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**RADIONUCLIDE MIGRATION IN
CRYSTALLINE ROCK FRACTURES**

LABORATORY STUDY OF MATRIX DIFFUSION

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Helsinki 2002

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Academic Dissertation

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ABSTRACT

Crystalline rock has been considered as a host medium for the repository of high radioactive spent nuclear fuel in Finland. The geosphere will act as an ultimate barrier retarding the migration of radionuclides to the biosphere if they are released through the technical barriers. Radionuclide transport is assumed to take place along water-carrying fractures, and retardation will occur both in the fracture and within the rock matrix. To be able to predict the transport and retardation of radionuclides in rock fractures and rock matrices, it is essential to understand the different phenomena involved. Matrix diffusion has been indicated to be an important mechanism, which will retard the transport of radionuclides in rock fractures. Both dispersion and matrix diffusion are processes, which can have similar influences on solute breakthrough curves in fractured crystalline rock.

In this work, the migration of radionuclides in crystalline rock fractures was studied by means of laboratory scale column methods. The purpose of the research was to gain a better understanding of various phenomena – particularly matrix diffusion – affecting the transport and retardation behaviour of radionuclides in fracture flow. Interaction between radionuclides and the rock matrix was measured in order to test the compatibility of experimental retardation parameters and transport models used in assessing the safety of underground repositories for spent nuclear fuel. Rock samples of mica gneiss and of unaltered, moderately altered and strongly altered tonalite represented different rock features and porosities offering the possibility to determine experimental boundary limit values for parameters describing both the transport and retardation of radionuclides and rock matrix properties.

The dominant matrix diffusion behaviour was demonstrated in porous ceramic column and gas diffusion experiments. Demonstration of the effects of matrix diffusion in crystalline rock fracture succeeded for the first time in a series of experiments where the experimental arrangements enabled very low water flow rates. FTRANS, a modified numerical code that can simulate both groundwater flow and the transport of radionuclides in porous or fractured medium, was tested in order to interpret laboratory scale migration experiments. The code was able to interpret

in-diffusion of calcium into altered tonalites. The elution curves of calcium for the altered tonalite fracture columns were explained adequately by the code when using parameters obtained from in-diffusion calculations. The K_d -values for intact rock obtained on the basis of the fracture column experiments were one order of magnitude lower than the K_d -values for crushed rock, indicating that batch experiments overestimate the retardation of sorbing radionuclides onto the rock matrices owing to the larger surface areas that are available. The greater sorption on altered tonalites was explained by the composition of the sorptive alteration minerals and the large specific surface areas.

In this research, sodium, calcium and strontium were used as tracers in order to compare various experimental techniques. Experiments with relevant nuclear waste nuclides are needed to enable more detailed discussion of the differences in K_d -values and the implication for performance assessment calculations. Data obtained from transport experiments conducted in well-defined laboratory conditions is the basis for the block scale and field experiments that are necessary to validate the radionuclide transport concept and to test the transferability of laboratory data to field conditions.

PREFACE

The work for this thesis was carried out in the Laboratory of Radiochemistry at the University of Helsinki as part of the Public Sector's Research Programme on Nuclear Waste Management (JYT). Financing from the Finnish Ministry of Trade and Industry is gratefully acknowledged. I appreciate the financial support of Posiva Oy and the Emil Aaltonen Foundation and the Jenny and Antti Wihuri Foundation.

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Life is not easy for any of us. But what of that? We must have perseverance and above all confidence in ourselves. We must believe that we are gifted for something and that this thing must be attained.

Maria Curie

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LIST OF PUBLICATIONS

This dissertation is based on the following publications:

- I P. Hölttä, A. Hautojärvi, M. Hakanen, Transport and Retardation of Non-Sorbing Radionuclides in Crystalline Rock Fractures, *Radiochimica Acta*, 58/59 (1992) 285-290.¹
- II P. Hölttä, M. Hakanen, A. Hautojärvi, J. Timonen and K. Väätäinen, The effects of matrix diffusion on radionuclide migration in rock column experiments. *Journal of Contaminant Hydrology*, 21 (1996) 165-173.²
- III P. Hölttä, M. Siitari-Kauppi, M. Hakanen, T. Huitti, A. Hautojärvi and A. Lindberg, Radionuclide transport and retardation in rock fracture and crushed rock column experiments. *Journal of Contaminant Hydrology*, 26 (1997) 135-145.²
- IV P. Hölttä, M. Siitari-Kauppi, A. Lindberg and A. Hautojärvi, Na, Ca and Sr Retardation on Crushed Crystalline Rock, *Radiochimica Acta*, 82 (1998) 279-285.¹
- V P. Hölttä, M. Siitari-Kauppi, M. Hakanen and V. Tukiainen, Attempt to model laboratory scale diffusion and retardation data. *Journal of Contaminant Hydrology*, 47 (2001) 139-148.²

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1. INTRODUCTION

Crystalline rock has been considered as a host medium for the repository of highly radioactive spent nuclear fuel in Finland and also in some other countries. The geosphere would act as the ultimate barrier retarding the migration of radionuclides to the biosphere if radionuclides are released through the technical barriers. Performance assessments are carried out in order to estimate how well the final disposal concept complies with the established requirements and to determine the consequences for human life and the natural environment if one or more of the protective barriers isolating the nuclear waste were to fail, thereby releasing radioactive substances from the repository – first to the surrounding bedrock, then possibly to organic nature.

Radionuclide transport is thought to take place along water-carrying fractures, with retardation occurring both in the fracture and within the rock matrix. To be able to predict the transport and radionuclide retardation in rock fractures and rock matrices, it is essential to understand the different physical and chemical phenomena involved. An understanding of relevant rock properties is also of great importance for the safe disposal of radioactive waste. Neretnieks (1980) showed that matrix diffusion is an important mechanism that will retard the transport of radionuclides in rock fractures.

In this research, laboratory scale column methods were used to study radionuclide migration in crystalline rock fractures. The general objective was to gain a better understanding of the physical and chemical phenomena – such as advection, dispersion, matrix diffusion and sorption – affecting the transport and retardation behaviour of radionuclides. Both dispersion and matrix diffusion are processes, which can have a similar effect on solute breakthrough curves in fractured crystalline rock. Experiments were conducted in order to demonstrate the effects of matrix diffusion and to distinguish matrix diffusion from other phenomena, e.g. hydrodynamic dispersion in fracture flow. Additional aims were to measure the interaction between radionuclides and the rock matrix and to test the compatibility of experimental retardation parameters and transport models used in assessing the safety of underground repositories for the spent nuclear fuel. The knowledge obtained through transport experiments performed in well-defined laboratory conditions is the basis for

block scale and field experiments done in order to validate the radionuclide transport concept and to test the transferability of laboratory data to in-situ conditions.

Papers I and II deal with physical phenomena – such as advection, dispersion and matrix diffusion – affecting transport behaviour in laboratory-scale fracture column experiments with non-sorbing radionuclides. Papers III and IV investigate the transport and retardation behaviour of sorbing radionuclides in order to compare sorption onto intact rock with sorption onto crushed rock. Paper V presents an attempt to test the modified migration model used in performance assessments, which was adapted for interpreting laboratory-scale experiments.

2. GENERAL

2.1. General background

In Finland, the repository for spent nuclear fuel will be excavated at a depth of about 500 metres in the fractured crystalline bedrock in Olkiluoto at Eurajoki, the site proposed by Posiva Oy. The safety of the final disposal of spent nuclear fuel is based on several technical and natural release barriers which prevent and slow down the release of radioactive materials from the final disposal repository into the bedrock and into the biosphere (Figure 1). These barriers include the solid state of the spent fuel, the double construction of the final disposal canister and the bentonite clay in which the canister is enclosed. The final barrier is formed by hundreds of metres of rock between the final disposal repository and organic nature. A final barrier this thick is thought to be enough to dampen the radiation to the level of natural background radiation. (Vieno and Nordman, 1999).

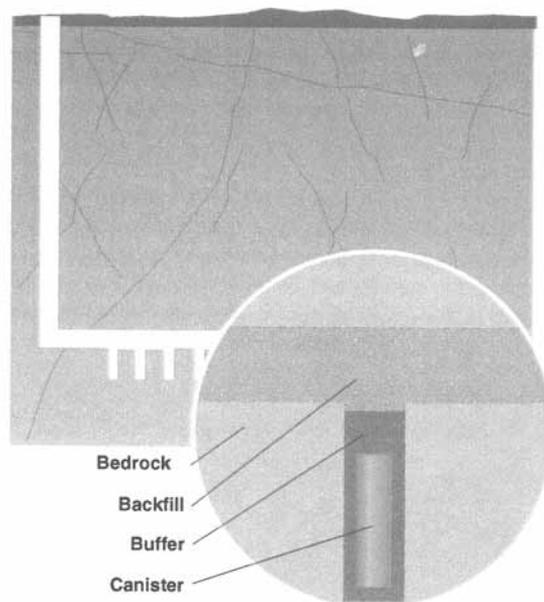


Figure 1. The KBS-3 concept for disposal of spent nuclear fuel (Posiva Oy, 2000).

Over very long time periods, radioactive substances may be released from a repository and then transported along water-conducting fracture zones. The radioactive substances move more slowly than the water due to the retardation effect of the surrounding rock. Owing to geochemical reactions with the bedrock – groundwater system, some of the dissolved radionuclides are attached to the fracture surfaces and fracture-filling materials along the water-carrying fracture. Some of the radionuclides will diffuse from the flowing water into the stagnant pore water of the rock matrix surrounding the fracture.

Final disposal of spent nuclear fuel in geological formation has been studied in many countries for more than twenty years. Crystalline rock has been considered as a host rock not only in Finland but also in Sweden, Switzerland, Canada and Japan. The other alternatives studied are clay formations, tuff and salt domains. In recent years, extensive research programmes have been involved in the development of various experimental and modelling methods in order to describe solute transport in rock fractures. In the laboratory, fracture flow and radionuclide transport have been studied in intact permeable cores (Fried et al., 1979; Dosch and Lynch, 1980; Rundberg et al., 1982; Drew and Vandergraaf, 1989; García Gutierrez et al. 1991; 1992; Smith et al., 1991; Perkins and Lucero, 2001), in single fracture columns (Fried et al., 1979; Neretnieks et al., 1982; Eriksen, 1983; 1984; Moreno et al., 1985; Reimus et al., 1995, Yllera de Llano et al., 1996; Callahan et al., 2000; Xu, 2000) and in block scale fractures (Grondin and Drew, 1988; Drew et al., 1990; Cliffe et al., 1993, Vandergraaf et al., 1996; 1997, Vilks and Bachinski, 1996, Park et al., 1997; Vilks and Baik, 2001). Experimental and modelling investigations have also been performed in-situ in many underground rock laboratories (Birgersson and Neretnieks, 1982; Abelin et al., 1982; 1986; 1991a; 1991b; Uchida and Sawada, 1995; Umeki et al., 1995; Hadermann and Heer, 1996; D'Alessandro et al., 1997; García Gutierrez et al., 1997; Vilks et al., 1997; Frieg et al., 1998; Johansson, 2000; Andersson et al., 2002). Evidences of phenomena affecting fracture flow have been also sought by means of natural analogue studies (Gancarz et al., 1980; Menet et al., 1992; Heath et al., 1992; Blomqvist et al., 2000). In performance assessments, modelling methodology has been developed to analyse the safety of the proposed nuclear disposal concept before it is adopted (Hadermann et al., 1985, Vieno, 1994; Smith et al., 1997; 2001).

2.2. Parameters affecting fracture flow

Natural rock consists of interconnected and intertwined networks of fractures and pores. This implies the existence of two distinct porosities to which the fractures or the pores contribute (Figure 2). The fractures provide the most effective transport paths even though most of the porosity derives from the pores. Transport processes along the pores and fractures are very different; transport occurs in the fracture network, while the porous matrix act as a capacitor charged by exchange with adjacent fractures. The surface of fractures is very rough, and the fracture aperture varies from point to point (Grenier et al., 1998).

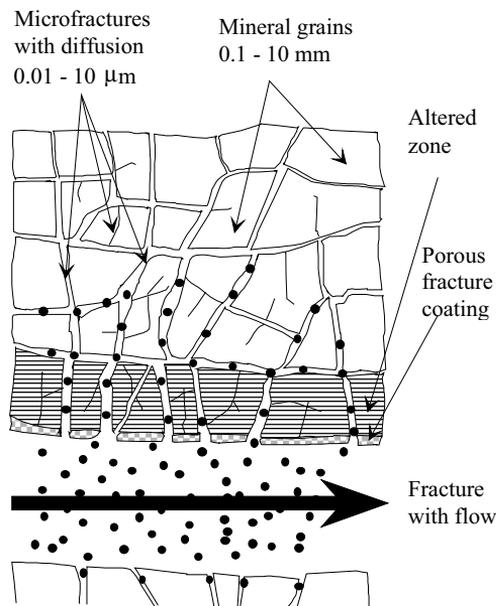


Figure 2. *Heterogeneous structure of the crystalline rock matrix (Rasilainen 1997).*

Because groundwater flows in few channels, the result is stagnant non-flowing areas in the fracture. Stagnant water is found also side fractures, microfissures and in pores within the rock matrix. As the groundwater moves, it will convey radionuclides along its path. The transport of radionuclides in the groundwater system is affected by various processes, such as advection, dispersion, channelling, matrix diffusion and sorption. Advection is the movement of the radionuclide with the groundwater flow. Dispersion is a process by which the concentration of radionuclide is diluted through

mixing with the fluid phase in a fracture. Matrix diffusion means the transport of radionuclides from the fracture conducting water to accessible microfissures and to pore water in the rock matrix surrounding the fracture. Sorption can be described as the ability of a radionuclide to attach itself to the rock matrix. Groundwater is found to flow primarily in limited areas of the fracture volume; this is called channelling. These processes can occur simultaneously or separately in groundwater flow. The diffusion of radionuclides into the rock matrix and their sorption onto the surfaces of the microfissures and pores are the main mechanisms retarding radionuclide transport. Effective diffusion coefficient, D_e , rock porosity, ϵ and mass-based distribution ratio, K_d are the parameters describing radionuclide retardation in transport models used in performance assessments.

2.2.1. Dispersion

Dispersion is a phenomenon which causes the spreading of solutes during transport through fractures (Grisak and Pickens, 1980; Neretnieks, 1980; 1983, Novakowski et al., 1985; Raven et al., 1988; Tsang et al., 1988; Lowell, 1989; Molyaner, 1989; Rundberg et al., 1991; Sahimi, 1995; Xu, 2000). Dispersion is caused by both a mechanical process and a physico-chemical process; the two are difficult to separate. When a radionuclide is diluted in the groundwater, it follows the path of normal flow and is called lateral dispersion. Hydrodynamic dispersion in fracture flow is caused by velocity differences in various areas of the flow channel and by transverse molecular diffusion coupled to the flow field. Molecular diffusion results from concentration gradients and the random motion of molecules, such as Brownian motion. At short time scales and in fast flows, the dispersion behaviour is dominated by the velocity distribution. With increasing transport times, molecular diffusions across the flow field tend to smooth out the effect of different velocities.

In Taylor's classical work, the convective diffusion was studied in a tube (Taylor, 1953). Taylor showed that after a sufficiently long time, the dispersion in a tube can be described by a constant dispersion coefficient. The time to reach the stationary dispersion depends on the tube diameter and the diffusion coefficient. The molecules of the solute have to diffuse across the channel and be advected essentially by all the velocities of the flow field before approaching the steady state.

When flow in fractures is being considered, bulk flow with Fickian dispersion is assumed. In practice, it is impossible to arrange an ideal bulk velocity distribution and, in addition, the velocity approaches zero at the channel walls. In fractures with a relatively narrow aperture but with a large width, the velocity distribution is nearly parabolic over the aperture; it can, however, have an uncontrollable distribution over the width. The simplified case of a lineary varying velocity field over the width of a fracture has been analysed by Taivassalo and Hautojärvi (1991). They showed that, in analogy with the dispersion in tubes, the dispersion in a fracture is initially unstable but develops later towards a steady state, the so-called Taylor dispersion.

For any velocity distribution, the dispersion coefficient remains the same apart from the numerical factor, which is defined by the distribution. In transport problems where the channel is confined, the dispersion in steady-state situation is Taylor dispersion, but the numerical factor in the dispersion coefficient is not known. The time it takes to reach steady-state behaviour in the solute transport depends on the channel width and the molecular diffusion coefficient. Experimental arrangements are based on these considerations, and the width of the channel is limited so that a readily controllable dispersion is applicable. This usually means widths of the order of millimetres in laboratory-scale transport lengths.

2.2.2. Matrix diffusion

Through-diffusion, in-diffusion and out-leaching have been the conventional methods used to determine matrix diffusion parameters (Relyea, 1980; Bradbury et al., 1982; Bourke et al., 1989; Siitari-Kauppi et al., 1994; Yamaguchi and Nakayama, 1998; Johansson, 2000; Xu et al., 2001). Siitari-Kauppi et al. (1994) and Siitari-Kauppi (2002) have compared different experimental approaches and discussed diffusion in homogeneous and heterogeneous rock matrices. Ohlsson et al. (2001) have determined rock matrix diffusivity in-situ by means of electrical conductivity measurements. Hartikainen et al. (1995) have determined rock matrix diffusivity in crystalline rocks by means of helium gas measurements. Matrix diffusion studies have also been performed as part of natural analogue research in which models were tested against in-situ observations over long periods of time (Heath et al., 1992; Rasilainen, 1997, Suksi, 2001).

The effect of matrix diffusion on solute transport through fractured media has been investigated theoretically, e.g. by Grisak and Pickens (1980), Neretnieks (1980; 2002) and Delay and Bodin (2001). Dispersion and matrix diffusion often result in similar effects on tracer breakthrough curves in fractured media. Solute diffusion into stagnant water areas in the fractures can also cause delay of the tracer. However, only matrix diffusion can cause significant changes in the shape of a breakthrough curve as a function of either elution time or the diffusion coefficient. When the dispersion can be controlled theoretically and experimentally at different flow velocities, it is possible to study the effects of matrix diffusion by making a series of tracer breakthrough measurements at several flow velocities. The lower the flow rate is, the more important the effect of matrix diffusion becomes.

In the case of crystalline rock, in short time scale laboratory experiments the residence times of tracers have been too short for matrix diffusion to occur, and hydrodynamic dispersion has dominated the transport behaviour of non-sorbing radionuclides. In laboratory-scale experiments, the effects of matrix diffusion have been demonstrated by Callahan et al. (2000). They investigated solute transport in fractured saturated volcanic tuff, which is significantly more porous than crystalline rock, allowing matrix diffusion to occur in a reasonable time. Groundwater flow in granitic rock has been found to be unevenly distributed, causing strong channelling effects (Tsang et al., 1988; 1991; Neretnieks, 2002). In block-scale and in-situ experiments, diffusion of solutes from flow channels into stagnant regions within fractures has been suggested while matrix diffusion was rejected as a significant mechanism explaining the spread of breakthrough curves (Raven et al., 1988, Cliffe et al., 1993).

2.2.3. Sorption

Sorption is defined as the uptake of a nuclide on a solid as a function of the nuclide concentration in a solution. Sorption depends on the properties of the rock matrix and the radionuclide. Sorption comprises all of the processes that retard radionuclide migration in solution. These mechanisms are sometimes difficult to distinguish clearly. However, the main sorption processes are physical adsorption and electrostatic adsorption (Serne, 1992). Physical adsorption is due to non-specific, long-range forces of attraction involving the entire electron shells of the radionuclide

in solution and of the adsorbing substrate. This process is rapid, reversible, and largely independent of temperature, nor does it depend on the chemical composition of the sorbent and or the ionic strength and composition of the solution. The presence of complexing ligands and the pH of the solution have appreciable influences on physical adsorption. Electrostatic adsorption is due to short-range coulombic forces of attraction between charged solute species and the adsorbing substrate. This process is rapid, largely reversible, somewhat dependent on temperature and strongly dependent on the composition of the sorbent and on the ionic strength and composition of the solution. Ion exchange is an example of this type of adsorption.

Owing to complicated interactions of radionuclides and the geologic barrier, several approaches to the measurement of radionuclide retardation have been developed and discussed (Erdal et al. 1980; Rundberg, 1992, Byegård, 1995; Johansson et al., 1998; Johansson, 2000, Rasilainen et al., 2001). Static batch technique has been the standard method for studying the interaction of radionuclides and different geological media, e.g. crystalline rock (Allard et al., 1979; Beall et al., 1980; Pinnioja et al., 1984a), tuff (Erdal et al., 1979), sedimentary rock (Dosch, 1979; Dosch and Lynch, 1980; Lynch and Dosch, 1980) and clay (Erickson, 1980). Sorption has also studied on minerals (Allard et al., 1980; Kamineni et al., 1983; Pinnioja et al., 1984b; Ticknor et al. 1989). Most of the research projects have involved a combination of diffusion and permeability based sorption, batch sorption and thin section sorption (Bradbury and Stephen, 1985; Muuronen et al., 1985; Suksi et al., 1989; Baston et al., 1992; Berry and Bond, 1992). Dynamic column methods have also applied to determine sorption parameters (Erdal et al., 1979; Vine et. al., 1981; Carlsen and Batsberg, 1982; Thompson, 1989; García Gutierrez et al., 1992; Triay et al., 1993; Cui and Eriksen, 1998). The retardation of neptunium was studied by Kumata and Vandergraaf (1998) under in-situ geochemical conditions over a range of groundwater flow rates in columns of crushed rock in a facility at the 240-level of the underground rock laboratory URL.

In transport models, radionuclide retardation has usually been taken into account by means of the K_d -concept, in which a retardation factor is used to apply the distribution ratio to radionuclide transport. The possibility of measuring the retardation factor directly in column experiments is a valuable test included in the K_d -concept.

K_d -values have been determined for crushed rock with different specific surface areas; these values may not be valid for modelling radionuclide transport in fractures. It may, however, be difficult to relate the parameters measured by the static method for crushed rock to a heterogeneous intact rock, owing to differences in mineral compositions and in the accessibility of minerals to the aqueous phase. Hydrologically homogeneous, crushed rock columns with a wide particle size distribution are an important intermediate stage between batch sorption and fracture column experiments. In the case of a crushed rock column, the same crushed rock as used in batch experiment can also be used in the column experiment, which makes the measured K_d -value more directly transferable. Of course, the time constants between respective batch and crushed rock column experiments may be different.

2.3. Column method

The column method using a flow-through fracture column is a direct approach for determining the parameters affecting the fracture flow described in radionuclide transport models. It is clear that in the geological scenarios, this technique would simulate the actual conditions to be expected better than static or crushed material packed in column methodologies. The water flow rate, the fracture dimensions and the porosity of fracture surfaces are the most important factors affecting the transport of solutes in fracture column experiments. Solute diffusion into the matrix from the fracture, aperture sizes and water velocity, dispersivity, porosity and distribution coefficient were investigated theoretically by Grisak and Pickens (1980). The column method for determining retardation factors was considered theoretically and experimentally by Relyea (1982). Numerical investigation of the influence of variable fracture aperture on the transport of non-sorbing solutes in a single fracture was done by Grenier et al. (1998). Experimental investigation of the influence of specific surface area and fracture aperture on the transport of sorbing solutes in a fracture was done by Wels et al. (1996).

The advantages and disadvantages of the dynamic column method in comparison to the static batch technique have been discussed by Relyea et al. (1979). Flow-through fracture column experiments allow the observation of nuclide migration rates and the calculation of nuclide K_d -values for porous materials without significant sample

alteration. Reversibility, multiple oxidation-state or species can be observed, and the physical transport of colloids and fine particles can be studied. A realistic solution to solid ratios for both porous and fracture flow can be determined. In fact, both unsaturated and water saturated flow can be studied. The disadvantages of the dynamic column method include the length of time necessary to perform the experiment, especially for strongly sorbing nuclides; inability to create practical flow rates in tight rock materials; experimental artefacts such as channelling and wall effects caused by the use of small column sizes; and greater difficulty in controlling Eh and pH. Because of the amount of equipment and the time required to complete an experiment, fewer experiments can be conducted simultaneously with the dynamic column method than with the static method. In order to produce short-term results, higher flow rates are used; in consequence, kinetic effects are often found to dominate the results. Separation of the solid and liquid phase is also less difficult in a column experiment, but the migration of small particles that may carry adsorbed nuclides has been shown to occur in columns of crushed material (Reimus et al., 1995).

The static and dynamic column methods for radionuclide geological media interaction studies are complementary. The static method is most useful for screening investigations of radionuclide behaviour in a variety of systems and for estimating the time needed to attain equilibrium. Static radionuclide adsorption distributions may thus be compared to retardation factors obtained from dynamic systems under similar conditions, to verify the results. Crushed or uncrushed material can be used in either method, and equilibrium solution compositions obtained from static tests can be used in dynamic experiments. The most pressing need is to determine the relationship, or to gain an understanding and to devise a measurement method, enabling us to relate the K_d -values obtained for crushed material to the variable and tortuous fissures and cracks expected to constitute the environment through which water would flow.

From the beginning of nuclear waste management research column methods were adapted in order to measure parameters essential for predicting radionuclide migration. A number of radionuclide migration experiments have been performed in columns of crushed material and in columns of intact cores or fractured cores. Many of these experiments have focused on the retardation of sorbing radionuclides. The elution times of non-sorbing tracers have been used to indicate the flow rate of the

groundwater in the fracture. Fracture flow and radionuclide transport have been studied in intact permeable cores of, e.g. tuff and dolomite, which have a sufficiently porous structure to permit direct percolation experiments (Fried et al., 1979; Lynch, 1979, Dosch and Lynch, 1980; Grisak et al., 1980; Perkins and Lucero, 2001). Owing to the great pressures needed to force water through the grain boundaries (Drew and Vandergraaf, 1989; García Gutierrez et al. 1991; 1992; Smith et al., 1991;), the flow-through fracture column method has been utilised for intact crystalline rocks in order to study radionuclide transport (Fried et al., 1979; Neretnieks et al., 1982; Rundberg et al., 1982; Eriksen, 1983; 1984; Moreno et al., 1985; Grondin and Drew, 1988; Reimus et al., 1995, Yllera de Llano et al., 1996; Callahan et al., 2000; Xu, 2002).

3. Interpretation of transport in a fracture

The processes considered in solute transport in an ideal fracture are advective flow along the fracture, Fickian dispersion, diffusion from the fracture into the rock matrix, and sorption within the rock matrix and onto the fracture surfaces. Solute transport in an ideal fracture has been described by, e.g. Neretnieks (1980) and Moreno et al. (1985; 1988). Following Fick's second law, diffusion into the rock in one dimension is described by Eq. (1). Assuming fast, linear and reversible adsorption, the transport of radionuclides in an ideal fracture with constant aperture is described by Eq. (2).

$$\frac{\partial C_p}{\partial t} = \frac{D_p}{R_p} \frac{\partial^2 C_p}{\partial z^2} \quad (1)$$

$$R_f \frac{\partial C_f}{\partial t} = -v_x \frac{\partial C_f}{\partial x} + \alpha_L v_x \frac{\partial^2 C_f}{\partial x^2} - \frac{D_e}{b_f} \frac{\partial C_p}{\partial z} \Big|_{z=b} \quad (2)$$

where C_f is the concentration in the fracture water ($\text{mol}\cdot\text{m}^{-3}$), C_p is the concentration in the pore water ($\text{mol}\cdot\text{m}^{-3}$), α_L is the dispersion length (m), v_x is the velocity of water in the fracture ($\text{m}\cdot\text{s}^{-1}$), b_f is the fracture half-aperture (m), D_e is the effective diffusivity ($\text{m}^2\cdot\text{s}^{-1}$), D_p is the pore diffusivity ($\text{m}^2\cdot\text{s}^{-1}$), R_f is the retardation factor in a fracture and R_p is the retardation factor in the rock matrix. The terms on the right-hand side of Eq. (2) represent advection, dispersion and matrix diffusion, respectively. The dispersion coefficient can also be expressed as

$$D_L = \alpha_l v_l + D_w \quad (3)$$

where α_l is the dispersivity (m), v_l is the mean groundwater velocity ($\text{m}\cdot\text{s}^{-1}$), and D_w is the molecular diffusion coefficient ($\text{m}^2\cdot\text{s}^{-1}$) (Grisak and Pickens, 1980). Advective transport of radionuclides takes place in the mean direction of flow and with a mean velocity in the fracture, whereas the dispersive term incorporates all effects caused by 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.

In dynamic models, sorption causes retardation of the radionuclides relative to the transport of an ideal, non-interacting tracer. The retardation factor expresses the ratio of water velocity to the radionuclide velocity. The inverse of the retardation factor represents the fraction of the total radionuclide inventory that is dissolved in the water and thus considered mobile. The retardation factors in a fracture (R_f) and in the rock matrix (R_p) are given by:

$$R_f = 1 + \frac{2}{2b} K_a \quad (4)$$

$$R_p = 1 + \frac{\rho_s(1-\varepsilon_p)K_d}{\varepsilon_p} \quad (5)$$

where $2b$ is the fracture aperture (m), K_a is the area-based distribution coefficient ($\text{m}^3 \cdot \text{m}^{-2}$), K_d is the mass-based distribution coefficient ($\text{m}^3 \cdot \text{kg}^{-1}$), ε_p is the porosity of the rock matrix, and ρ_s is the bulk rock density ($\text{g} \cdot \text{cm}^{-3}$). K_d can be derived from K_a through multiplication by the specific surface area of the rock:

$$K_d = K_a a_f \quad (6)$$

where a_f ($\text{m}^2 \cdot \text{kg}^{-1}$) is the specific surface area of the rock.

The two diffusivities in the rock matrix (D_e and D_p) are interlinked and can both be derived from molecular diffusivity (Relyea, 1980; Olin, 1994; Rasilainen, 1997)

$$D_p = \frac{\delta_D}{\tau^2} D_w \quad (7)$$

$$D_e = \varepsilon_p D_p \quad (8)$$

where δ_D is the constrictivity of the pore network, τ^2 is the tortuosity of the pore network, D_w is the molecular diffusivity in free water ($\text{m}^2 \cdot \text{s}^{-1}$), and ε_p is the porosity of the rock matrix. The factor δ_D/τ^2 is called the geometric factor, and it takes into account the fact that molecular diffusion does not take place in free water, but in a complicated network of irregular pores.

In performance assessments, all sorption processes are grouped together and characterised by the mass-based distribution coefficient K_d :

$$K_d = \frac{C_{rock}}{C_{solution}}, \quad (9)$$

where C_{rock} is the concentration of nuclides per solid mass ($\text{mol}\cdot\text{kg}^{-1}$) and $C_{solution}$ the concentration of nuclides in the pore water ($\text{mol}\cdot\text{m}^{-3}$). The parameter is used to quantify sorption, which is kinetically fast, reversible and independent of the concentration of the sorbing solute.

4. EXPERIMENTAL ARRANGEMENT

In this work, radionuclide migration in crystalline rock was studied by means of different laboratory-scale methods. The experiments and the methods applied are aggregated into a scheme in Figure 3.

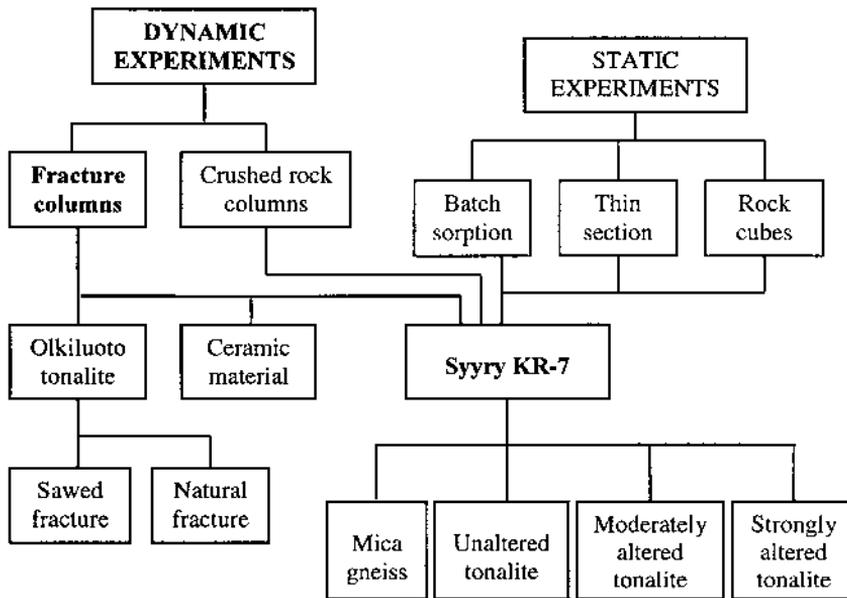


Figure 3. Scheme of the methods utilised in this study.

4.1. Rock samples

In order to test the experimental arrangement, early rock fracture columns were made out of tonalite drill core sections obtained from the Olkiluoto nuclear power plant site on the west coast of Finland. Tonalite is a homogeneous, medium-grained and slightly foliated synorogenic rock. The main minerals were plagioclase (47%), biotite (25%), quartz (17%) and hornblende (7%). The intact rock matrix is dense, but the alteration products on the fracture surfaces are highly porous. The porosity of the intact rock was 0.1 – 0.3% (Hellmuth et al., 1992, Hölttä et al., 1993).

Radionuclide migration in crystalline rock was studied systematically using rock samples obtained from hole SY-KR7 drilled in the Syry area in Sievi in western Finland. The rock samples – mica gneiss, unaltered, moderately altered and strongly altered tonalite – represented different rock features and porosities, thereby making it possible to determine experimental boundary limit values for parameters describing both the transport and retardation of radionuclides and the rock matrix properties. Syry was one of the five sites selected by Teollisuuden Voima Oy for preliminary investigations concerning the final disposal of spent nuclear fuel in Finland.

Drill hole SY-KR7 (Lindberg and Paananen, 1992) intersects a medium-grained slightly schistose tonalite zone containing fine-grained and homogeneous mica gneiss inclusions. The mica gneiss core section originated from the mica gneiss zone at the drilling depth of 209 m. The grain size in mica gneiss was very small (0.1–0.3 mm), and there was clear foliation. The main minerals were quartz, plagioclase and biotite and the accessories found were chlorite, calcite, muscovite/sericite, sphene, apatite, epidote and opaques. The unaltered tonalite core section was from a drilling depth of 70.2 m. The main minerals in coarse-grained tonalite were plagioclase, quartz, biotite and hornblende. The accessory minerals were chlorite, apatite, sphene, muscovite/sericite, calcite, epidote, opaques and analcime. The moderately altered tonalite drill core section representing medium- grained, porous rock was from the depth of 180.6 m. The strongly altered tonalite drill core section representing very porous rock was from the depth of 190.5 m. In altered tonalites, plagioclase has been altered to sericite and partly to kaolinite, hornblende had been altered to epidote and biotite to chlorite. Particularly in moderately altered tonalite, the mineral grains were cemented by analcime. A detailed mineral characterisation of SY-KR7 rock samples is presented in Paper III.

4.2. Characterisation of the rock structure

The total porosity and the surface areas of mineral grains available for sorption in intact rock and migration of species were determined by means of the $^{14}\text{CPMMA}$ method (Hellmuth et al., 1992, 1993; Fernandez-Merayo et al., 1996; Siitari-Kauppi, 2002). In this method, a dried rock sample is impregnated with ^{14}C -labelled methyl-

methacrylate and then gamma irradiation polymerised and sliced for autoradiography. The autoradiographs were then digitally processed. The total bulk porosities of the rock matrices were also determined by means of water impregnation. The pore aperture distribution was evaluated on the basis of Hg-porosimetry determinations (Hellmuth et al., 1995). The pore apertures and geometry of the mineral phases were analysed by the means of scanning electron microscopy (SEM/EDX) using carbon coated polished rock sections. The minerals were quantified by means of energy dispersive X-ray microanalysis. The surface areas for the solid rock pieces and crushed rock samples were determined by means of the BET method, using krypton for solid and nitrogen for crushed rock samples (Hellmuth et al., 1995).

The characterisation of the mica gneiss, unaltered tonalite, moderately altered tonalite and strongly altered tonalite rock samples is given in Table I. The mica gneiss was fine grained and intra granular porosity dominated as a result of the homogeneous distribution of biotite grains in the matrix. Unaltered tonalite was from fine to coarse grained, and the biotite content was lower than in mica gneiss. On the basis of the autoradiographic study, intergranular porosity was found to be dominant, resulting in higher pore apertures than in mica gneiss. The spatial porosity was found to be heterogeneous in mm-scale. Strongly altered tonalite contained visible mm-scale round pores in the matrix. Hg-porosimetry determination showed a wide variation of pore apertures, implying a high surface area inside the matrix. The pore structure in moderately altered tonalite was similar to that in strongly altered tonalite. A detailed characterisation of the structure of the SY-KR7 rock samples is presented in Paper III and in Siitari-Kauppi et al. (1997).

The crushed rock samples were sieved into fractions ranging in size from 0.01 mm to 3.15 mm. The specific surface areas for each fraction given in Table I were determined by the BET nitrogen adsorption method. A qualitative mineral composition for the different fractions was determined by means of X-ray diffraction, which gives the best possible estimation of how minerals are divided by crushing and sieving. The distribution of minerals within different fractions was highly similar for all except the softest minerals (chlorite and micas) – which were slightly enriched in the fine end – and the brittle, hard minerals (quartz, feldspars) in the roughest fraction.

Table I. Characterisation of the Syryy KR-7 rock samples.

	Mica gneiss	Unaltered tonalite	Moderately altered tonalite	Strongly altered tonalite
Specific surface area (m²·g⁻¹)				
Grain size (mm)				
0 – 0.1	0.40	0.40	3.35	1.95
0.1 – 0.3	0.30	0.22	1.73	2.17
0.3 – 0.5	0.17	0.11	1.26	1.37
0.5 – 0.8	0.17	0.19	0.89	1.23
0.8 – 1.0	0.13	0.10	0.90	0.66
1.0 – 2.0	0.12	0.09	0.55	1.35
2.0 – 3.15	0.08	0.11	0.61	1.24
Intact rock	0.07	0.05	0.4	0.5
Porosity ε (%)				
¹⁴ CPMMA	0.2 - 0.8	0.16	2.0 - 7.5	2.0 - 7.5
Water	0.1	0.12	7 - 9	7 - 9
Hg	0.62	0.16 - 0.57	5.85	6
Density ρ (g·cm⁻³)				
	2.79	2.80	2.4	2.4

4.3. Static experiments

Static diffusion and sorption experiments were performed to support the column experiments and to provide independently obtained data.

4.3.1. Batch experiments

The rock samples for batch experiments were equilibrated with the synthetic granitic groundwater for 20-30 days by changing the water six times. The synthetic granitic groundwater (Allard and Beall, 1979) used in all of the experiments was of low salinity and was typical of granitic groundwater in Finland. The sodium, potassium, magnesium and calcium concentrations were followed by atomic adsorption spectroscopy determinations. Spiked solutions containing ²²Na, ⁴⁵Ca or ⁸⁵Sr came into contact with crushed rock in polypropylene centrifuge tubes, which were shaken gently. The initial strontium concentration was 10⁻⁵ M. The initial concentrations of calcium and sodium tracers were negligible when compared to the elemental

concentrations in the groundwater. Experiments were carried out for mass/liquid ratios of 1:10. After a 7-day contact period, the groundwater and crushed rock were separated by centrifugation (G 12100) and the samples were washed five times. The mass distribution ratio, K_d , was determined in batch experiments as the ratio of the radionuclide concentration in the solid phase to the aqueous concentration.

4.3.2. Thin section experiments

The sorption of tracers onto different minerals was estimated from autoradiographs taken from the thin sections. The thin sections were equilibrated with the synthetic granitic groundwater for seven days by changing the water three times. After a 7-day contact period, washed thin sections were exposed to a β film (Hyper film β max) and an X-ray film (Kodak X-OMAT MA). ^{22}Na and ^{45}Ca had suitable beta energies for rough autoradiographic measurement, i.e. the range of beta particles were below the size of mineral grains. The surface-based distribution coefficient, K_a , was calculated using a geometric sorption area determined by a digital image processing of autoradiographs. The K_d -values were calculated from the K_a -values, using a thin section thickness of 30 μm and densities of 2.4 $\text{g}\cdot\text{cm}^{-3}$ for altered rock type and 2.8 $\text{g}\cdot\text{cm}^{-3}$ for unaltered rock type.

4.3.3. Rock cube experiments

In-diffusion of calcium into mica gneiss and into unaltered, moderately and strongly altered tonalite was determined using 2 x 2 x 2 cm rock cubes. The rock samples for in-diffusion experiments were evacuated and equilibrated with the synthetic granitic groundwater for two weeks. Equilibrated rock cubes were immersed in spiked solution, containing ^{45}Ca . The initial concentrations of calcium tracer were negligible when compared to the elemental tracer concentrations in the groundwater.

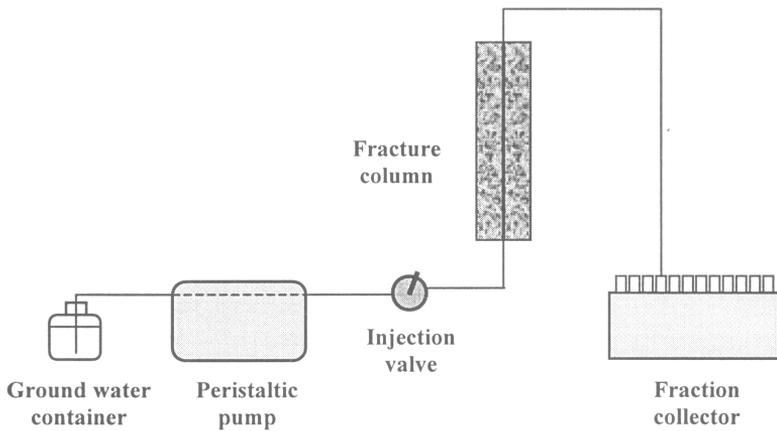


Figure 4. Schematic diagram of the fracture column apparatus.

4.4. Dynamic experiments

4.4.1. Experimental set-up

The arrangement for the fracture column experiments is schematically illustrated in Figure 4. Filtered groundwater was continuously pumped through the fracture. Tracers in a known volume of water were injected as a short pulse into the water flow. The effluent was continuously fed to the fraction collector for determining the breakthrough concentration of the tracer. The fractions were collected dropwise into polyethylene vials, and the radioactivity in the collected samples was measured using liquid scintillation counting or γ -counting.

4.4.2. Columns

The fracture column dimensions are given in Table II. The arrangement for the column experiments was constructed and tested using columns made of tonalite drill core sections obtained from the Olkiluoto. One axial fracture was induced mechanically in each core by sawing or opening along the natural fracture. The cylindrical outer surfaces of the drill cores were sealed with urethane lacquer to

prevent any water leakage from the rock except through the outlet end of the fracture. The cylinders were mounted between two Plexi-glass end pieces with two bores at both ends leading to the groove at the face in contact with the fracture.

In order to demonstrate the effects of matrix diffusion in a breakthrough of non-sorbing solutes, a high porosity ceramic column with a narrow fracture width was introduced. The porosity of the material was determined by the water impregnation method to be $30 \pm 1\%$ and was two orders of magnitude higher than the porosity of the rocks. The column with a narrow fracture width was made of two rectangular pieces in the same way as the rock columns; however, the inlet and outlet tubes were connected directly to the fracture in order to minimise the dead volume.

Table II. Fracture column dimensions, tracers used in the experiments and range of the volumetric flow rate.

	Length (m)	Width (m)	Aperture (m)	Tracers	Flow rate ($\mu\text{l}\cdot\text{min}^{-1}$)
Olkiluoto tonalite					
Sawed fracture	0.068	0.035	$1\cdot 10^{-4}$	^3H , ^{36}Cl , ^{99}Tc ^{22}Na	1 – 60 0.8 – 11.5
Natural fracture	0.083	0.035	$1\cdot 10^{-4}$	^3H , ^{36}Cl , ^{99}Tc ^{22}Na	1 – 60 0.8 – 11.5
Ceramic column	0.145	$4 \cdot 10^{-3}$	$1\cdot 10^{-5}$	^3H , ^{36}Cl , ^{99}Tc	1 – 12
Syyry KR-7					
Mica gneiss	0.190	0.01	$4\cdot 10^{-5}$	He ^3H , ^{36}Cl ^{22}Na , ^{45}Ca , ^{85}Sr	60 – 250 0.002 – 10 5 – 10
Unaltered tonalite	0.213	0.008	$5\cdot 10^{-5}$	^3H , ^{36}Cl ^{22}Na , ^{45}Ca , ^{85}Sr	0.4 – 10 5 – 10
Moderately altered tonalite	0.085	0.015	$1\cdot 10^{-4}$	^3H , ^{36}Cl ^{22}Na , ^{45}Ca , ^{85}Sr	1 – 10 5 – 10
Strongly altered tonalite	0.225	0.006	$1.7\cdot 10^{-4}$	He ^3H , ^{36}Cl ^{22}Na , ^{45}Ca , ^{85}Sr	80 – 360 0.7 – 10 5 – 10

Rock fracture columns were made by first sawing a narrow slice along the axis from the middle part of a cylindrical drill core section; the slice was then cut into halves, the cutting surfaces were polished, and the polished surfaces were set against each other. Inlet and outlet tubes were connected directly to the fracture, and the whole column was sealed from outside in order to prevent leaks.

Crushed rock columns were made by loading plastic columns with crushed rock that had been in contact with groundwater. A loaded column was inserted into the apparatus used in the fracture flow experiments, to replace the fracture column. The parameters of the crushed rock columns are given in Table III.

Table III. Crushed rock column parameters.

Grain size (mm)	Column length (cm)	Column diameter (cm)	Interstitial volume (cm ³)	Interstitial fraction ϵ_i	Particle density ρ_p (g·cm ⁻³)
Mica gneiss					
0 – 0.071	4.0	0.5	0.79	0.46	1.27
0.3 – 0.85	3.8	0.5	0.75	0.48	1.34
0.85 – 1.25	4.0	0.5	0.79	0.46	1.27
Unaltered tonalite					
0 – 0.071	4.4	0.4	0.55	0.65	1.81
0.3 – 0.85	3.8	0.4	0.48	0.75	2.09
0.85 – 1.25	3.8	0.4	0.48	0.75	2.09
0.3 – 0.5	3.2	1	1.16	0.46	1.51
0.5 – 0.8	8.5	1	3.50	0.52	1.33
0.8 – 1.0	2.5	1	1.02	0.52	1.34
1.0 – 2.0	4.7	1	1.67	0.45	1.53
2.0 – 3.15	3.3	1	1.30	0.50	1.40
Moderately altered tonalite					
0 – 0.071	4.0	0.5	0.79	0.53	1.27
0.3 – 0.85	3.7	0.5	0.73	0.57	1.38
0.85 – 1.25	4.2	0.5	0.83	0.55	1.21
0.3 – 0.5	3.9	1	1.46	0.48	1.26
0.5 – 0.8	4.1	1	1.54	0.48	1.25
0.8 – 1.0	3.1	1	1.09	0.45	1.33
1.0 – 2.0	3.3	1	1.03	0.40	1.45
2.0 – 3.15	5.5	1	1.95	0.45	1.32
Strongly altered tonalite					
0 – 0.071	4.4	0.4	0.55	0.75	1.77
0.3 – 0.85	3.8	0.4	0.48	0.87	2.09
0.85 – 1.25	3.9	0.4	0.49	0.85	2.04

4.4.3. Flow experiments

Before the tracer experiments, the fracture surfaces were saturated for at least two months with degassed synthetic granitic groundwater (Allard and Beall, 1979). The experiments were carried out under oxygen conditions of ambient air. The volumetric flow rate was determined before and after each experiment by collecting water over known time periods and weighing the amount collected. Blank runs were made to determine transit times through the dead volume of the apparatus. The mean flow velocity u ($\text{m}\cdot\text{s}^{-1}$) in the column was determined using the equation:

$$u = \frac{qL}{V} = \frac{q}{2bW} \quad (10)$$

where q is the volumetric flow rate ($\mu\text{l}\cdot\text{min}^{-1}$), V the volume (m^3), L the length (m), W the width (m) and b half of the aperture of the column (m). The fracture aperture was estimated from the determined volume of the water filling the fracture and from the width and length of the fracture.

In the slow flow experiments, the water flow was controlled by hydrostatic pressure instead of by pumping. Fractions were collected by feeding the effluent into water in a sealed vial in order to avoid evaporation at the tip of the tube during the collection. The flow rate was monitored by weighing every fraction. The lowest flow rate obtained was $0.02 \mu\text{l}\cdot\text{min}^{-1}$. The transport of non-sorbing radionuclides was studied in order both to gain an understanding of the physical phenomena affecting the transport of solutes in fracture flow and to distinguish matrix diffusion from other phenomena, e.g. hydrodynamic dispersion in fracture flow. The radionuclides used as non-sorbing tracers were tritiated water (HTO) and chloride (^{36}Cl), which were injected simultaneously in all experiments. Radionuclide retardation was determined using sodium (^{22}Na), calcium (^{45}Ca) and (^{85}Sr) as sorbing tracers. A non-sorbing tracer was injected simultaneously with a sorbing tracer. The tracers and the range of the volumetric flow rate used in the fracture column experiments are presented in Table II. In crushed rock column experiments, uranine dye tracer was used to demonstrate the possible flow paths in a column. The isotopes were provided by Amersham International, U.K. A series of elution curves for the tracers was determined using different water flow rates.

5. RESULTS AND DISCUSSION

5.1. Fracture column experiments

5.1.1. Olkiluoto tonalite

The experimental arrangement for the rock fracture column method was tested by using sawed and natural fracture columns made of Olkiluoto tonalite drill core sections (Paper I, Hölttä et al., 1991; 1993). In the sawed fracture, the transport behaviour of non-sorbing tracers was explained using the calculation for dispersion only. Symmetrical elution curves and agreement between the experimental and calculated results showed that hydrodynamic dispersion dominated the transport of non-sorbing tracers. To estimate the diffusion distance (x_D) from the fracture into the matrix, the following equation was used:

$$x_D = \sqrt{2D_e\tau} \quad (11)$$

where D_e is the effective diffusion coefficient and τ is the mean solute residence time in the fracture. Calculations for the case of the effective diffusion coefficient determined for the Olkiluoto tonalite (Hölttä et al., 1993) illustrated that the residence times were too short for matrix diffusion to occur. No basic difference was observed between the elution times of tritiated water and the anionic tracers in the sawed fracture column. The transport of sodium was delayed more than non-sorbing tracers; this resulted from weak sorption onto fracture surfaces. In the sawed fracture, the transport of sodium, too, was explained by dispersion only. Experimental and calculated elution curves of sodium for sawed fracture are shown in Figure 5.

In the natural fracture column, the relative residence times of the tracers were longer and the elution peaks more spread than in the sawed fracture column. Experimental and calculated elution curves of sodium for natural fracture are shown in Figure 6. For sodium, higher retardation with lower flow rates and effects analogous to matrix diffusion were observed. Tracer transport, including the diffusion of solutes from the fracture into the matrix, was interpreted. However, the required value of the effective diffusion coefficient, D_e , was unreasonably high for the crystalline rock matrix,

suggesting solute diffusion into the fracture filling material or stagnant pore water areas near the uneven fracture surface. The change in the flow rate had no significant effect on the shapes of the elution curves, and it was impossible to extract the effects of matrix diffusion from other phenomena that cause dispersion. Tritiated water was dispersed and retarded more than chloride. This delay could be explained by weak interaction with altered fracture surfaces. Another possible explanation is that anion exclusion of chloride was responsible for the faster chloride transport.

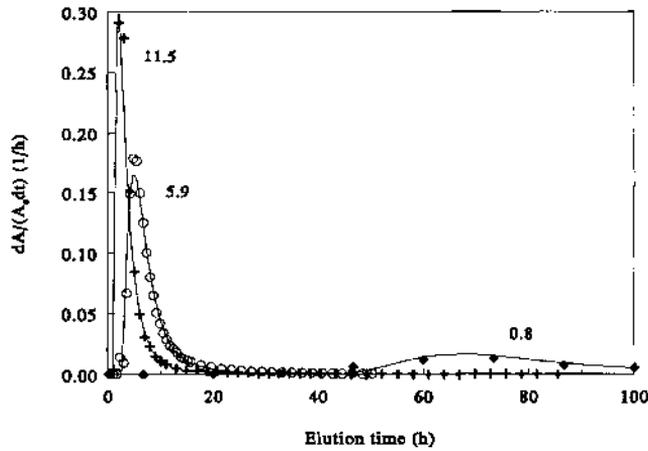


Figure 5. Experimental and calculated elution curves of sodium for the Olkiluoto tonalite sawed fracture column.

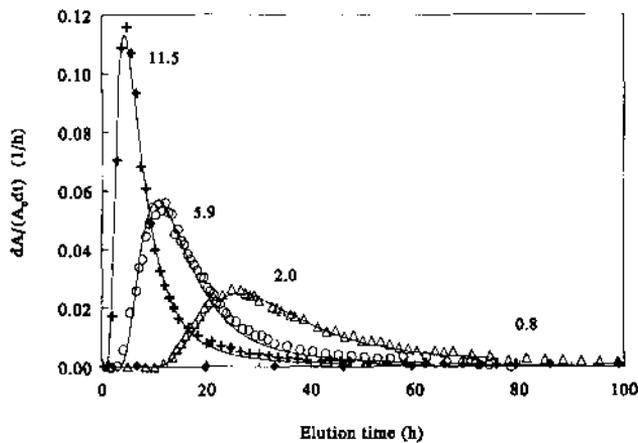


Figure 6. Experimental and calculated elution curves of sodium for the Olkiluoto tonalite natural fracture column.

5.1.2. Ceramic column

The effects of matrix diffusion in the elution curves of the non-sorbing tracers were demonstrated by the use of a high-porosity ceramic column. A porosity of two orders of magnitude higher than the porosity of crystalline rock allowed matrix diffusion to occur with the use of routine volumetric flow rates. The transport of tritiated water and chlorine through the ceramic fracture column was interpreted using a widely known analytic solution to the advection-matrix diffusion problem, with semi-infinite boundary conditions in the matrix and a sudden release of the tracer at the inlet based on the solution by Carslaw and Jaeger (1959):

$$\frac{dA}{A_0 dt} = \frac{\sqrt{D_e \epsilon_p} x}{2bu\sqrt{\pi}(t-t_w)^{3/2}} e^{-\left[\frac{D_e \epsilon_p x^2}{(2bu)^2(t-t_w)}\right]} \quad (12)$$

where A_0 is the injected total radioactivity, D_e the effective diffusion coefficient, ϵ_p the diffusion porosity of the matrix, x the distance in the flow direction, $2b$ the fracture aperture, u the flow velocity and t_w the flow time ($= x/u$). The breakthrough of the tracer is given as a fraction with radioactivity over injected radioactivity as a function of the elution time. Standard deviation of radioassay (± 1) was smaller than the marker height in the elution curves.

Experimental and calculated elution curves for tritiated water and chloride from runs with different flow rates are shown in Paper I, Figure 5. The consistency obtained between the experimental data and the calculated results showed that the transport of the non-sorbing tracers in the porous ceramic fracture column was affected by matrix diffusion. Longer rise time of the elution curve, lower peak height and increased tailing with lower flow rates are the main effects of matrix diffusion on the elution curves. With faster flow rates, the agreement between the calculated and experimental elution curves was good. As the flow rates decreased, there was increasing inconsistency between the curves. In the case with the lowest flow rate, the experimental curve obtained was considerably different from the calculated curve. This disagreement was caused by limitation in matrix diffusion, which was a consequence of the shallow matrix depth of the column: 9 mm. With reflective boundary conditions, the tracer transport approach a steady state where, statistically,

all the molecules experience the same velocities with equal column transport time within a Gaussian distribution. The experimental data for the lowest flow rate were interpreted using a numerical code, FTRANS (INTERA, 1983). Excellent consistency between the experimental results and the model were found, and the existence of reflective boundaries in the limited matrix diffusion was confirmed (Paper I, Figure 6).

5.1.3. Syyry KR-7

Radionuclide transport and retardation in a single crystalline rock fracture were studied systematically using mica gneiss and unaltered, moderately altered and strongly altered tonalite drill core samples from hole SY-KR7.

Helium

The matrix diffusion properties of the mica gneiss and strongly altered tonalite columns were estimated by the gas flow method before the water flow experiments (Väättäinen et al., 1993; Hartikainen et al., 1995) using nitrogen as the carrier gas and helium as the tracer gas. The effects of matrix diffusion that had been demonstrated in ceramic column experiments were seen in the gas flow experiments. For strongly altered tonalite, the experimental and calculated breakthrough curves for helium with three different flow rates are shown in Paper II, Figure 1. Dotted lines show how the breakthrough curves would look if dispersion alone were effective. The solid lines are curves calculated using the numerical compartment model with a matrix diffusion included. The best fit of the measured curve was obtained for $D_e = 4.9 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$; this corresponds to a value of $1.4 \cdot 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ for D_e in the water flow experiments estimated on the basis of the gas to water diffusion coefficient ratio of $3.5 \cdot 10^4$. For mica gneiss, an upper limit of $2 \cdot 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ was estimated for the effective diffusion coefficient, D_e in the corresponding water flow experiments.

Non-sorbing tracers

Instead of analytical models, a numerical compartment model developed for near-field modelling, REPCOM (Nordman and Vieno, 1994), was modified to calculate the

advection and hydrodynamic dispersion in the fracture columns. Owing to the limited dimensions of the columns, the boundary conditions have an important effect on the hydrodynamic dispersion of the transported tracer towards the end of the column. With decreasing flow rates, the longitudinal diffusion increases in importance, and it is no longer possible to model the tracer plume adequately using conventional approximate analytical models appropriate for longer distances and higher velocities. Based on the retention time distribution without matrix diffusion in the column, the effect of matrix diffusion was calculated for each short time interval by means of analytic expression of the matrix diffusion (Eq. 12). These results were then summed up to give the final breakthrough curve. This procedure allows the modelling of any kind of hydrodynamic dispersion, including non-Fickian distribution types (Hartikainen et al., 1995).

In order to demonstrate the effects of matrix diffusion in the elution curves for crystalline rock, a series of very low flow rate experiments was performed in the mica gneiss column. According to estimation from gas diffusion experiments, the lowest water flow rate of $0.02 \mu\text{l}\cdot\text{min}^{-1}$ would enable demonstration of the dominating matrix diffusion behaviour in water flow experiments. A series of experimental and calculated elution curves of tritiated water and chloride for the mica gneiss column is shown in Figure 7. The transport of the tracers was calculated using a dispersion model with and without the inclusion of matrix diffusion. Each experiment was modelled using the same parameters throughout the flow rate range.

In the experiments with the two fastest flow rates, 1.2 and $0.7 \mu\text{l}\cdot\text{min}^{-1}$, hydrodynamic dispersion dominated the transport of the tracers. Adding matrix diffusion gave a somewhat better fit with the experimental values but the difference was not significant. In an experiment with a flow rate of $0.1 \mu\text{l}\cdot\text{min}^{-1}$ adjusted by hydrostatic pressure, the fraction collection frequency at the leading edge of the elution peak was sparse because of manual fraction collection. However, the experimental values at the trailing edge agree with the calculated curve that includes the effect of matrix diffusion. Scaling of the time axis and the mass flux values with the flow rates clearly reveals the change in the shape of the elution curve for the lowest flow rate of $0.02 \mu\text{l}\cdot\text{min}^{-1}$, indicating matrix diffusion behaviour.

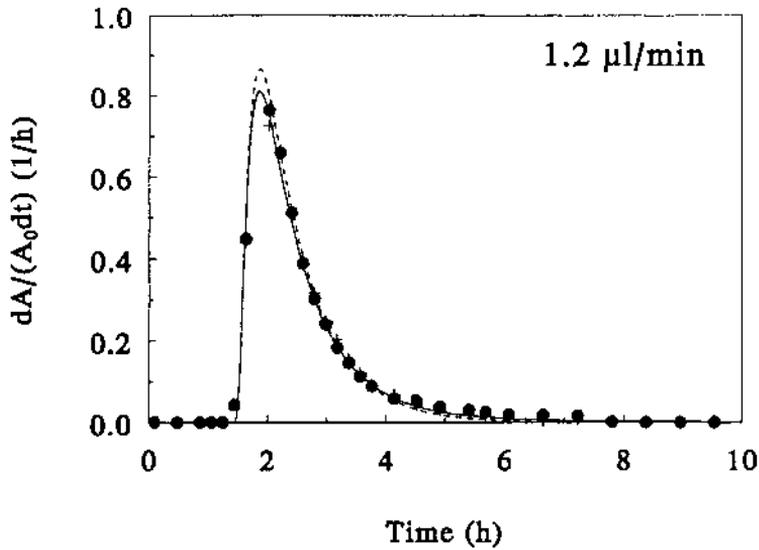


Figure 7a. Experimental and calculated elution curves of tritiated water and chloride for the mica gneiss fracture column. Flow rate of $1.2 \mu\text{l}\cdot\text{min}^{-1}$ controlled by pump.

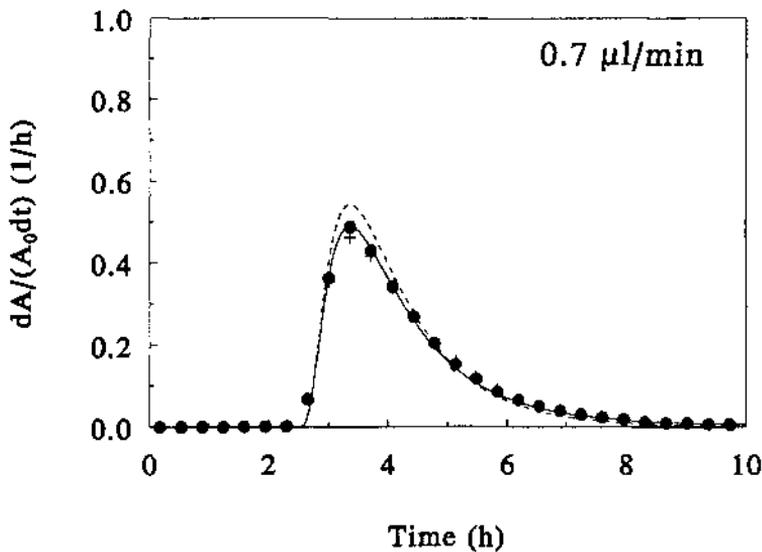


Figure 7b. Experimental and calculated elution curves of tritiated water and chloride for the mica gneiss fracture column. Flow rate of $0.7 \mu\text{l}\cdot\text{min}^{-1}$ controlled by pump.

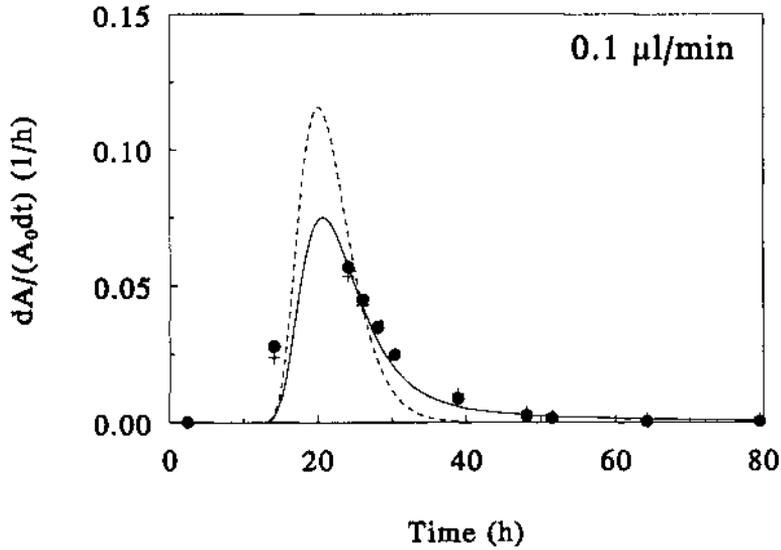


Figure 7c. Experimental and calculated elution curves of tritiated water and chloride for the mica gneiss fracture column. Flow rate of $0.1 \mu\text{l}\cdot\text{min}^{-1}$ controlled by hydrostatic pressure.

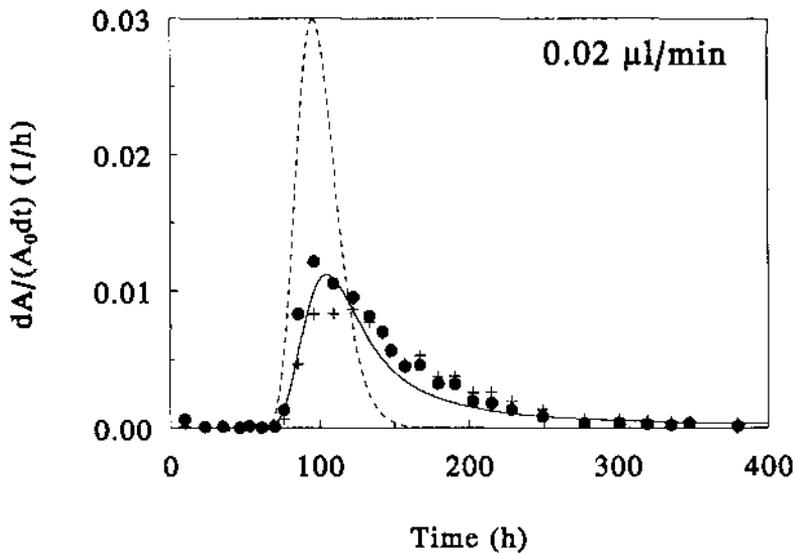


Figure 7d. Experimental and calculated elution curves of tritiated water and chloride for the mica gneiss fracture column. Flow rate of $0.02 \mu\text{l}\cdot\text{min}^{-1}$ controlled by hydrostatic pressure.

An effective diffusion coefficient D_e -value of $2 \cdot 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ estimated from gas flow experiments and a porosity of 0.5%, gave the best overall fit between the experimental results and the model calculations. According to the model calculations, hydrodynamic dispersion alone does not explain the experimental results. The best agreement with the experimental and calculated curves was obtained for the model, which includes the effect of matrix diffusion. The narrow and rather long flow channel as well as the sawed and polished fracture surfaces indicated that diffusion into the stagnant water areas of the fracture should not be operative in these experiments.

With flow rates of 0.4 and $0.1 \mu\text{l} \cdot \text{min}^{-1}$, hydrodynamic dispersion dominated the transport of tritiated water and chloride also in the unaltered tonalite column (Figure 8). Despite the strong role of dispersion, matrix diffusion was seen in the elution curve at the lowest flow rate of $0.4 \mu\text{l} \cdot \text{min}^{-1}$. At the flow rate of $1.5 \mu\text{l} \cdot \text{min}^{-1}$, the experimental and calculated curves showed inconsistency owing to dominating advection.

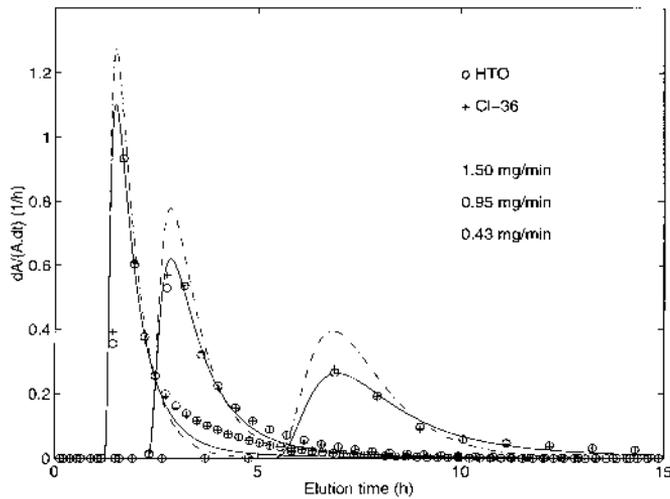


Figure 8. Experimental and calculated elution curves of tritiated water and chloride for the unaltered tonalite fracture column.

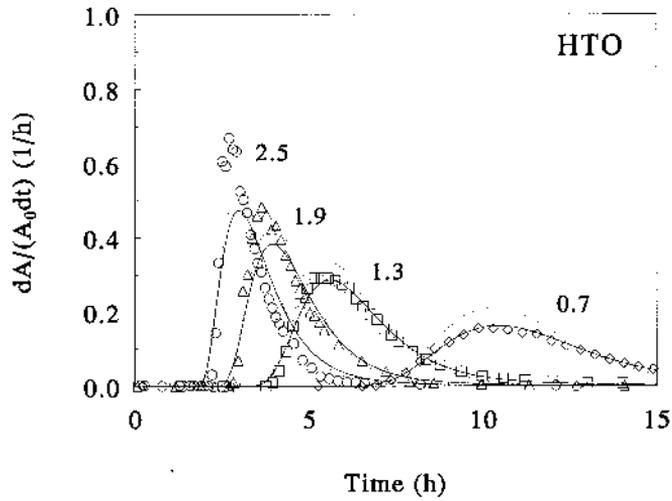


Figure 9. Experimental and calculated elution curves of tritiated water for the strongly altered tonalite fracture column.

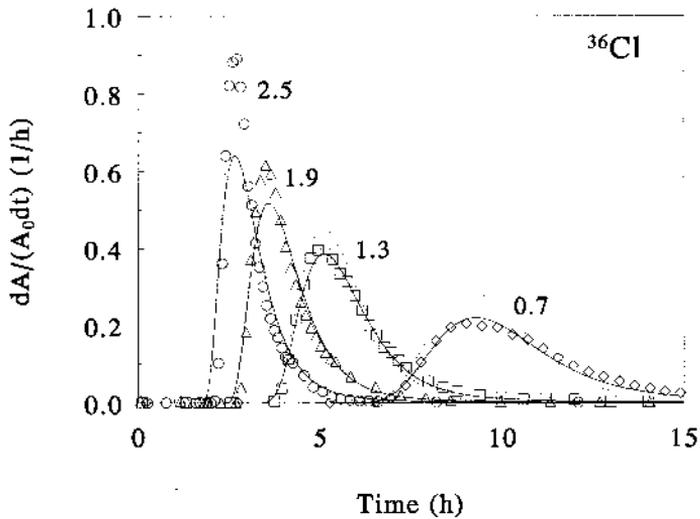


Figure 10. Experimental and calculated elution curves of chloride for the strongly altered tonalite fracture column.

Experimental and calculated elution curves of tritiated water for strongly altered tonalite are shown in Figure 9, and elution curves for chloride are shown in Figure 10. Model calculations for dispersion with and without the inclusion of matrix diffusion indicate that hydrodynamic dispersion dominated the transport of tracers. At lower flow rates, the experimental curves were lower and spread out more, indicating more diffusion into the matrix or stagnant pore water areas. With a D_e value of $2.8 \cdot 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ and a ϵ_p value of 5%, the chloride series showed better overall agreement. Compared to model curves for chloride, the addition of a retardation factor of 1.35 gave better agreement for tritium. At the fastest flow rates, the experimental and calculated curves showed inconsistency owing to dominating advection.

The residence times in the fracture were too short for transverse diffusion to smooth out velocity differences. At the lowest flow rates, the dispersion domination was obvious, though the effects of matrix diffusion were seen in the elution curves. On the basis of gas diffusion calculations in strongly altered tonalite column, it was estimated that some matrix diffusion behaviour could be seen in water flow experiments, at a flow rate as high as $0.7 \mu\text{l} \cdot \text{min}^{-1}$. The dominating matrix diffusion effects would, however, require flow rates of a lower order of magnitude.

For rock fracture, demonstration of the dominating effects of matrix diffusion succeeded in a mica gneiss column experiment series where the experimental arrangements enabled very low water flow rates. The numeric compartment model was able to interpret hydrodynamic dispersion in the column at the fastest flow rates. Adequate knowledge of the dispersion behaviour in the column gives good reason to assume that the effects seen in the very slow flow rate elution curves are the result of matrix diffusion. In intact mica gneiss, homogeneously distributed intragranular porosity also enabled matrix diffusion to occur. Owing to mainly intergranular, heterogeneous spatial porosity in unaltered tonalite, the probability of the tracer atom hitting the connected network of pores or microfissures is lower than in mica gneiss. In altered tonalites, the porosity consisted of mesopores and macropores, implying a high specific surface area of the rough fracture surface and inside the matrix, making it difficult to distinguish between real matrix diffusion and diffusion into stagnant water areas.

Sorbing tracers

Sorbing tracers would not require flow rates as low as those required by the use of non-sorbing tracers in order to see the effects of matrix diffusion. Fracture column experiments were conducted using slightly sorbing sodium and moderately sorbing calcium and strontium in order to test different processes affecting the transport of radionuclides in fractures. The flow conditions and transport behaviour of sodium, calcium and strontium in fracture columns were interpreted using a numerical compartment model. Each experiment was modelled using the same parameters throughout the flow rate range.

The exact K_d -value able to explain the experimental elution curves depends on the effect of surface retardation in the fracture. The amount of surface retardation is not known precisely and this has a slight effect on the K_d -values used in the matrix diffusion calculations. The calculations take both retardation in the rock pore volumes and surface retardation into account. In the matrix diffusion calculations, the retardation in rock pore volumes, R_p , is related to the mass distribution ratio, K_d , by means of equation (5). Retardation of radionuclides in column experiments was estimated by using a retardation factor that was determined as the ratio of tracer velocity to groundwater velocity. In the fracture column experiments, the surface retardation factor, R_a , is related to the sorption distribution ratio, K_a , determined by means of equation (4).

The experimental and calculated elution curves of calcium for mica gneiss are shown in Figure 11, and elution curves of strontium are shown in Figure 12. The diffusion parameters used in the matrix diffusion calculations were estimated on the basis of gas diffusion and MMA out-diffusion determinations (Siitari-Kauppi et al., 1997). Retardation in rock pore volumes estimated from the mass distribution ratios determined by static batch sorption experiments and surface retardation was used as fitting parameters. The elution curves for sodium indicated that matrix diffusion had a stronger effect on sodium in altered tonalite columns than on sodium in mica gneiss and unaltered columns. This finding is in agreement with the K_d -values of sodium obtained from batch experiments. The use of sorbing tracers enabled demonstration of matrix diffusion behaviour in the water flow experiments at a flow rate of $10 \mu\text{l}\cdot\text{min}^{-1}$.

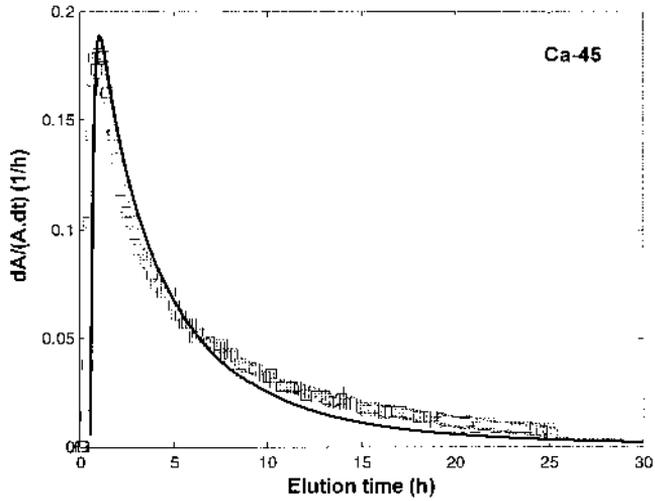


Figure 11. Experimental and calculated elution curves of calcium for the mica gneiss fracture column.

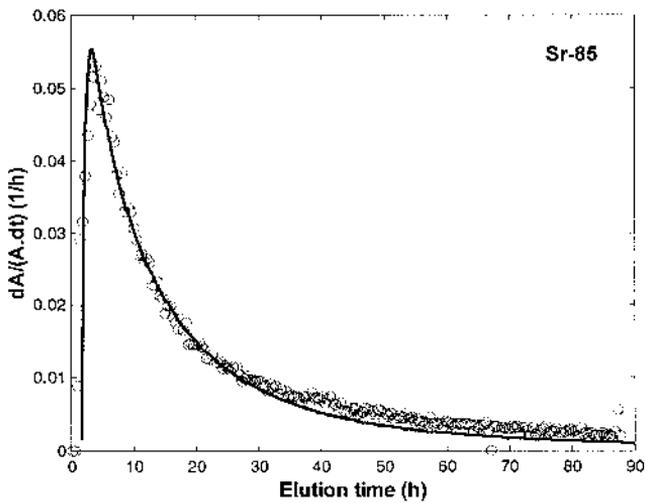


Figure 12. Experimental and calculated elution curves of strontium for the mica gneiss fracture column.

5.2. Interpretation of laboratory-scale experiments

Because of the moderate amount of sorption, calcium was chosen as the tracer for testing a model based on a numerical code, FTRANS, which was adapted for interpreting laboratory-scale migration experiments. FTRANS is a 2-dimensional code that can simulate groundwater flow and transport of radionuclides in a porous or fractured medium (INTERA, 1983). In-diffusion into rock cubes was introduced in order to determine the effective diffusion coefficient, D_e , and to predict retardation in fracture columns. The in-diffusion of calcium into the rock cubes was then interpreted FTRANS (Tukiainen, 2000; Hölttä et al., 2001). The rock cubes were assumed to be porous which means that there is a connected network of water-filled microfissures and pores running through the whole cube.

A numerical code was able to interpret the in-diffusion of calcium into altered tonalites in which the rock matrix was assumed to be saturated (Paper V, Figures 2b, 3b). Owing to the insignificant decrease in the calcium concentration in the solution after a three-month follow-up period, the code was not able to interpret the in-diffusion of calcium into low porous mica gneiss and unaltered tonalite rock cubes. The extent of diffusion of the tracer into the rock cubes was supported by earlier through-diffusion experiments, for which samples of a similar rock type were cut at the end of the experiments, and the cut surfaces were then autoradiographed (Hölttä et al., 1993; Johansson, et al., 1998).

The experimental and calculated in-diffusion and elution curves of calcium for moderately altered tonalite are shown in Figure 13. The corresponding curves of calcium for strongly altered tonalite are shown in Figure 14. The elution curves of calcium for the moderately and strongly altered tonalite fracture columns were interpreted using a modified code. Calcium retardation in the altered fracture columns was explained adequately by the code when using parameters obtained from in-diffusion calculations.

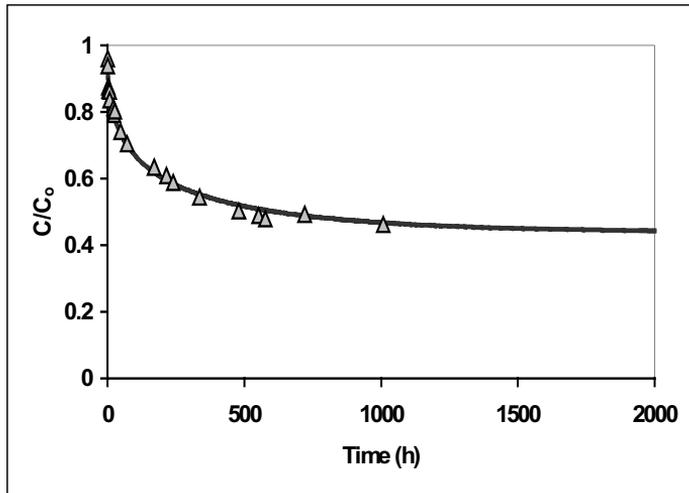


Figure 13a. Experimental and calculated in-diffusion of calcium for moderately altered tonalite rock cube. The model curve was calculated using the FTRANS code. $R=250$, $D_e=3.9 \cdot 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, $K_d=0.002 \text{ m}^3 \cdot \text{kg}^{-1}$.

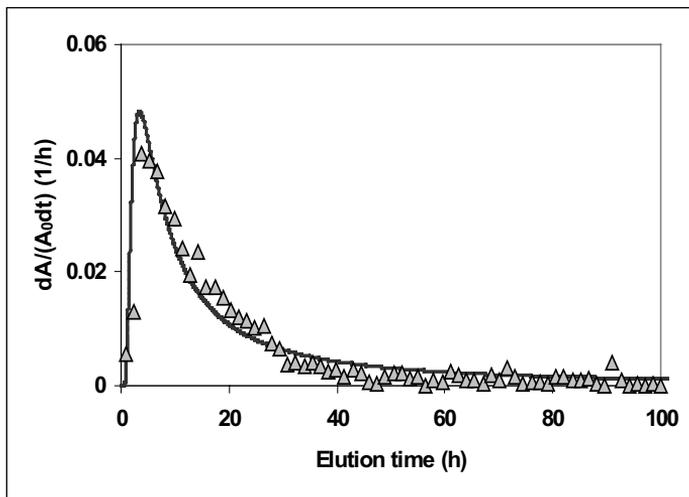


Figure 13b. Experimental and calculated elution curves of calcium for the moderately altered tonalite fracture column. The model curve was calculated using the FTRANS code; $D_e=3.9 \cdot 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, $K_d=0.002 \text{ m}^3 \cdot \text{kg}^{-1}$.

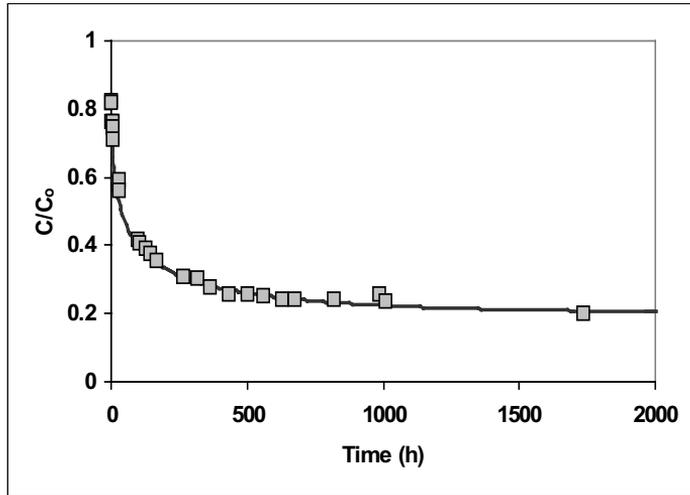


Figure 14a. Experimental and calculated in-diffusion of calcium for strongly altered tonalite rock cube. The model curve was calculated using the FTRANS code. $R=600$, $D_e=8.3 \cdot 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, $K_d=0.008 \text{ m}^3 \cdot \text{kg}^{-1}$.

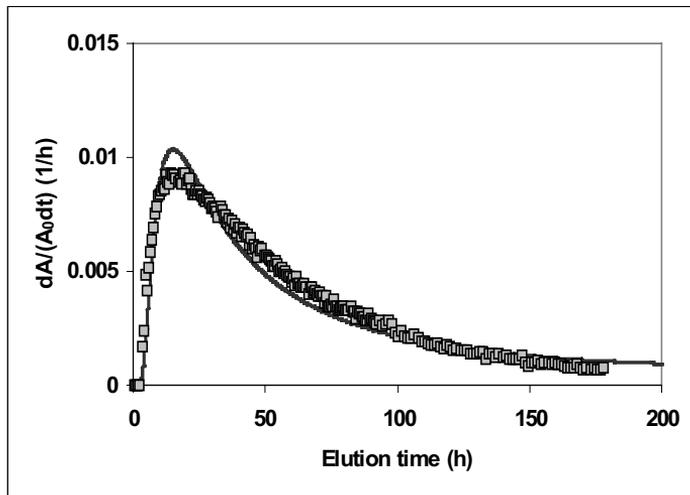


Figure 14b. Experimental and calculated elution curves of calcium for the strongly altered tonalite fracture column. The model curve was calculated using the FTRANS code. $D_e=8.3 \cdot 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, $K_d=0.008 \text{ m}^3 \cdot \text{kg}^{-1}$.

5.3. Crushed rock column experiments

The numerical compartment model used in fracture column experiments was applied to the crushed rock column elution curves in order to interpret the flow conditions and transport behaviour of radionuclides. In the calculations for porous flow, the retardation factor, R_f , is related to the mass distribution ratio, K_d , which is measured in batch experiments by means of the equation:

$$R_f = 1 + \frac{(1 - \varepsilon_i)}{\varepsilon_i} K_d \rho_p \quad (13)$$

where ρ_p is the particle density in the column ($\text{g}\cdot\text{cm}^{-3}$) and ε_i is the interstitial fraction, i.e. the effective porosity of the media. The mass distribution ratio, K_d , calculated from the retardation factor is an approximation because, in the course of the column experiment, equilibrium between sorbed and dissolved species may not have been attained. The transport of radionuclides in porous media is controlled by kinetic processes (André et al., 1998; Compere et al., 2001; Delay et al. 1997). Kinetic processes were not taken into account in the calculation, which may be a source of additional inaccuracy.

In crushed rock columns, the elution curves of tracers were in fair agreement with the dispersion calculations although the model for fracture flow may not be adequate in the case of crushed rock (Paper III, Figure 3). The transport of tracers was explained by dispersion and surface retardation only. Adding matrix diffusion gave better fit with experimental elution curves only for altered tonalites. Effects analogous to matrix diffusion in the elution curves may indicate diffusion into the particles, but possibly also into stagnant areas in the flow field. Retardation in the rock pore volume estimated on the basis of the mass distribution ratios determined by means of static batch sorption experiments and surface retardation were used as fitting parameters. The exact K_d -value able to explain the experimental elution curves depends on the effect of surface retardation in the column. Owing to inaccuracy in the dispersion calculations for the crushed rock columns, the experimental and calculated elution curves showed slight inconsistency.

5.4. Comparison of sorption parameters

The mass distribution ratios, i.e. the K_d -values, for Syyry KR-7 samples were determined from standard static batch, thin section and rock cube experiments in order to obtain supporting data for the column experiments and to provide data obtained independently. In batch experiments and in-diffusion experiments, the mass distribution ratios, K_d , were determined as the ratio of the radionuclide concentration in the solid phase to the radionuclide concentration in the aqueous phase.

The K_d -values ($\text{m}^3 \cdot \text{kg}^{-1}$) of calcium are compared in Table IV. The K_d -values ($\text{m}^3 \cdot \text{kg}^{-1}$) of sodium, calcium and strontium obtained by means of different approaches are compared in Table V. Values from batch and crushed rock column experiments are given for the largest fraction size. The sorption of sodium, calcium and strontium on mica gneiss and unaltered tonalite was slight, and no difference due to fraction size was observed. Higher sorption and fair dependence on fraction size was detected for altered tonalites, owing to the larger specific surface areas and composition of sorptive alteration minerals. The effect of fraction size and specific surface area on radionuclide sorption has been discussed more in Eriksen and Locklund (1989), Hölttä et al. (1997) and Siitari-Kauppi et al. (1999).

The K_d -values calculated on the basis of thin section K_a -values were in agreement with those obtained on the basis of the batch experiments, indicating that the specific surface area usable in the thin section experiments was equal to that in the batch experiments. The K_d -values for calcium obtained on the basis of in-diffusion into rock cube were an order of magnitude lower than the values of the batch experiments, indicating that the batch experiments overestimate the retardation of calcium onto the rock pore surfaces. The K_d -values obtained on the basis of the crushed rock column experiments were lower than those of the batch experiments. The K_d -values obtained on the basis of the fracture column experiments were an order of magnitude lower than the K_d -values of the batch experiments.

Table IV. Comparison of the K_d ($m^3 \cdot kg^{-1}$) values of calcium obtained by means of different approaches. * Values obtained by means of FTRANS calculations.

Grain size (mm)	Mica gneiss	Unaltered tonalite	Moderately altered tonalite	Strongly altered tonalite
Batch				
0 - 0.1	0.013	0.004	0.025	0.039
0.1 - 0.3	0.012	0.006	0.018	0.043
0.3 - 0.5	0.010	0.004	0.019	0.035
0.5 - 0.8	0.011	0.008	0.014	0.032
0.8 - 1.0	0.015	0.013	0.035	0.044
1.0 - 2.0	0.013	0.011	0.028	0.035
2.0 - 3.15	0.017	0.009	0.027	0.030
Crushed rock column				
0 - 0.071	0.008	0.004	0.014	0.030
0.3 - 0.85	0.006	0.002	0.017	0.021
0.85 - 1.25	0.003	0.001	0.014	0.011
0.3 - 0.5		0.004	0.009	
0.5 - 0.8		0.005	0.010	
0.8 - 1.0		0.009	0.009	
1.0 - 2.0		0.004	0.007	
2.0 - 3.15		0.004	0.008	
Thin section				
	0.002	0.004	0.017	0.029
Rock cube				
	0.0004	0.0004	0.003 0.002*	0.01 0.008*
Fracture column				
	0.0008	0.001	0.002	0.008

Table V. Comparison of the K_d ($m^3 \cdot kg^{-1}$) values of sodium, calcium and strontium obtained by means of different approaches.

	Thin section	Batch	Rock cube	Crushed rock column	Fracture column
Mica gneiss					
Na	0.006	0.003	–	0.001	0.0006
Ca	0.002	0.008	0.0004	0.003	0.0008
Sr	0.003	0.035	–	0.003	0.004
Unaltered tonalite					
Na	0.006	0.003	–	0.001	0.0003
Ca	0.004	0.009	0.0004	0.001	0.001
Sr	0.007	0.036	–	0.002	0.004
Moderately altered tonalite					
Na	0.33	0.39	–	0.020	0.05
Ca	0.02	0.02	0.003	0.015	0.002
Sr	0.02	0.06	–	0.023	0.0015
Strongly altered tonalite					
Na	0.15	0.15	–	0.01	0.02
Ca	0.03	0.02	0.01	0.01	0.008
Sr	0.03	0.04	–	0.02	0.015

6. CONCLUSIONS

In this work, radionuclide migration in crystalline rock fractures was studied by means of laboratory-scale column methods in order to gain a better understanding of different phenomena, particularly matrix diffusion, affecting the transport and retardation behaviour of radionuclides in fracture flow.

The research generated additional knowledge with regard to various relevant phenomena, such as advection, dispersion, matrix diffusion and sorption. In short time scale rock fracture column experiments with flow rates faster than $1 \mu\text{l}\cdot\text{min}^{-1}$, hydrodynamic dispersion alone was sufficient to explain the spread of the elution peaks of non-sorbing tracers. The addition of matrix diffusion gave only a slightly better fit with experimental values. In relatively short and narrow columns with flow rates over $10 \mu\text{l}\cdot\text{min}^{-1}$, fracture flow was dominated by the advective velocity field and the ordinary dispersion theory was not applicable.

The dominant matrix diffusion behaviour was demonstrated in the porous ceramic column and gas diffusion experiments. The fast gas flow method made it possible both to determine the rock diffusion properties in advance and to obtain estimates for optimal experimental conditions in water flow experiments. In rock fractures, demonstration of the effects of matrix diffusion succeeded in an experiment series where the experimental arrangements enabled very low water flow rates. The effects of the dominant matrix diffusion were seen convincingly only in very low flow rate ($0.02 \mu\text{l}\cdot\text{min}^{-1}$) elution curves for the mica gneiss column. Despite of the domination of dispersion, the influence of matrix diffusion was seen in the elution curves at flow rates of $0.4 - 1 \mu\text{l}\cdot\text{min}^{-1}$. In these experiments, the use of slightly and moderately sorbing tracers enabled demonstration of the matrix diffusion behaviour in water flow experiments at flow rates of $1 - 10 \mu\text{l}\cdot\text{min}^{-1}$.

The test in which a model based on a numerical code, FTRANS, was adapted and then used to interpret laboratory-scale migration experiments gave promising results. The numerical code was able to interpret the in-diffusion of calcium into altered tonalites.

Because the follow-up periods were too short, the code was not able to interpret the in-diffusion of calcium into low porous unaltered rock cubes. The elution curves of calcium for the altered tonalite fracture columns were explained adequately by the FTRANS code when using parameters obtained from in-diffusion calculations.

The K_d -values for intact rock obtained on the basis of the fracture column experiments were one order of magnitude lower than the K_d -values for crushed rock. This finding indicates that batch experiments overestimate the retardation of sorbing radionuclides onto the rock matrices, owing to the fact that the surface areas available are larger. The greater sorption on altered tonalites was explained by the composition of sorptive alteration minerals and large specific surface areas.

In these studies, sodium, calcium and strontium were used as tracers in order to compare various experimental techniques. Experiments with relevant nuclear waste nuclides are needed to enable more detailed discussion of the differences in the K_d -values and methods and the implication of these differences for performance assessment calculations. Knowledge based on transport experiments in well-defined laboratory conditions is the basis for the block scale and field experiments needed both to validate the radionuclide transport concept and to test the transferability of laboratory data to field conditions.

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