type	K (m²)	N
Amfibolite	$2 \cdot 10^{-19}$	2
Diorite	$4 \cdot 10^{-18}$	7
Gneiss	$2 \cdot 10^{-19}$	22
Granite	$3 \cdot 10^{-19}$	53
Granodiorite	$2 \cdot 10^{-19}$	10
Tonalite	$9 \cdot 10^{-19}$	12

Table 4. Permeability results by regions.

Region	K (m²)	N
Hästholmen	$1 \cdot 10^{-18}$	14
Kivetty	$1 \cdot 10^{-18}$	4
Olkiluoto	$1 \cdot 10^{-18}$	20
Palmottu	$5 \cdot 10^{-18}$	5
Romuvaara	$4 \cdot 10^{-19}$	32
Äspö	$1 \cdot 10^{-19}$	13

Channel flow results

The channel flow measurement data is not normally distributed (Tables 5 and 6). The average products $D_e \cdot \varepsilon_p$ for rock types and regions are only rough estimates because insufficient statistics were available to determine the data distribution.

Table 5. Channel flow results by rock type.

Rock type	$D_e \cdot \varepsilon_p$ (m²/s)	N
Amfibolite	$8 \cdot 10^{-14}$	3
Gneiss	$8 \cdot 10^{-14}$	22
Granite	$3 \cdot 10^{-14}$	36
Granodiorite	$8 \cdot 10^{-14}$	12
Tonalite	$9 \cdot 10^{-14}$	18

Table 6. Channel flow results by regions.

Rock type	$D_e \cdot \varepsilon_p$ (m²/s)	N
Hästholmen	$1 \cdot 10^{-14}$	18
Kivetty	$5 \cdot 10^{-13}$	15
Olkiluoto	$7 \cdot 10^{-14}$	20
Romuvaara	$2 \cdot 10^{-14}$	32

Disturbed vs. intact samples results

Details of the characterization of the excavation disturbance caused by drilling (see main text) have been published earlier. The porosity, diffusion coefficient and permeability of disturbed rock samples are clearly higher than those of undisturbed samples (Table 7). Also, if the rock has a schistositic structure, diffusivity and permeability are found to have larger values in the direction of the schistosity.

Table 7. Channel flow results by degree of disturbance.

Rock type	ε_p (%)	D_e (m²/s)	K (m²) *	N
Intact	0.17	$9.4 \cdot 10^{-10}$	$1 \cdot 10^{-19}$	14
Disturbed	0.20	$5.6 \cdot 10^{-9}$	$1.4 \cdot 10^{-18}$	14

* For permeability N = 12.

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Title

Retardation mechanism studies for performance assessments

Abstract

Performance assessments of geological repositories for nuclear waste require information about how possibly escaping radionuclides will be transported through the bedrock. Retardation mechanism studies provide an important part of the database required. So far Finnish performance assessments have considered sorption and matrix diffusion as retardation mechanisms. In this report we discuss how the data supplied by experimental retardation mechanism studies meet those required by performance assessments in the Finnish case.

Experimental structural studies on small-scale pore network are discussed in detail. The C-14-PMMA method and helium-gas methods provide porosity, diffusivity and permeability data. The effort within the Palmottu natural analogue project that aimed to locate large-scale flow channels is described briefly. Specific retardation mechanism studies are discussed. The laboratory studies cover column experiments and anion exclusion studies. Column experiments provide data on sorption and matrix diffusion. The natural analogue studies cover work done in the Palmottu, the Hämeenlinna boulder, and the Hästholmen projects. Studies at Palmottu provide in situ data about sorption and matrix diffusion.

This review indicates that data required by current migration models in performance assessments can be met by existing experimental methods. But the situation changes if more detailed modelling is wanted. In that case, a strategic question must be answered: what is a reasonable level of detail and conceptual rigour in performance assessment modelling, considering the unavoidable overall uncertainties due to long time scales and heterogeneous bedrock? The results obtained so far in natural analogue studies indicate that there is room for improvements in sorption modelling. The current K_d based approach could be supported by parallel mechanistic sorption modelling. It is acknowledged, however, that mechanistic sorption modelling is possible for neither all nuclides, nor all minerals, nor all geochemical conditions. Notwithstanding this, it would nevertheless better utilise the current state-of-the-art understanding of sorption.