R-04-48

RETROCK Project

Treatment of geosphere retention phenomena in safety assessments

Scientific basis of retention processes and their implementation in safety assessment models (WP2)

Work Package 2 report of the RETROCK Concerted Action

October 2004

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Work performed as part of the European Atomic Energy Community's (Euratom) framework of the specific research and training programme, Key Action Nuclear Fission, within the RETROCK Concerted Action, "Treatment of geosphere retention phenomena in safety assessments", contract No FIKW-CT-2001-20201

Keywords: Retention, Retardation, Transport, Radionuclide, Geosphere, Modelling, Safety assessment, Performance assessment, Safety analysis, Radioactive waste, Final disposal.

ABSTRACT

This report considers the present-day understanding and approaches to take into account retention and transport processes in the performance assessment (PA) models used in the evaluation of the long-term safety of deep geological repositories for radioactive waste. It is a product of Work Package 2 in the RETROCK Concerted Action, a part of EURATOM's research and training programme.

The processes emphasised in RETROCK are the influences of the flow field, matrix diffusion, and sorption on radionuclide transport characteristics. These processes, and radioactive decay, provide the key terms to the transport equations of the PA models. The following processes are handled more cursorily: colloid-facilitated transport, microbial activity, gas-mediated transport, precipitation/coprecipitation, and off-diagonal Onsager processes.

The environment in question is saturated sparsely fractured rock in the repository far-field. The fracture network offers flowpaths for the groundwater transporting radionuclides away from a repository. The radionuclides in various chemical forms interact physically and chemically with other matter in groundwater, fracture surfaces, fracture infills and the rock matrix adjacent to the fractures. These interactions typically result in significant retardation, and decay, of radionuclides compared to the velocity of the groundwater.

The PA models usually take into account retention phenomena using simplified concepts that are justified by their conservatism. They are complemented by a large variety of more detailed and realistic process-specific models that can be used to support the choice of data for PA models, as well as specific arguments made in safety cases. While the fundamental understanding, the conceptualisations of the phenomena, the models and the computing resources develop, the extensive data requirements often become a most restrictive factor to the use of a model. The difficulties in obtaining data tend to hinder the utilisation of the most realistic mechanistic models, but major challenges are also encountered in obtaining relevant and defensible data for the principal simplified PA models.

In the RETROCK project the current report serves as a tool for further judgement of understanding and approaches, and for an assessment of the development needs.

ACKNOWLEDGEMENTS

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The following external experts reviewed a mid-term draft of the report providing helpful comments and suggestions:

- R. Haggerty with the Department of Geosciences, Oregon State University, USA
- D. Read with Enterpris Ltd, University of Reading, United Kingdom
- J. Bruno with Enviros Spain SL, Spain
- P. Robinson with Quintessa Limited, United Kingdom

In addition, the active participants of the Specialist Workshop, arranged at San Lorenzo de El Escorial in Spain in October, 2003, offered valuable feedback to the project.

The project partners wish to acknowledge the credit of the Scientific Officers of the European Commission in their encouraging administrative support:

- H. Ritter von Maravic
- M. Raynal

AUTHORS AND PROJECT ORGANISATION

The participating organisations and their representatives in RETROCK are presented in Table 1 and the authors of the report in Table 2. The project organisation is constituted by a regulator, four implementors, and a mixture of research institutes, universities and consultants, assuring the diversity of the views. In addition, four external experts, (see Acknowledgements) reviewed a draft of this report at the midterm of the project. At the same time, feedback was received from a Specialist Workshop.

RETROCK is divided into three work packages:

- Work Package 1 (WP1)
    - Assessment of the level of understanding and treatment of retention and transport processes in recent safety assessments.
    - Lead contractor: Nagra
- Work Package 2 (WP2)
    - Description of the current theoretical basis, data needs and modelling practices.
    - Lead contractor: SKB
        - Management of the two Working Groups: ENRESA and SKB
    - *This report was produced within WP2*
- Work Package 3 (WP3)
    - Integration of the results of RETROCK and assessment of development needs
    - Lead contractor: SKI

The duration of the project is three years. The project is co-ordinated and managed by Safram.

Table 1. The participating organisations and their representatives in RETROCK.

Organisation	**Short name**	**Representatives**	**Role**[1, 2]	**Country**
Safram Oy	Safram	M. Nykyri	CO	FI
Empresa Nacional de Residuos Radiactivos S.A.	ENRESA	P. Hernán	CR	ES
Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas	CIEMAT	F. Recreo	MB	ES
Technical University of Catalonia	UPC	J. Carrera C. Ayora (CSIC) J. Soler (CSIC)	MB	ES
Nationale Genossenschaft für die Lagerung radioaktiver Abfälle	Nagra	J. Schneider	CR	CH
Paul Scherrer Institute	PSI	A. Jakob	MB	CH
Posiva Oy	Posiva	A. Hautojärvi J. Vira	CR	FI
Technical Research Centre of Finland	VTT	A. Poteri	MB	FI
Svensk Kärnbränslehantering AB	SKB	J-O. Selroos	CR	SE
The Royal Institute of Technology	KTH	V. Cvetkovic I. Neretnieks	MB	SE
JA Streamflow AB		J. Andersson	SC	SE
Göteborg University		K. Pedersen	O	SE
Bergab		B. Åhlén	O	SE
The Swedish Nuclear Power Inspectorate	SKI	B. Strömberg E. Simic	CR	SE
The Swedish University of Agricultural Sciences	SLU	A. Wörman	MB	SE
Independent consultant Dr. Neil Chapman		N. Chapman	SC	GB
Clearwater Hardrock Consulting		J. Geier	O	US
Galson Sciences		S. Wickham & T. Hicks	O	GB

1) Roles of organisations in RETROCK:

CO: Coordinator and project manager
CR: Principal Contractor
MB: Member
SC: Subcontractor
O: Other organisation/person without a formal role in the EC contract.

2) The indents indicate relationships of the members, subcontractors and others to the principal contractors.

Table 2. The authors of the different parts of the report.

Chapter	**Authors**
Abstract	M. Nykyri (MN)
Acknowledgements	MN
Authors and project organisation	MN
Table of contents	–
1 Introduction	MN
2 Processes commonly modelled in Pa's	–
2.1 Influence of flow field on transport and retention	I. Neretnieks
2.2 Water chemistry and sorption	C. Ayora & J. Soler
2.3 Matrix diffusion	A. Jakob
2.4 Radioactive decay incl. decay chains	A. Wörman & B. Strömberg
3 Processes discussed in PA's	–
3.1 Colloids	S. Wickham & T. Hicks
3.2 Precipitation and dissolution	C. Ayora & J. Soler
3.3 Microbiologically mediated processes	K. Pedersen
3.4 Gas mediated transport	B. Åhlén
3.5 'Off-diagonal' processes	J. Soler
4 Implementation of processes in PA's	–
4.1 Influence of flow field on transport and retention	A. Poteri & J. Andersson
4.2 Water chemistry and sorption	C. Ayora & J. Soler
4.3 Matrix diffusion	A. Jakob
4.4 Radioactive decay incl. decay chains	A. Wörman & B. Strömberg
4.5 Colloids	S. Wickham & T. Hicks
4.6 Precipitation and dissolution	C. Ayora & J. Soler
4.7 Microbiologically mediated processes	K. Pedersen
4.8 Gas mediated transport	B. Åhlén
4.9 Off-diagonal processes	J. Soler
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APPENDIX 2	I. Neretnieks & A. Jakob
Overall editing	MN

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1 INTRODUCTION

The report was produced within Work Package 2 of the RETROCK project, "Treatment of Geosphere Retention Phenomena in Safety Assessments". In RETROCK it is examined how the retention and transport of radionuclides are and should be recognised in the performance assessment (PA) models for deep geological repositories of radioactive waste in saturated sparsely fractured rock. The principal aim is to summarise the underpinning knowledge and modelling practices and to appraise the development needs. An additional aim is to enhance the communication between the different parties connected to the PA modelling, especially between the PA modellers and the process researchers.

The domain under consideration is the repository far-field, i.e. the geosphere between the so-called repository near-field and the biosphere. Radionuclides migrate with the groundwater in various chemical forms in fracture networks and interact with other matter in water, fracture surfaces, fracture infills and rock matrix between the fractures. The retention and transport processes emphasised in RETROCK are the influence of flow field, matrix diffusion, and sorption on radionuclide transport characteristics. The following processes are handled more cursorily, principally from the point of view of their effects on retention and transport: colloid-facilitated transport, microbial activity, gas-mediated transport, precipitation/coprecipitation, radioactive decay, and off-diagonal Onsager processes.

In the beginning of RETROCK, in Work Package 1, a questionnaire was used to acquire information of the level of understanding and the treatment of these processes in a few recent safety assessments. A synthesis of the replies with the identified issues was then fed to Work Package 2 for further processing. In Work Package 2, the project team judged the current theoretical basis, modelling practices and data needs in-depth. The work resulted in this relatively comprehensive report that allows its authors to present also their individual views. At the end of RETROCK, in Work Package 3, the findings of the project are integrated, discussions on disputatious issues continued, and development needs appraised. The Work Package 3 report or the final project report summarises all the results concisely and corresponds as closely as possible to the common views of the project partners and the external collaborators. The Work Package 3 report thus delivers the prevailing consensus on the subject.

The report is structured so that the processes commonly modelled explicitly in PAs are first discussed in Chapter 2. In Chapter 3 processes not modelled explicitly but considered in the safety cases are discussed. Finally, the implementation of processes in the PA models is described in Chapter 4.

Despite the attempts to arrive at generally accepted definitions of the terms 'retention' and 'retardation', different definitions and usages of the terms are found in scientific papers. The authors of this report follow their personal preferences in this respect.

2 PROCESSES COMMONLY MODELLED IN PA'S

2.1 INFLUENCE OF FLOW FIELD ON TRANSPORT AND RETENTION

This section describes the basic ideas for modelling dissolved radionuclide transport in water saturated fractured rocks. The nuclides are transported by flowing water. Many nuclides are cationic and will sorb on mineral surfaces. This will retard their movement in relation to the water velocity. The interior of the rock matrix has micropores with stagnant water and sorbing surfaces that together are much larger than the surfaces of the fractures with the moving water. The matrix pore waters and the inner surfaces can be reached by molecular diffusion, which is a slow process. During PA time scales the inner surfaces can often be more important to retard the nuclides than the fracture surfaces themselves including the retardation by any infill in the fractures.

The fracture networks give rise to complex flowpaths. Models are used to simulate the water flow and the solute migration. The contact surface between the flowing water and the fractures of the rock where the water flows, the Flow Wetted Surface, FWS, is an important entity. The larger the FWS is for a given water flowrate the larger will be the matrix uptake and retardation of the nuclides. The understanding and modelling of the flowpaths in the fracture system and the assessment of the FWS to flowrate ratio are very central in the models.

Two main approaches used in PA modelling are described. One is based on approximating the flow in the rock as if it were a porous medium. The other is to model the rock as a fracture network. In both cases stochastically variable rock hydraulic properties are used in the models. One of the challenges is to obtain and interpret data from the field for use in the models.

2.1.1 Introduction to the transport modelling approaches

In water saturated hard rock formations, a very important mechanism to retard solutes (nuclides) carried by the water is what is called matrix diffusion. The nuclides diffuse into the pores of the rock matrix within which they are sorbed on the micro fractures. Section 2.3 describes the transport in the matrix. This chapter describes how the flowing water comes in contact with the flowing fracture surfaces over which the transport into the matrix can take place. Obviously, for a given flow, the larger the surface over which the transport can take place the more efficient will be the uptake into the matrix.

This section gives an overview of the basic processes that govern the transport of solutes through fractured rocks. It emphasises the basic mechanisms and how they are implemented in different models used in safety analysis. Differences in the models are brought out but also common traits that exist and that may not always have been clearly stated in the model descriptions. Some issues that are still under discussion are also treated.

There are two basically different ways to model the transport of a solute through fractured rocks. One way is to describe the rock as a heterogeneous *porous medium* and calculate the flow field of water. (In practice made numerically by e.g. a finite difference or finite element method applied to the rock mass described in two or three-dimensional space.). In principle the transport equations can also be solved in two or three dimensions. This is, however, seldom done for Performance Assessment, PA, applications because it is deemed that transverse mixing is not very important on a large scale and much computing effort can be saved.

When solving for a three-dimensional flow field, the solution of the flowrate equations gives information on flowrate distribution and trajectories of the flowing water. At steady state the trajectories are streamlines. The streamlines can be followed to assess the residence time distribution of the water if information on the flow porosity is available. It is practical to introduce the stream tube concept. A streamtube is a fictitious tube where a stream of water flows without any of the water or its solutes passing the walls. One can then follow a stream along the tube and the fracture surfaces within the tube that the stream encounters.

The notion of streamlines and streamtubes is based on an idealisation of a fluid. A real fluid consists of molecules subject to random thermal motion. On the molecular level it is not possible to follow the fluid flow by tracing out the paths of the molecules because of the random movements. One may think of following a tiny volume of the fluid as in the streamline concept and this often gives an illustrative visualisation of the flow. However, it must be recognised that solute molecules will randomly pass the "impermeable" boundaries of the streamtube by molecular diffusion. If one chooses the streamtube to be wide in comparison to distance the molecular diffusion transports the molecules, the errors can be made acceptable.

Streamtubes are constructed based on the trajectory and flowrate information obtained by solving the flow model. Thereafter the solute transport equations including any reactions are solved for each stream tube. There is no mixing between stream tubes but within the streamtube there is interaction e.g. surface sorption and matrix diffusion. The streamtube concept is based on a continuum representation of the bedrock in this case and treats transport as one-dimensional along the streamtubes.

In another approach the rock is modelled as a *fracture network* where each fracture may have different properties. In this approach the flow in every fracture in the network is solved for. In some implementations of this model every fracture is assumed to have constant properties within it. In other implementations further refinements in detail are incorporated in the fracture network models by letting the properties within each fracture also vary stochastically.

In both the porous media models and the network models the same interaction mechanisms between solute and rock are accounted for.

In both the porous medium and the fracture network models it is necessary to assess when the streamtube approximation is permissible as this assumes non- mixing between streamtubes.

Mixing between flowpaths is studied in order to assess when the streamtube approximation can be used and when mixing must be accounted for. In the porous media models mixing between adjacent streams is modelled as taking place by molecular diffusion and by what is called dispersion. The latter will be discussed more, later in this chapter. In the fracture network models the same mixing method may be used. In addition, however, it is commonly assumed that at the intersection of two or more channels there is total mixing of the incoming streams before the water exits by one or more other fractures. Table 3 compiles the main traits of the two approaches.

Table 3. Comparison of porous medium and fracture network models.

	Porous medium	**Fracture Network**
Flowrate distribution obtained by solving	Darcy's law in porous medium	Darcy's law in the whole network. Network Information on Conductive Fracture Frequency, CFF
Solute transport for non interacting solutes I	Streamtubes: No mixing between tubes, dispersion in flow direction. Flow porosity needed for water residence time	Flowpaths(s) in every fracture, mixing at fracture intersections. CFF and apertures needed for water residence time
Solute transport for non interacting solutes II	Full 3D formulation of Advection Dispersion equation, AD-equation. Flow porosity needed for water residence time	2D formulation of AD-equation in every fracture, mixing at fracture intersections. CFF and apertures needed for water residence time
Solute transport for interacting solutes I	Streamtube: Matrix diffusion equation solved with information on Flow Wetted Surface per volume of streamtube	Flowpath in every fracture, mixing at fracture intersections. FWS of individual fractures known from definition.
Solute transport for interacting solutes II	Full 3D: Matrix diffusion equation solved with information on Flow Wetted Surface per volume of rock	2D formulation of AD-equation in every fracture, mixing at fracture intersections. FWS of individual fractures known from definition.

In all models the basic interaction mechanisms between the solute carried by the water and the rock are modelled based on the same mechanisms, namely surface sorption and matrix diffusion.

In the porous media models the magnitude of the contact surface between the flowing water (in the streamtubes) and the rock is estimated from observations in boreholes of the number of conducting fractures per volume of rock.

In the network models the surface over which the solutes can diffuse into the rock matrix is given by the Discrete Fracture Network, DFN, model itself where the fracture geometry is simulated from fracture size, orientation, transmissivity and density distributions. The fracture density is preferably expressed as total fracture area per volume of rock (P_{32}, see e.g. Dershowitz et al., 1998). The DFN-parameters can be estimated from field data, mostly borehole observations, but will be formulated differently for use in different models (Moreno and Neretnieks 1993, Andersson et al. 1998, Outters and Shuttle 2000). The frequency of and flowrates in conducting fractures encountered in a borehole is used to obtain data for the network models. The Conductive Fracture Frequency, CFF, in boreholes is often the prime source of obtaining the information needed for the network models.

The CFF, the orientation of the fractures, their clustering and other information that can be derived from observations defines the network and thus the surface that a little stream will “see” as it proceeds from fracture to fracture through the network. Because the different fractures have different transmissivities, and thus flowrates, this information must also be supplied to the network. Also this information is obtained from the borehole measurements.

In the performance assessment time perspective the rate of migration of the nuclides is dominated by the flowrate of water, by matrix diffusion and sorption within the matrix, and radioactive decay and ingrowth in the case of nuclide decay chains. The discussion will therefore focus on this mechanism and how it is and may be incorporated in the different models.

The different approaches are discussed in more detail below.

2.1.2 Basic mechanisms

Solute transport in fractured rocks takes place by the water flowing in the rock fractures. The water flow is unevenly distributed over the fracture plane. Observations indicate that a large part of the flow takes place in a limited part of the fracture. Other parts of the fracture carry less water. The term channelling has been proposed to describe the uneven flow distribution. It is understood that this does not mean that there are fixed channels but that for a specific gradient direction the water seeks out the easiest pathways. Another gradient direction will lead the water in other paths. Thus already in a fracture different paths will behave differently.

Solutes that are carried by the water interact in different ways with the rock. The rock is slightly porous, typically 0.1- 0.5 %. (Ohlsson and Neretnieks, 1995) Small solutes can enter into the porous rock matrix by molecular diffusion. The stagnant water volume in the rock matrix is much larger than the flowing water in the rock fractures. The solutes that enter the rock matrix can therefore attain a longer residence time than the flowing water. The differences can be considerable and one to two orders of magnitude spread is typical for nonsorbing solutes such as e.g. iodide. Solutes that can sorb on the mineral surfaces will encounter much larger sorption surfaces in the interior of the rock matrix than on the flowing fracture surfaces. The interior surfaces can be typically 3 to 6 or more orders of magnitude larger than the flowing fracture surfaces. The additional retardation by sorption on the internal surfaces can vastly add to slowing down sorbing nuclides (Neretnieks 1980). However, not all the interior surfaces can be utilised because the nuclides will not have time to reach all the interior surfaces. The retardation due to matrix diffusion and sorption on the interior surfaces is a very important retardation mechanism for the nuclides. The contact surface between the flowing water and the rock will determine the size of the surface over which the nuclides can enter the matrix. This is called the Flow Wetted Surface, FWS.

The volume of the channel and the flowrate determine the residence time of the water and so of the radionuclides that do not interact with the matrix. For the sorbing radionuclides the residence time is mainly determined by the ratio between the FWS and the flowrate in the flowpath. This ratio will determine the interaction between the rock and the radionuclide. The main interaction mechanisms are diffusion in the porous matrix and sorption on the internal surfaces. The fracture surface itself and any infill in the fracture may also contribute to the retardation of sorbing nuclides.

In field experiments, much higher flowrates, shorter distances and shorter times are used than what is of interest for a repository situation. In the experiments both the water residence time and the retardation effects due to the matrix interaction may contribute to determine the residence time of slightly sorbing solutes. Different mechanisms may dominate for different time scales. In field experiments sorption on the fracture surfaces, on infill and diffusion into stagnant waters may have the dominating influence on the Residence Time Distribution, RTD, of a tracer. For PA time scales the diffusion into the rock matrix over the fracture surface will have a dominating influence on the RTD. Therefore field experiments cannot directly be used to extrapolate to longer time scales. A detailed understanding of the interaction mechanisms is essential in order to make credible extrapolations.

The problem to assess the RTD of a solute can be divided in two distinct parts. In the first part the flowrate distribution of the water in the rock mass from release point to exit points must be determined. This would make it possible to follow a minute stream of water along the flowpath. It flows in a "streamtube" where no mass can pass over the walls of the tube. The tube walls can be thought of as being bounded by a large number (infinite) of very closely located streamlines.

For illustrative purposes we use the one-dimensional formulation of the transport equations. This is adequate, for the moment, because that is what is done in many present day safety analyses models. The flowpaths and the fluxes in the three dimensional space are assumed to be known from hydraulic modelling. Thus the transport of a nuclide in a streamtube forms the basis for the following description and discussions.

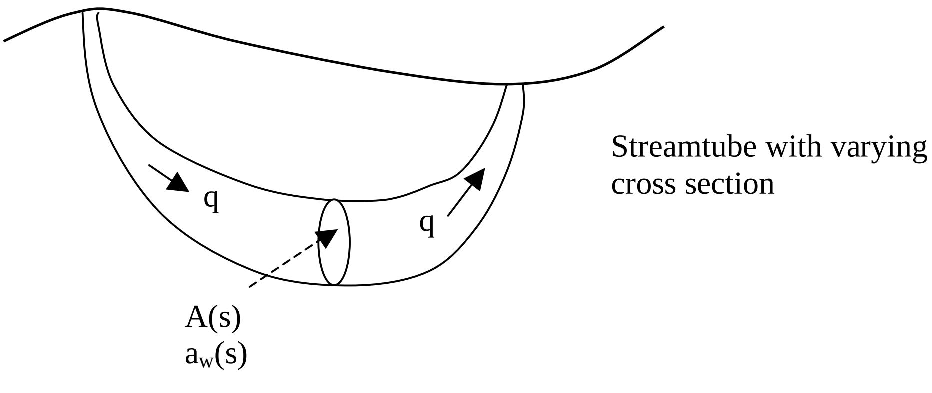

Figure 1. Illustration of the concept of a streamtube. Mass can enter and exit at in- and outlet only, not over boundaries. The flowrate q is constant in streamtube. Cross section A, water velocity and contact surface between water and rock fracture, a_w, varies along the streamtube.

The streamtube concept is used to describe the flow in fluids and also in porous media where it is implicitly assumed that the solid particles making up the porous medium are so small that one can disregard that the streamlines have to move around them.

Notation is found in APPENDIX 2.

The commonly used advection-dispersion model, with interaction with the rock matrix included, can be formulated by the following differential mass balance. The conventional mathematical form in continuum formulation is

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} = D_L\frac{\partial^2 c}{\partial x^2} + a_w D_p \varepsilon_p \frac{\partial c_p}{\partial z} \quad (z=0) \tag{1}$$

This is the basic equation upon which most solute transport models are based. The models differ mostly in how the equation is implemented in different conceptualisations of the rock mass.

The equation describes a mass balance of a solute. It was originally formulated for transport in a porous medium but can be applied to fractures in fractured rocks also. It will form the basis for further discussions.

In Equation (1) u is the water velocity in the x direction, D_L the dispersion coefficient, a_w the contact surface between the flowing water and the rock per volume of flowing water. $D_p\varepsilon_p$ is the effective diffusivity in the rock matrix. The last term accounts for the exchange of the nuclide with the porous rock matrix. The diffusion is directed in the z-direction into the rock matrix.

Note that the third term describes diffusional mixing in the flow direction. It is commonly taken to describe also “hydrodynamic dispersion”. This is, however, not a mixing mechanism that actually causes mixing as molecular diffusion does. Furthermore, field observations indicate that the dispersion coefficient is not a constant, as the equation assumes, but that it increases with distance. This, in fact, implies that it is wrong to use the equation, solving it with a constant D_L. It is, however, commonly used as an approximation. Because velocities in the different streamtubes vary much this causes a larger “dispersion” than that within the individual tubes and thus introduces a negligible error if the waters in several streamtubes are collected and mixed.

Another major difficulty is that all the water-rock interaction surface, the so called Flow Wetted Surface, in a cross section of the stream tube must be averaged to one value, here denoted by a_w. As in fact the streamtube encompasses a multitude of fractures with different flowrates and different flow velocities, this averaging causes considerable difficulties that have not yet been adequately resolved. The difficulty can be illustrated in the following way. In a section of the streamtube one large portion of the water flows in one of the fractures. The remaining small water portion flows in, say, nine fractures. Shall we consider that on the average all fracture surfaces make up the flow wetted surface, or be prudent and say that we are more concerned with how much rock surface most of the water contacts and thus use only a tenth of the flow wetted surface. This is the other main fundamental problem with the advection-dispersion model applied to a porous medium formulation. A simple example in Section 2.1.9 will illustrate this question.

A special difficulty arises when the streamtube concept is to be applied to a medium where the “particles” of the porous medium are larger than the resolution needed to describe details of the streamlines. This is the case for fractured rocks as is illustrated in Figure 2 below.

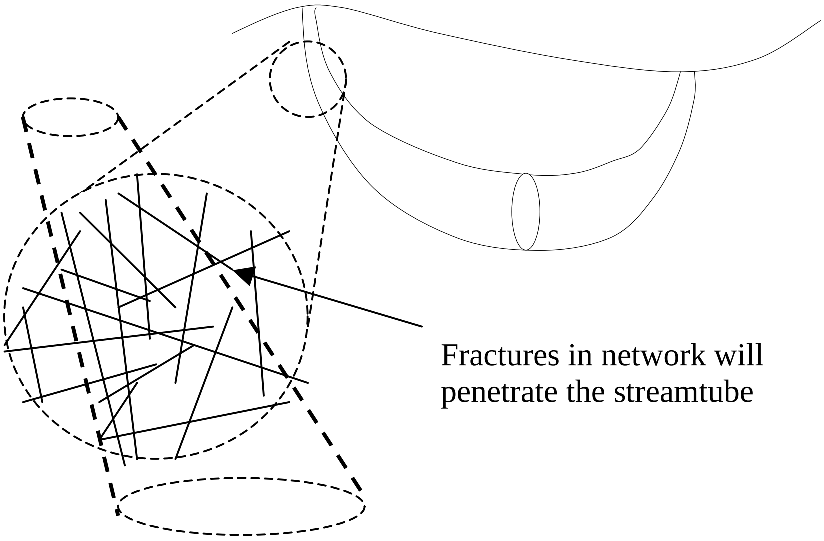

Figure 2. In the enlarged section of the streamtube it is seen that the rock fractures penetrate the wall of the streamtube. This permits water and solutes to penetrate the" streamtube" wall. This then may not be a good approximation of a streamtube.

This is a weakness in using the streamtube concept to describe large-scale flow in fractured rock masses. However, it will be argued later that the errors introduced by this approach are not deemed to be larger than those caused by other uncertainties in data and in other model concepts.

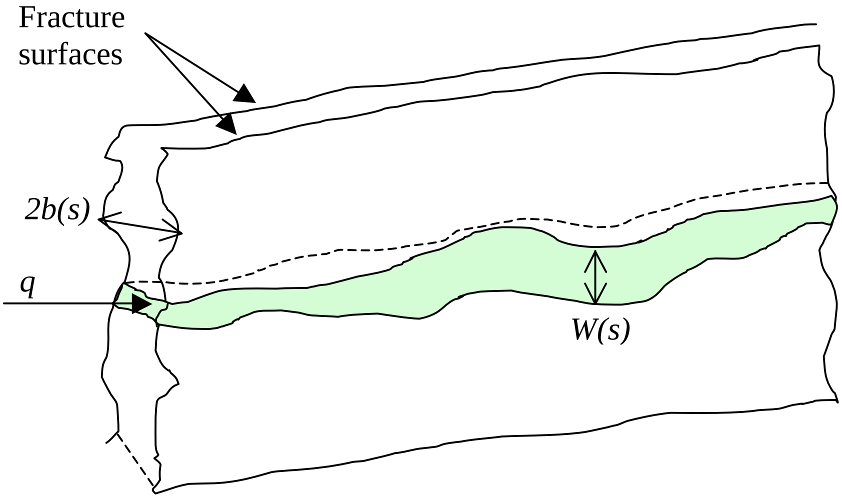

Figure 3. A stream with flowrate q flows through a thin fracture with variable aperture 2b(s). The stream also varies in width, W(s), and is exposed to a variable contact surface to the fracture as it passes along the flowpath.

The use of Equation (1) is illustrated in Figure 3 for a little section of the rock containing a fracture in which water flows. It can be related to the streamtube concept and by thinking of it as a path carrying the identifiable volume with constant flowrate *q* and a part of rock that the path is in contact with.

By following an identifiable stream with flowrate *q*, that does not mix with other adjacent streams, from location to location through the whole pathway, the residence time distribution of the solute in the streamtube can be assessed. Later in this section the conditions for diffusional mixing with adjacent streams will be discussed. It will be found that in PA applications stream widths much larger than tens of cm behave as streamtubes and streams with widths smaller than a mm do not.

Provided the flow model contains information on the flow path cross section *A(s)* along the path *s*, the water residence time t_w for the stream with the flowrate *q* along this streamtube, from $s = 0$ to $s = L$ is simply obtained by determining the integral volume of the water in flowpath V_q and dividing this by the flowrate. Thus for a streamtube *in the fracture*

$$t_w = \frac{\int_0^L A(s)\,ds}{q} = \frac{\int_0^L W(s)2b(s)\,ds}{q} = \frac{V_q}{q} \tag{2}$$

For a streamtube in *a porous medium*

$$t_w = \frac{\int_0^L \varepsilon_f(s)\,A(s)\,ds}{q} = \frac{V_q}{q} \tag{3}$$

Here ε_f is the local porosity of the streamtube. For the streamtube in the water in a fracture the porosity $\varepsilon_f = 1$. One important observation is that in the streamtube concept there is no need to identify the residence times of parts of the flowpath to obtain the total residence time for the whole flowpath. It suffices to assess the water volume in the whole stream tube.

The above result seems trivial but points to the need to track the cross section *A(s) =W(s) 2b(s)* along the flowpath in the fracture. In the same way, to determine the RTD of an interacting solute we need to determine the area exposed to flow along the flowpath where the stream travels. The flow wetted surface that the stream with flowrate *q* in the streamtube contacts is denoted A_q.

The transport model thus needs to have information on the surface area of the rock in the stream tube that the stream *q* contacts. Denoting local width of the channel by *W(s)* the total flow wetted surface on both sides of the fracture along the flowpath is

$$A_q = 2\int_0^L W(s)\,ds \tag{4}$$

Similarly for a porous medium

$$A_q = \int_0^L A(s)\,a_R(s)\,ds \tag{5}$$

a_R is the specific flow wetted surface per volume of rock. It is about four times the conductive fracture frequency, CFF found in boreholes in a rock with fractures that are randomly oriented in space. This entity is mentioned here to relate the terminologies between different models. The relation between the *CFF*, a_R and a_w is

$$a_R = a_w \varepsilon_f = 4 \cdot CFF \tag{6}$$

a_R is the total area of both sides of the fractures in a given volume of rock, m^2 flow wetted surface/m^3 rock volume. This entity or the *CFF* is directly related to observable physical entities whereas the use of a_w needs information on the flow porosity ε_f, which seldom is known. It will further be demonstrated that for PA applications the water residence time commonly has a negligible influence on the residence time of the nuclides. This simplifies the task considerably as the fracture apertures and/flow porosities are difficult to measure.

The CFF or a_R is estimated from observations of the frequency of conductive fractures in boreholes. This will be discussed more, later in this section.

These trivial but important results can be applied to a rock mass containing a multitude of fractures forming a connected network. It has been shown (Neretnieks and Rasmuson 1984) that in the same way as for the water residence time, the total FWS, irrespective of its variations along the streamtube can be used to account for the interaction with the rock matrix, including matrix diffusion effects.

The flow, as already pointed out, on every portion of the flow wetted surface in a volume of rock will not influence the RTD of the solutes equally. In the streamtube in the porous medium the flow is divided over a multitude of fractures, each with a different flowrate. In this use of the streamtube concept the flowrate in the streamtube is averaged over the cross section. Also the FWS is averaged over the streamtube. This way of independently averaging the flowrate and the area exposed to flow leads to a loss of information. There is a considerable difference between how the solutes in a small stream and a large stream interact when they are exposed to the same size of surface. This is an inherent difficulty in using the streamtube concept over large volumes of rock. There is at present no simple way of compensating for this loss of information and in PA applications the magnitude of the flow wetted surface is sometimes taken to be considerably smaller than the strict average value obtained from observations of the CFF (SITE-94 1996).

2.1.3 Fracture network concept

The above observations have led to the idea to follow a multitude of individual paths through the different fractures as they flow through the network of fractures. This can be done in different ways. If the flow in the fractures is described by a 3D flow model, then the streams may be traced out as described above. However, in the models used, the flow in the fractures is described by 2D elements due to computer limitations and because we do not have the information to resolve the small-scale 3D flow field. Also as will be shown later it is not meaningful to solve too detailed flowpaths across the fracture aperture because the random molecular movements quickly transport molecules across “streamlines”. This allows the tracing of trajectories in the fracture plane *but not across the aperture of the fracture.* At a fracture intersection where a stream splits in two it is no longer possible to trace the trajectory when molecular diffusion is active. This is because there is no resolution of the trajectory across the fracture aperture because of the random thermal movement of the molecules. This is illustrated in Figure 4.

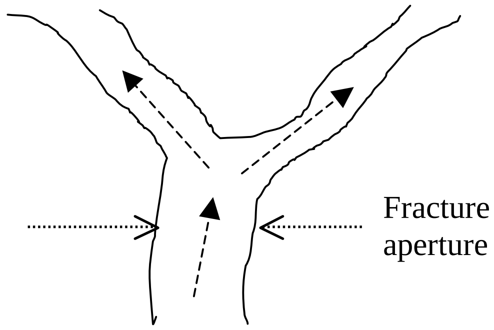

Figure 4. View perpendicular to the fractures. At a fracture intersection the stream splits in two. The incoming stream has the same concentration over the fracture aperture and the two leaving streams have the same concentration.

The mixing of a stream across the fracture aperture will be discussed later and it will be shown that any concentration differences across the aperture at the inlet of a channel will even out very quickly for PA applications. The situation is somewhat different for the case where two or more streams come to a fracture intersection and leave in one or more outgoing streams. The time for mixing at the intersection is much less than when two adjacent streams use the whole residence time through the fracture to mix. This mixing at intersections is illustrated in Figure 5.

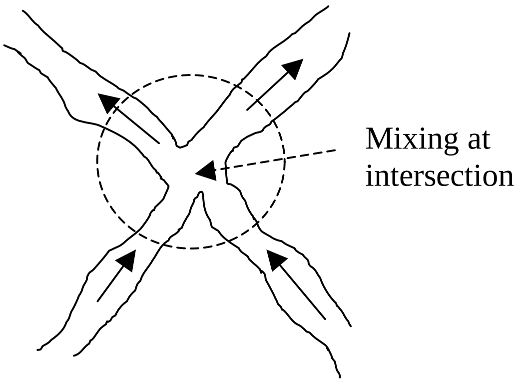

Figure 5. View perpendicular to the fractures. At a fracture intersection two streams meet and then divide again. The time for mixing is only the residence time in the intersection.

In the section on diffusional mixing, later in this chapter, it will be shown that for PA applications it is not always assured that full mixing will occur, although commonly it will. For the rest of this section we make the assumption that full mixing will occur.

The network approach is based on the use of fracture networks with stochastic fracture properties. Observations in boreholes give information on the density (frequency) of water bearing fractures. In a fracture network model a network with the observed CFF can be modelled.

Networks can also be made to include effects of fracture clustering, orientation of families of fractures, correlations of orientations and hydraulic properties and other entities found in the field observations.

The hydraulic properties of each fracture vary strongly and are randomly chosen so that they can reproduce observations in boreholes. The stochastic assignment is necessary for the majority of the fractures in the background rock because it is not possible to measure each individual fracture. Known large-scale features such as fracture zones extending over hundreds of meters can be deterministically included in the model. The flow in such a model is solved in principle in the same way as the porous medium models. One difference is that the flowrate in each fracture is obtained directly. Another difference is that the fractures have a transmissivity in the plane of the fracture only, in contrast to the elements in a finite element (or difference) model used in the porous medium approach. This leads to differences in solute spreading, especially in the direction perpendicular to the main flow direction.

However, it should be noted that in practice it is not yet possible to use fracture network models for large rock masses using the full, observed fracture densities because of computer memory and speed limitations. So, also for the fracture network approach, an average for a number of fractures is lumped into one fracture to generate a coarser network. Different approaches to simplify the models have been suggested and tried in order to make the handling of the models tractable.

In practice one must always choose a finite size of the resolution of details in a fracture. Some modellers use finer grids than others. Some approximate a variable transmissivity fracture by one with the same transmissivity everywhere in the fracture. Other models again, substitute the whole fracture by a channel or tube. However, the variability of transmissivities between the different fractures is kept.

In fracture network codes that use variable aperture fractures one can trace out the pathways within a fracture and how the pathway continues in the next fracture even if the stream splits. A multitude of pathways can be traced by using particle tracing. This method allows the tracing of particles also at intersections. In contrast to the stream-tubes the pathways will have a stochastic nature as the particle has to choose which way to go at a fracture intersection.

If the diffusional movement in the fracture could be neglected a “particle” could be followed by streamline routing through the network. As will be shown later the molecular diffusion across the narrow fracture aperture is mostly so large that essentially full mixing takes place across the distance of the fracture aperture. Because of this mixing in the fracture the particle will randomly choose the exit paths in proportion to the flowrates in the outgoing streams. This is commonly assumed for network models in PA applications.

When two or more streams meet at an intersection and exit in two or more fractures it is also assumed that they have mixed at the intersection. As in the porous medium case it is then possible to sum up the volume of each pathway to obtain the residence time for the stream of water. Also the fracture surface contacted by the stream that is traced out by the particle can be determined.

It may be noted that in the strict application of the streamtube concept all particles originating from the same point will follow the streamtube to the same exit point. With particle tracking, particles from the same point can follow different paths and end up in a multitude of different locations.

The particle tracking can be seen as equivalent to tracing very thin streamtubes through the system. It can be understood from the following. Consider a very large number of particles released from one point. The number is chosen so large that however many divisions at fracture intersections the original mass of particles has to make, there are still sufficient particles to split at the next intersection. Follow particle # 1 through all divisions, then particle # 2 etc. They will have taken different flowpaths in general. Some pathways will carry more particles than others and can be identified as being more preferred than others. Every particle will have seen its portion of the FWS according to Equation (4) and (5) when it arrives at the observation point.

The entity of interest is A_q/q. This avoids the difficulty to conceptualise the ever-smaller streams and ever-smaller surfaces these streams contact. The smaller the stream q is the smaller the A_q will be but the ratio will still be a non-vanishing number.

One still not fully explored question is how fine a resolution in the 2D fracture is meaningful. A very fine discretisation becomes meaningless if the diffusion between this and other adjacent streams in the fracture plane cannot be neglected. This will be discussed in a later section.

Equation (1) is solved for every pathway traced out by the particles in the fracture. By using a multitude of fine pathways this method is equivalent to using streamtubes, especially if the dispersion along the streamlines is disregarded. “Dispersion” will still be observed in this case because the RTD along each pathway is different. By collecting the waters from different paths into one stream as they enter the biosphere (or any other cross section we choose) a tracer pulse will seem to have dispersed because it arrives at different times through the different paths. This effect usually dominates over the effect of “hydrodynamic dispersion” in an individual pathway.

2.1.4 Common traits of the models

In both the porous medium and the fracture network approach the hydraulic properties of the system contains some deterministic information and some stochastic information. Deterministic information is e.g. location of a canister, topographic information and location of major fracture zones. The properties of the rest of the rock mass are assigned values for the different parameters that are taken from a stochastic distribution based on field observations.

A large number of different realisations of rock masses are made and for each realisation the flow field and solute RTD are calculated for the multitude of particle pathways. The resulting information can be summed as ensemble averages and give e.g. breakthrough curves for a nuclide at a location of interest. Also the variability of the breakthrough curves can be estimated from the differences between the different realisations. The multitude of different pathways is found to have different lengths, volumes and FWS surfaces.

In practice the particle tracks are obtained in the following way in many models. A particle is introduced into a stream at a chosen inlet location. As the particle arrives at the first intersection it is directed to one of the intersecting channels, randomly, in proportion to the flowrates of the exiting channels at that intersection. A multitude of particles is released, one after another, and each will follow a different path through the network. The RTD from a release point to the biosphere is obtained by making a histogram of the number of flowpaths in different residence time intervals. The random assignment of different routes at the channels intersections is equivalent to stating that waters from two ore more channels that meet at a point are fully mixed before they enter the effluent channels.

2.1.5 The RTD of solutes along a flowpath or a streamtube

Having traced out the flowpath or the stochastic flowpaths by particle tracking we now turn to how to assess the RTD of solutes along a path. This entails the determination of how the solutes that interact with the matrix by molecular diffusion will behave along the flowpath.

Equation (1) describes the solute as it travels with the water along a flowpath including the interaction with the rock matrix. Account for this interaction is made by a mass balance equation that describes the migration and sorption in the matrix. It is given by Equation (7) below

$$\frac{\partial c_p}{\partial t} = \frac{D_p}{R}\frac{\partial^2 c_p}{\partial z^2} \tag{7}$$

$$R = 1 + K\frac{1-\varepsilon_p}{\varepsilon_p} \tag{8}$$

For a case where the penetration depth into rock matrix is smaller than the distance between fractures and the diffusion and dispersion along the flowpath is negligible, the residence time distribution of a solute can be described by a simple relation, Equation (9), that shows the effluent concentration, c_f, from a streamtube that is instantaneously injected with a given mass, *M*, of solute (Neretnieks 1980). The relation is obtained by solving Equation (1), neglecting the dispersion term, and Equation (7) together with the appropriate initial and boundary conditions. There are other models that include dispersion and limited matrix diffusion but it suffices for the purposes of this document to discuss the properties of Equation (9). For an instantly injected mass of tracer M at the inlet the concentration at the outlet of the stream tube can be obtained from

$$c_f q = \dot{m} = \frac{MG}{2q\sqrt{\pi}}\frac{e^{-\frac{G^2}{4q^2(t-t_w)}}}{(t-t_w)^{3/2}} \tag{9}$$

For a step input with a concentration c_o the effluent concentration is

$$\frac{c}{c_o} = erfc\left(\frac{G}{2q\left(t-t_w\right)^{1/2}}\right) \tag{10}$$

where

$$G = 2\int_0^L MPG(s)W(s)\,ds \cong 2MPG\int_0^L W(s)\,ds \tag{11}$$

and

$$MPG(s) = \varepsilon_p \sqrt{D_p(1+\frac{(1-\varepsilon_p)K}{\varepsilon_p})} = \sqrt{D_p\varepsilon_p(\varepsilon_p + (1-\varepsilon_p)K} \cong \sqrt{D_p\varepsilon_p K} = \sqrt{D_e K} \tag{12}$$

The Materials Property Group, MPG, contains information on pore diffusivity D_p, sorption coefficient K and matrix porosity ε_p. All these entities may vary along the flowpath s. For sorbing nuclides the approximation of the two rightmost expressions in Equation (12) can be used.

In several publications the term *G/q* is expressed differently e.g. in SITE-94 (1996) and in SR 97, Poteri and Laitinen (1999), Cvetkovic et al (1999) but the meaning is the same. This has lead to some confusion. Furthermore some authors base their equations on fracture aperture and velocity whereas others prefer to use fracture width and flowrate. It is shown here, Equation (13), that the formulations are equivalent.

Not carrying the term MPG through the equation the following is obtained

$$\frac{G}{q}\frac{1}{MPG} = \frac{A_q}{q} = 2\int_0^L \frac{W(s)}{q}ds = 2\int_0^L \frac{W(s)2b(s)}{q2b(s)}ds = 2\int_0^L \frac{1}{u(s)2b(s)}ds \tag{13}$$

It is seen in Equation (13) that integrating *W(s)* over the flowpath is equivalent to integrating *1/[u(s)2b(s)]* over the same flowpath. We choose here to use the formulation with the flowpath width *W(s)* because it is easily related to an “observable” physical entity whereas the aperture *2b(s)* is not easily measured and must also everywhere be coupled to the aperture and the local velocity. The property of the streamtube that the flowrate q of the stream is constant throughout makes the conceptualisation of the physics of the process rather simple.

The most important equation to discuss is Equation (11). This shows the influence of the FWS for the stream where q is constant and that this can be simply added (integrated) from inlet to outlet of the stream or flowpath as stated in Equations (4) and (5). This was shown previously by (Lee et al 1990). APPENDIX 1 gives a full derivation of the equation for variable properties along the flowpath.

Thus when matrix diffusion is active the total FWS of the flowpath is the entity that determines the matrix diffusion effects. It should be noted that although the MPG is formally under the integration sign and can vary along the flowpath it is commonly assumed to be constant because of lack of data and Equation (11) simplifies to Equations (4) and (5) times the MPG.

It is found that in PA applications the group *G/q* has such values that Equations (9) and (10) give results that very often depend little on the residence time of the water t_w. This also applies when the flow is through complex networks or streamtubes in the porous medium approximation. The reason is that the matrix interaction is so strong that it totally dominates the process. The solutes (nuclides) are so strongly retarded by this effect that the water residence time is negligible.

2.1.6 Some different implementations of fracture network models

Because there is no need to differentiate between what a stream does during its passage through one fracture and the next, different implementations of the fracture network models have chosen slightly different ways of approximating the fracture structures.

Some models, e.g. NAPSAC (Hartley 1998), discretise every fracture into small elements. This permits tracking the particles in the detail that the discretised elements have. Other models e.g. the CNM (Moreno and Neretnieks, 1993) and FracMan (http://fracman.golder.com) commonly average the properties over the whole fracture although FracMan also can treat variable aperture fractures. Using the same size computers, the discretisation within in the fractures will allow fewer fractures.

There are two commonly used programs that implement detailed information of fracture sizes and orientation, NAPSAC (1998) and FracMan.

In a simplified fracture network model specifically designed for tracing radionuclides and their matrix interaction, the Channel Network Model, CNM, (Moreno and Neretnieks, 1993) the fracture is taken to be a path with constant transmissivity. Each path is called a channel in this model. One special trait of the model is that it specifically includes flow conduits *along* the fracture intersections. This has been observed to occur in fractured rocks.

In applications of these models the flowrate in every fracture/channel in the network is calculated for a given situation. Thereafter an injection point is selected and a particle is tracked through the system. For every channel the stream passes, the fraction of the volume of the fracture that the stream passes is added according to Equation (14) and the FWS of the channel is added according to Equation (15). The fraction is simply obtained as the same fraction of volume (or surface) as the fraction of our stream to the total flowrate in the fracture or channel.

$$\frac{V_q}{q} = t_w = \sum_i \frac{\mathrm{V_i}}{Q_i} \tag{14}$$

$$\frac{A_q}{q} = \sum_i \frac{\mathrm{A_i}}{Q_i} \tag{15}$$

V_i and A_i stand for the volume and FWS of fracture "*i*". By making q arbitrarily small even the smallest Q's can be accommodated.

The essence of this method of obtaining the FWS along a flowpath is used in e.g. Moreno and Neretnieks (1993), Poteri and Laitinen (1999) and in the FracMan model (http://fracman.golder.com).

After having passed all fractures to the effluent point the total t_w and the total G is obtained. If information is available on the variation of the *MPG* along the flowpath this information is also used in integrating Equation (11). Equation (9) then can be used to determine the RTD along this flowpath. Models that discretise within the fracture, average over the area of the discretised element, whereas the other models implicitly average over a whole fracture.

As a particle may stochastically chose different channels at every fracture intersection, a large number of particles are tracked. Also because the network itself has stochastic properties a fair number of realisations are made of different networks. The ensemble RTD of the different paths and networks make up the total RTD of the case studied.

To illustrate the use of a network model the simplest of them is used. In the CNM (Moreno and Neretnieks, 1993) the channels are modelled as flat features connected in a three-dimensional network. The hydraulic properties of the channels are taken from a stochastic distribution based on observations in boreholes. The water is assumed to be fully mixed in the direction perpendicular to the flow direction. Also at every fracture intersection the waters in incoming fractures are fully mixed before they divide the water into the outgoing fractures. A further trait is that flow may be specifically allowed along the fracture intersections themselves by assuming that these also are conduits. The fracture density and the hydraulic transmissivity distribution are taken from observed distributions in boreholes. The fracture statistics and especially the CFF contain information that allows to assess the specific FWS, a_R, of a given volume of rock.

In order to model very large rock masses where many millions of fractures would have to be included the number of fractures are reduced and the network is made sparser. In order to preserve the same FWS per volume of rock, a_R, and flowrate in the whole rock mass, the “surface” of each channel and the transmissivity of the channel is increased by the same factor that the *CFF* was reduced. This preserves the total FWS/q of the rock mass.

The fracture apertures are in practice poorly known and various assumptions can be used to relate aperture to transmissivity. None of them seem to be generally valid (Neretnieks 2002). For the purposes of this report where primarily conditions that are of interest for PA are discussed, this is of little importance. We discuss primarily the RTD of nuclides in slowly seeping water from a deep geologic repository. Then the matrix interaction effects on the RTD totally dominate over the water residence time itself. This reduces the need to determine the actual fracture apertures. If needed, the water residence times along the different pathways are obtained as shown by Equations (2) and (3).

2.1.7 Mixing between streams, across fracture apertures, along fractures and at fracture intersection

It is of some interest to consider how mixing takes place or does not take place in various situations. This will indicate whether the streamtube approach is permissible or not. It will also indicate when a higher spatial resolution is not needed or even would counteract the expected higher accuracy.

In laminar flow or in stagnant liquids, mixing takes place by molecular diffusion. Consider a stream of water d thick, originally pure, that is suddenly exposed to a constant concentration c_o of a species at one side of the stream. The stream is invaded by the diffusing species and will eventually attain the concentration that is maintained at the surface. The concentration profile in the stream will evolve over time as shown in Figure 6. d could be the half aperture or half the stream width of a stream exposed at both sides to concentration c_o. The figure shows how the diffusing species penetrates further and further into the stream with time. For dimensionless time, Dt/d^2, less than

0.01 the diffusing species have penetrated a very short distance. For a dimensionless time larger that 1 the stream has practically equilibrated with the surface concentration (Carslaw and Jaeger 1959).

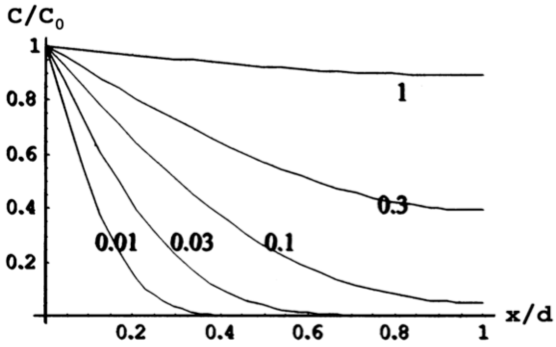

Figure 6. Concentration profile in a stream that has been exposed to a surface concentration for different dimensionless times Dt/d^2.

With these simple criteria one can readily determine weather there is good or poor mixing in a stream or between streams.

First consider the diffusional mixing across the fracture aperture. The diffusivity in water of small molecules is on the order of $D_w = 10^{-9}$ m^2/s. Typical fracture apertures range from 0.5 mm and downwards. The time needed for full mixing, $Dt/d^2 = 1$, across a 0.5 mm fracture, d=0.25 mm is 60 seconds. This is a very short time compared to the residence times expected in fractures under PA conditions. Thus if two different streams meet and travel in a fracture, flat side touching flat side, they will be fully mixed after a very short time.

Two different streams that enter a fracture side by side, touching as shown in Figure 7, will need a longer contact time and will travel a longer distance before they loose their identity as we conceive them to be wider that the aperture.

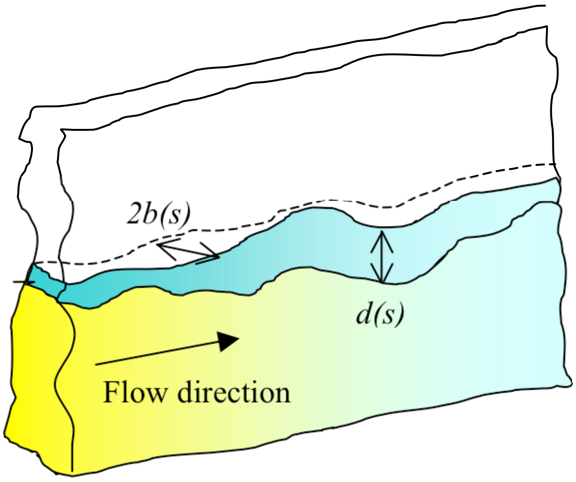

Figure 7. Two streams travel side by side in a fracture and exchange dissolved species with one another by molecular diffusion.

As an example consider a case where the rock has a hydraulic conductivity of $K = 10^{-8}$ m/s, a flow porosity of $\varepsilon_f = 3\text{x}10^{-4}$ and there is hydraulic gradient $i = 0.003$. These are not unusual values encountered in fractured rocks at depth and for PA conditions.

The average water velocity is $u = 10^{-7}$ m/s or 3 m/y in the fractures. The residence time in a 3 m long fracture is 1 year. A stream would then be totally mixed and loose its identity if it is less than 0.2 m wide.

Sorbing species will be retarded in their sideways diffusion. A surface retardation factor of e.g. $R_a = 100$ for a sorbing species would make streams larger than 2 mm keep their identity during the same time. However, as the sorbing species will be retarded in the flow direction also by the same factor the sorbing species in the stream will have more time to spread sideways with approximately a factor equal to the retardation factor. Thus also the sorbing tracer pulse will spread out sideways by tens of cm in one fracture in this example. Another way of visualising these phenomena is to look at the boundary between two wide streams and study the diffusional fringe at the contact between the streams.

In a fracture with ten times lower transmissivity, streams more than half a meter wide would loose their identity over the same distance.

In fracture network models that do not explicitly account for diffusion in the flowing water it would not seem necessary to discretise finer than tens of cm to a meter. In network models that model diffusion in the fracture plane on the other hand the discretisation must be finer in order to resolve details in the diffusional mixing.

Mixing at intersections such as that depicted in Figure 5 can also be assessed with this method. The water passing an intersection 0.5 mm long will have a residence time of 5000 s using the velocity in the previous example. This is much larger than the 60 s needed for full mixing.

In summary: It is assured that there is a negligible concentration difference across a fracture aperture and probable that two streams that meet flat side by flat side at an intersection will have good chance of mixing fully. Streams that travel side by side in a fracture may or may not mix well depending on their widths. Mixing is expected to take place over distances ranging from tens of cm to meters in PA conditions. However, full mixing over the width of large fractures is not assured.

The often-used assumption in fracture network models that streams mix at intersections and across fracture apertures is reasonable when they meet flat side by flat side.

2.1.8 Experiments and observations to obtain data for the models

Below, the main issues and general approaches of data gathering are outlined. Different organisations emphasise different issues and adapt the investigations to their specific sites and needs.

The porous media based models that calculate the flow field by solving the Darcy equation in three dimensions typically use bulk hydraulic conductivities as a basis for the calculations. Often a stochastic approach is used where every cell or element in the discretised space is assigned a conductivity value. Typically, if the discretised element in the model has a linear extent of 30 m, an average value of the conductivity for a 30 m cube or tetrahedron would be used. Average values are estimated from e.g. double packer hydraulic conductivity measurements with a packer distance of 30 m in boreholes. Such a measurement is assumed to average the transmissivities of the different fractures in the 30 m sections. However, there are a number of reasons why this assumption may not be valid, including the fact that borehole diameter is commonly orders of magnitude smaller than the size of rock block.

Another approach is to use detailed flowrate (transmissivity) measurements from boreholes where much narrower packer or otherwise isolated distances or other more modern techniques such as incremental flow logging have been used to identify practically every flowing fracture and obtain data on the individual fracture transmissivities. Then average values for the 30 m volume are obtained by using a fracture network model covering volumes of 30 m cubes and assessing the average transmissivities and variances of a multitude of such volumes. If fracture orientations also are known then direction dependent transmissivities can be assessed.

Measured flowrates Q of the individual fractures give information on the flowrate distributions $f(Q)$. The flowrates have been obtained using an imposed head difference. These are usually used to estimate the transmissivity distribution $f(T)$ of the fractures.

The determination of the $f(T)$ is model dependent. For use in a network model, $f(T)$ should ideally be determined by making the modelled network $f(Q)$ in the model boreholes agree with the observed $f(Q)$. The mean and variance of the $f(T)$ distribution are obtained by minimizing the difference between observed and modelled $f(Q)$ distributions in the boreholes.

In a network model with variable transmissivity fractures the same model must be used to determine the $f(T)$ of the fractures. An inherent assumption then is that all fractures have the same $f(T)$. In models that assume that each fracture has a constant transmissivity the $f(T)$ of the fractures should be determined using that specific model.

In the network models the $f(T)$, CFF and possibly orientation information, in essence contain the information needed to obtain the flowrate distribution and information to do the particle tracking to obtain the residence times and A_q/q's along the tracks.

For the porous media models there remains to assess the specific FWS in the rock, a_R, for use in Equation (5). One way to do this is described in Moreno and Neretnieks (1993) and Moreno et al. (2001). In essence it is based on the following idea. If there is a fracture spacing S between flowing channels as measured in the boreholes then there must be a FWS, a_R m^2/m^3 of rock, on the average of 2/S if all the channels lie in parallel planes and have an infinite extent. They of course are not infinite but if they are finite in widths then the same applies because there would have to be as many more channels to be intersected on the average at a distance S. Because the channels can be (randomly) oriented in space in many different directions the specific FWS for random 3D orientation is larger. The relation between the measured average fracture distance S, the FWS a_R and the CFF, for a uniformly random 3D orientation is

$$a_R = \frac{4}{S} = 4 \cdot CFF \tag{16}$$

This relation is a simplification but conveys the essentials. Geier (1996), Andersson et al., (1998), Holmén and Outters, (2002) discuss the finer details and the biases involved.

There is no information on how large a portion of a fracture that the measured local *Q* represents and thus the relation between a flowrate and the sample surface size. It is therefore commonly (and implicitly) assumed that all measurements represent the same surface areas irrespective of the magnitude of the flowrate. This problem is partly circumvented if the same model is used to determine the distribution *f(T)* from the flowrate distribution *f(Q)* as later used in simulations.

The transmissivity distribution *f(T)* in the channels and a_R for the rock mass are determined for the experimental site as described in the example below.

However, as discussed previously an a_R determined in this way may not be well applicable to porous media models for solute transport because it is at present not clear how a weighted average should be made, considering the very different flowrates in fractures with different transmissivities.

An example of a transmissivity distribution of individual fractures is shown in Figure 8. The data are from the Äspö Site (Neretnieks and Moreno 2003). 162 0.5 m sections were measured for flow. Of these 112 were found to carry water. In addition, a few sections varying in length between 1 and 8 m were found to carry water. These sections were not used in the analysis. About 30 % of the 0.5 m sections had flowrates below the detection level. This number indicates that the average channel distance is slightly smaller than the section length 0.5 m (Moreno et al., 2001).

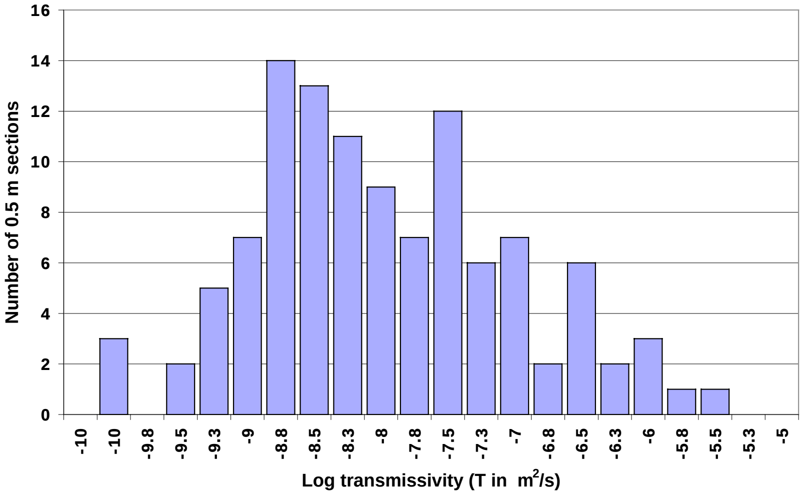

Figure 8. Frequency of transmissivities in five boreholes around Feature A at Äspö.

Measurements are made in the rock that makes up a three dimensional network of fractures with strongly varying transmissivities in the fracture plane and probably also varying transmissivities between different fractures. The flowrate from or into an individual fracture is measured when the head in the borehole has been changed. The flow in an individual fracture is not directly proportional to the local transmissivity.

Local gradients are unknown and may be very different from fracture to fracture. A highly conductive fracture e.g. cannot be fed much water from the low conductivity fractures that feed into it. The transmissivity of such a fracture would be underestimated if some average gradient were used. This difficulty is circumvented using a fracture network model to obtain the observed flowrate distribution by adjusting the parameters of the transmissivity distribution that goes into the model.

The difficulty may be illustrated as follows. A packed section of a borehole intersects one fracture. The flowrate in this section together with all other sections is to be used to assess the transmissivity distribution of the fractures and the local FWS. For the latter the question is if each measurement of a transmissivity represents an equally large region around the borehole.

The following assumption is inherently made for the FWS of the flowpaths:

The flowrates measured in the packed of sections in the boreholes represent equally large areas of a fracture.

This is an important assumption. It implies that the flowrate distribution also is a distribution of flowrate to flow wetted surface, q/A_q. It does not matter that we at first do not know what surface area the measurements actually represent, because the measurements also give the total specific FWS, a_R. Every fracture (or part of fracture in models that use variable aperture fractures) in the model is then implicitly assigned the same FWS. These matters should be further studied.

Detailed fracture network models based on fractures with variable properties in the fracture planes will typically first solve the detailed flow field in fractures and network and then follow the flowpaths by e.g. particle tracking. There will be several flowpaths in every fracture that may be thought of as channels in the channel network sense.

One question to address in the network models is how to average and scale the hydraulic properties when decreasing the spatial resolution in the fracture. Averaging the flow in a variable transmissivity fracture over a whole fracture plane will lead to a smaller variance between the averaged fractures than the variance of the elements or “patches” in the fractures. The variance of the transmissivity along a path is expected to decrease inversely proportional to the number of elements the path has traversed. This effect does not yet seem to have been discussed much.

Recently a detailed plan on how to gather relevant information from field experiments and observations has appeared (Rhén et al., 2003).

2.1.9 Discussion on differences between models

For sorbing species, provided the same FWS/q is used, comparisons between the models give similar results when they model the same case. This is illustrated in the following example.

The RTD in a rock mass modelled with a network model is compared to that obtained by a porous medium model. Comparisons are made for the same input data. A cube with 100 m sides is subjected to a pressure difference between two parallel sides. The other sides are closed.

There are about 36 000 channels arranged in the cubic grid. The specific FWS in the rock a_R is 1 m^2/m^3 and it is divided up equally among the channels. The average transmissivity of the channels is chosen such that a hydraulic conductivity, $K_h= 10^{-8}$ m/s is obtained.

The flowrate in the channels in the CNM is determined for the chosen gradient, which is the same in the porous medium model.

For the porous medium model there is a need to have a dispersion coefficient D_L in order to obtain the same dispersion for the water as in the network model. The approach here is that D_L should be such that a non-interacting tracer will have the same dispersion in the two models. D_L for the AD model is obtained in the following way.

For the CNM a number of realisations were made using a chosen standard deviation of the transmissivities. It is taken to be 1.6 on the ^{10}Log scale, which is in the range of values observed in boreholes. In each realisation 25 release points were selected as shown in Figure 9.

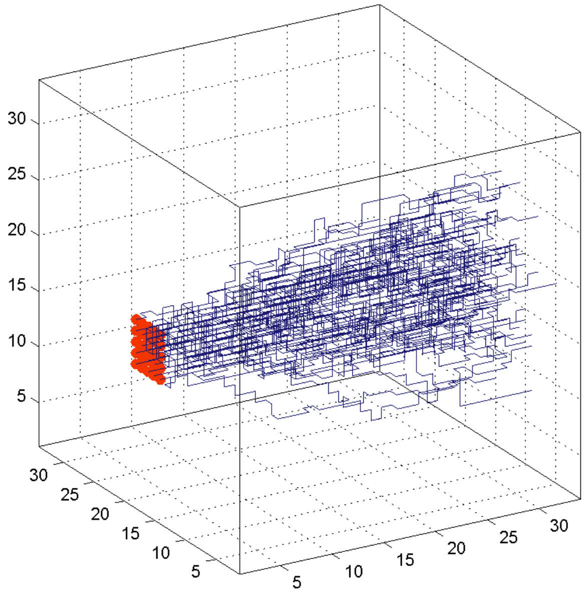

Figure 9. Trajectories in a 100 m cube space for the above example for a group of nearby release points.

Figure 9 shows one example of the distribution of a number of trajectories obtained in the CNM.

Breakthrough curves were generated for the particles following the water and at first not accounting for any interaction with the rock. The cubic law is assumed to be valid to obtain the relation between aperture and transmissivity. The breakthrough curves give the residence time distribution of the water. From this the dispersion coefficient D_L can be determined. The dimensionless Peclet number is used to summarise the dispersion effects. The average Peclet number for all the realisations was found to be about 14.

The solution to the AD model used that derived by Tang et al. (1981). It is based on the transport in a single fracture with an infinite matrix and with hydrodynamic dispersion. It is the solution to Equations (1) and (7). The network model uses the same equations, but for each individual channel in the network, and without the dispersion term. Thus so far the network model and the AD model give the same flowrate and RTD for a non-interacting tracer. The network model, being a stochastic model, does this on the average.

Next, matrix interaction is included in the CNM. The swarm of breakthrough curves is shown in Figure 10. The data used are given in the list below. They are within the range of values found for fractured rock in Sweden and for PA conditions.

The breakthrough curve for the AD model with the same data and the same flow wetted surface to flowrate ratio, *FWS/Q*, and a Pe of 14 is then used to determine the Break Through Curves, BTC, for the AD model by Tang et al. (1981). The sorption coefficient is chosen such that the penetration depth into the matrix is much smaller than the distance between the channels.

In addition the case for no dispersion in the AD model is included. The results are shown in Figure 10.

The following data are used in the example. They are reasonably representative for fractured rocks in Sweden and for PA conditions.

Data used in the example:

$K_h = 10^{-8}$ m/s
$L = 100$ m
$i = 0.003$ m/m
$D_p = 2 \cdot 10^{-11}$ m^2/s
$Pe = 14$
$K = 1$
$\varepsilon_f = 3 \cdot 10^{-4}$
$\varepsilon_p = 5 \cdot 10^{-3}$
$a_R = 1$ m^2/m^3
$\sigma_{cLog10} = 1.6$

Derived entities:

$u_f = K_h \cdot i / \varepsilon_f = 10^{-7}$ m/s –> 3m/a
t_w –> 32 a

Results for the case of no dispersion, and for dispersion for the porous media cases are shown (the two full lines) and also results for a number of different realisations for the channel network. The latter show an earlier breakthrough than the two other cases.

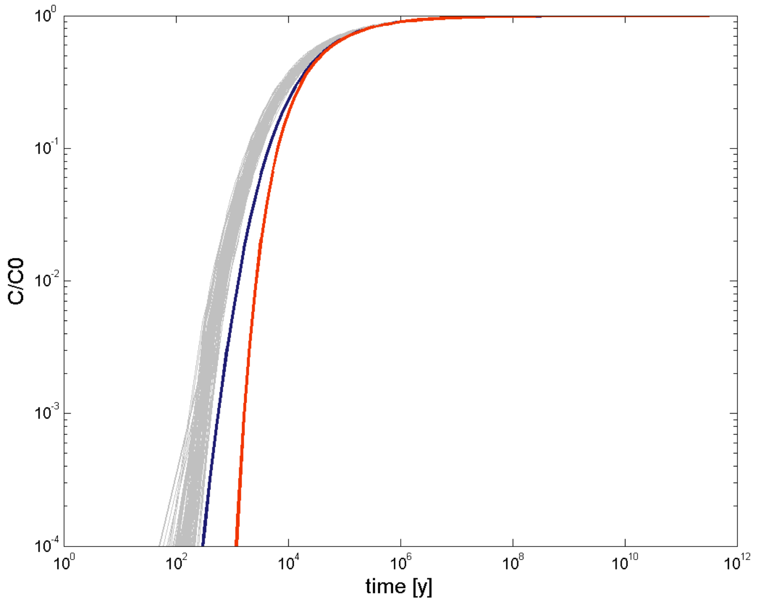

Figure 10. BTC's from left to right for CNM (swarm) Moreno and Neretnieks (1993), Tang et al (1981), and single channel (Neretnieks 1980).

The porous media and the network models predict rather similar break-through curves. The non-dispersion case is included to illustrate that dispersion effects cannot be neglected. The results are sensitive to the transmissivity distribution in the network model and the dispersion in the porous medium model, especially for the early times. They are extremely sensitive to the magnitude of *FWS/Q*. The influence of *FWS/Q* is very much larger that that of all other entities and will dominate the uncertainties even between the two model concepts. An increase of the FWS by a factor of three would shift the curves to the right by nearly a factor of ten in time.

Thus although the porous medium and the network models are seemingly very different the RTD for nuclides that interact with the rock matrix by diffusion are not very different, provided the same data are used in both model approaches.

It is somewhat unexpected that the porous medium model and the network model give rather similar results. It has generally been expected that the averaging of the FWS and the flowrate *q* independently, as done in the porous medium model, would over-emphasise the interaction between the water and the rock compared to the network models where the large flowrates in some passages will not be exposed to so large a surface. The differences are so small that it seems possible to use the AD model and streamtube approach at least for scoping calculations.

2.1.10 Simplified rules to assess whether a flowpath may be important

Some pathways will transport the solutes very slowly. Paths with solute residence times that are much longer than the times of interest for the safety assessment can be given much less attention than more important paths in the detailed PA. A simple way of making a first estimate of the importance of a flowpath is to calculate the early arrival along a path from Equation (10), which gives the relative effluent concentration for a constant input. A choice of what "early arrival" means is arbitrary. Choosing the argument, *arg*, of the erfc(*arg*) function to be unity gives a time $t_{c=0.16}$ for a the outlet concentration to be 16 % of that at the inlet. The relation is simply

$$t_{C=0.16} = t_w + (\frac{G}{2q})^2 \tag{17}$$

Choosing instead a concentration of 10^{-5} gives $t_{C=0.00001} = t_w + 0.01\,(\frac{G}{2q})^2$.

A similar approach can be used to assess the fate of a specific nuclide that decays with a decay constant λ. The radionuclides decay during their transport through the rock and when the rate of decay is large in relation to the rate of transport the nuclides may decay to insignificant concentrations. It is possible to make a simple estimate of this effect for a nuclide injected as a pulse or as a decaying band release.

For a nuclide that is released into a stream from the source with a concentration $c_o\, e^{-\lambda t}$ and

travels through a streamtube the effluent concentration is directly obtained from Equation (10) multiplied by the decay. For cases when t_w can be neglected the expression can be simplified to

$$\frac{c}{c_o} = \operatorname{erfc}\left(\frac{G}{q\left(t-t_w\right)^{1/2}}\right)e^{-\lambda t} \cong \operatorname{erfc}\left(\frac{1}{\sqrt{\tau}}\right)e^{-\Lambda\tau} \tag{18}$$

Where

$$\Lambda = \lambda\,(\frac{G}{q})^2 \tag{19}$$

$$\tau = \frac{t}{(\frac{G}{q})^2} \tag{20}$$

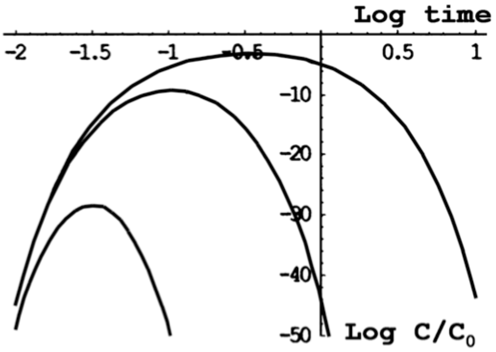

Figure 11. Effluent concentrations for a decaying nuclide for Λ=10, 100 and 1000 from right to left.

It is seen in Figure 11 that for Λ larger than 1000 the nuclide effluent concentration will be less than 10^{-30} of that at the start of the release. This simple result can be useful to identify which nuclides will not have to be considered further in large detail.

2.1.11 Revisiting some assumptions and simplifications in the models

The previous model descriptions were made with an emphasis on simplicity in concepts and models in order to bring out the main traits of the models. Many assumptions and simplifications were implicit and not specifically highlighted. In this section some of these are discussed and their possible impact on the PA are mentioned.

The model for solute transport and interaction with the porous rock matrix is originally based on the idealised flow between two flat surfaces whereas real fractures have varying apertures. This leads to a varying flow in the fracture. This is handled by introducing variable aperture fractures in the network models. However, the data needed for such models are seldom, if ever, at hand. Numerical studies using different assumption on the aperture variability are therefore commonly used to assess the sensitivity to aperture variations.

Data on the transmissivity of any channels formed by and in fracture intersections are not available. Flowrates and patterns can be influenced by such channels.

Positive correlations between fracture sizes and transmissivities are deemed probable and can give rise to fast pathways over long distances. Correlation data are sparse and numeric tests are made to explore the impact of such correlations.

There are still questions about the extent of the connected matrix porosity. Should the connectivity extend only a short distance (a few cm) the retardation due to matrix diffusion could be less than if many tens of cm or more are connected.

Flow porosity, which directly influences water residence time, is poorly known but does not seem to have an important influence on the nuclide flux. In the PA studies it is found that the non-retarded nuclides such as I^{129} and C^{14} will not have time to decay irrespective if the water travel time is one year or 1000 years. The sorbing nuclides are very little influenced by the water travel time as has been shown previously.

The measurement of conducting fractures and interpretations to obtain the CFF/FWS and the further use of this information in the models is not straightforward and much work is still done in this area. In general there is the question whether we sufficiently understand the basic structure of fractures, fracture intersections, fracture aperture and transmissivity variations etc. This lack of data and understanding is deemed to be a considerable cause of uncertainty.

There is usually very limited information on transport properties of and in fracture zones and thus there are considerable uncertainties when modelling solute transport in these features.

There are observation of what is deemed to be unusually fast pathways. There is not a full understanding of what might cause such effects.

It is accepted that there will be varying flowrates, flowpaths and flow directions over the very long times that are considered in many PAs. Work has commenced to study the impact on nuclide migration in time varying systems.

The uncertainties mentioned above and others not mentioned must be handled in PAs. In some cases it can be made credible that one can use “conservative” data to insure that not too optimistic results are obtained. This is not always possible, however, especially in the cases where the underlying structures and interpretation of the data are not unequivocal. Often a number of different assumption and their consequences are explored in the PA calculations with the aim of bounding possible uncertainties. A considerable effort, both computational and in meetings and workshops is usually spent on these matters.

2.1.12 Some issues that are further studied

Solute transport under conditions of flow varying in time due to changing boundary conditions has been studied by Moreno et al. (2004) and Svensson at al. (2004). It is found that under e.g. situations where the shoreline changes there can be considerable changes in flowrates and flow directions.

Salt density effects on flow are studied by Svensson et al. (2004), They include the diffusional release of salt from brines in the rock matrix to the water flowing in the fractures. The impact on flowrate distribution can be considerable.

Power law distributions of fracture sizes have been observed on several outcrops and this is being incorporated in flow and transport models. Correlations between size and transmissivity of fractures are also being studied in the Swedish program and at the Äspö laboratory.

The penetration depth of rock matrix by diffusion is studied in deep boreholes using electrical conductivity methods. Löfgren and Neretnieks (2003). Early results suggest that the penetration depth is at least on the order of metre(s).

2.2 WATER CHEMISTRY AND SORPTION

2.2.1 Water chemistry

The sorption properties of minerals depend on the chemistry of the solutions that interact with them. Chemical reactions affecting solution chemistry can be

- homogeneous, i.e., when reactants and products are all in the liquid phase, and
- heterogeneous, i.e., when there is an interaction between solid and liquid. Heterogeneous reactions include all types of sorption, precipitation/dissolution and coprecipitation.

In this section, attention is paid to homogeneous reactions. Two main types are distinguished: (i) Aqueous complexation and (ii) redox reactions.

2.2.1.1 *Aqueous complexation reactions*

Aqueous solutions are conceptualised as a medium where dissolved ions are in a state of continuous motion and are surrounded by a limited number of water dipoles. The numerous collisions make the formation of ion pairs and other more complex associations possible. Ions, ion pairs and complexes are called aqueous species. Since these reactions are almost instantaneous, they can be effectively considered as equilibrium reactions:

$$\nu_A A^{z_-} + \nu_M M^{z_+} \Leftrightarrow (A_{\nu_A} M_{\nu_M})^{\nu_M z_+ - \nu_A z_-} \tag{21}$$

The total number of species in solution can be distributed between N_c primary species and N_x secondary species. The number of primary species N_c, which is the number of independent chemical components in the system, will be given by the total number of species minus the number of independent chemical equilibria relating them. The different equilibrium relationships can be written as the production or destruction of one mole of secondary species, and take the form

$$A_i \Leftrightarrow \sum_{j=1}^{N_c} \nu_{ij} A_j \qquad (i = 1,2,...N_x) \tag{22}$$

where A_j and A_i are the chemical formulas of the primary and secondary species, respectively, and ν_{ij} is the number of moles of primary species j in one mole of secondary species i. The chemical equilibria provide an algebraic link between the primary and secondary species via the law of mass action for each reaction. The concentration x_i (mol/kg water) of a secondary species i is given by

$$x_i = K_i^{-1} \gamma_i^{-1} \prod_{j=1}^{N_c} \left(\gamma_j c_j\right)^{\nu_{ij}} \qquad (i = 1,2,...N_x) \tag{23}$$

where K_i is the equilibrium constant of reaction (22), c_j is the concentration (mol/kg water) of primary species j, and γ_j and γ_i are the activity coefficients of the primary and secondary species, respectively. The value of these activity coefficients depends in turn on the concentration of the species and can be calculated according to formulae more or less grounded in the electrolytic theory and empirical coefficients.

The total dissolved concentration of a given component or primary species C_j can be written in an explicit form as

$$C_j = c_j + \sum_{i=1}^{N_x} \nu_{ij} x_i \tag{24}$$

where N_x is the number of secondary species. Notice the difference between the concentration of an aqueous species arbitrarily considered as primary, c_j, and the total concentration C_j. Intuitively, C_j is coincident with the total analysed solute. In the case of protons, however, C_j could be positive or negative and is a measure of the 'total acidity' of the solution.

2.2.1.2 Redox reactions

The transfer of electrons between two different atoms changes their chemical oxidation state. This transfer is known as an oxidation-reduction reaction and is of special interest for the retention/migration of radionuclides. The redox potential of a chemical system can be described by means of redox pairs such as O_2/H_2O, SO_4^{2-}/H_2S, Fe^{3+}/Fe^{2+}, CO_2/CH_4, etc. Usually, the most abundant redox pair governs the redox potential. Even though this approach seems to be the most adequate, it is rarely used due to the difficulty of obtaining the analytical concentrations of the two species of a redox pair.

Among the different alternative approaches to describe redox reactions, the external approach considers a hypothetical activity of electrons as an aqueous component or a master species. The definition of this virtual concentration is useful because it allows completing the redox half-reactions and treating them as the rest of the chemical reactions in the aqueous phase. Each half-reaction is completed by adding electrons as transferable species:

$$\nu_e e^- + M^{z_+} \Leftrightarrow M^{z_+ - \nu_e} \tag{25}$$

Once the “free electron concentration”, $\boldsymbol{c_e}$, is known, the calculation of other redox indicators, such as the counter-part species of a redox pair, the concentration of dissolved oxygen ($O_{2(aq)}$), or the fugacity of oxygen gas ($O_{2(g)}$), can be easily calculated according to Equation (23).

Similar to acid-base reactions, the total concentration of electrons C_e represents the net electron balance or "electron excess" for all redox reactions, and may take on positive or negative values. In this way, redox reactions can be treated in the same way as the rest of equations. Contrary to the protons, which exist in reality as dissolved species, the free electron concentration is a hypothetical variable, and c_e does not participate in the calculation of the total electron excess (Equation (24)).

An alternative approach to describing redox processes is to write the redox reactions as whole-cell reactions. In this case, it is not necessary to consider the concentration of electrons in the system. An example of a whole cell reaction, describing the reduction/oxidation of iron in solution, can be written as

$$Fe^{3+} + 0.5H_2O \Leftrightarrow Fe^{2+} + 0.25O_2(g) + H^+ \tag{26}$$

It should also be noted that homogeneous redox reactions are usually slow and in many cases microbiologically mediated or catalyzed. The dynamics of these reactions cannot be described from purely thermodynamic considerations and are described by kinetic rate laws (Michaelis-Menten or Monod–type rate laws, or even more complex kinetics). These reactions are characterized by occurring in a well-defined sequence (e.g., in a reducing environment, oxygen consumption, denitrification, iron reduction, manganese reduction, sulphate reduction, methane generation). This type of reaction dynamics may cause zonation in redox conditions along flow lines.

2.2.2 Sorption

Sorption is a broad term describing the process of attachment of dissolved species to mineral surfaces. Although physical Van der Waals interactions are also possible, sorption is mainly referred to attachment by chemical bonding. The crystalline structure of the solids is interrupted at the solid surface, where a number of chemical bonds remain as functional groups, which provide a diversity of interactions with the aqueous species present in solution (Figure 12). It is a process limited by the availability of surface. Sorption is also considered as a reversible process. Sorption as a first step to form a solid solution is treated as precipitation and coprecipitation (see Section 3.2).

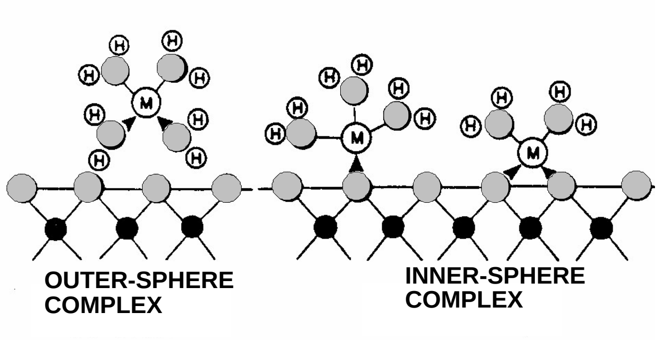

Figure 12. Structural arrangement of aqueous complexes at an oxide surface. In the outer-sphere complex, the metal (M) is attached to the surface without losing the hydration sphere of water dipoles. In the inner-sphere complex, the metal partly or totally loses the hydration sphere and establishes chemical bonds with the atoms in the crystalline structure. The grey circles represent oxygens and the small solid circles represent metal ions in the solid. The solid is below the horizontal line. (From Brown, 1990).

Sorption of aqueous species on solids has been described according to several models. A first group of models are empirical: they only describe by means of coefficients the experimental partition between the solute in solution and the solute adsorbed. Another group of models aims at representing the mechanism of the sorption reactions with a thermochemical formulation (thermodynamic sorption models, or TSM). These are the surface complexation and the ion exchange models.

2.2.2.1 Empirical models

Empirical models describe the experimental relationships between the concentration of solute in solution and the concentration of solute sorbed on the solid. As the experiments are performed at constant temperature these models are also known as isotherms. The most currently used are the linear (K_d), Freundlich and Langmuir isotherms.

Linear isotherm (constant K_d model)

It describes the process when the concentration of sorbed solute C_{XM} is linearly dependent on the concentration in solution C_M. This relationship is given by

$$C_{XM} = K_d \; C_M \tag{27}$$

The adsorption reaction of a metal can be written as

$$X + M = XM \tag{28}$$

where X means the surface sorbing site (no reactions with H^+ and OH^- are considered), M is the metal in solution and XM is the sorbed metal. No electric charges are required for this model. The equilibrium constant for the reaction will be given by

$$K_{ads} = \frac{a_{XM}}{a_X \, a_M} \tag{29}$$

Comparing Equations (27) and (29) one can deduce that the constant K_d model is based on the following assumptions:

- The concentration of surface sorbing sites is very large and is not affected by the amount of sites occupied by sorbed metals, i.e., there is no competition between species for a particular site ($a_X = 1$).
- The amount of surface sites occupied by metals is very small and has no influence on the behaviour of the rest of sites, i.e., the sorbed metals behave ideally and the standard state is a solid with a concentration of sites occupied by metal equal to 1 mol/kg water ($a_{XM} = c_{XM}$, in mol/kg water).
- There is only one species of a given metal in solution, i.e., $C_M = c_M$.
- The solute behaves ideally in solution ($\gamma_M = 1$).
- $K_{ads} = K_d$ (assuming that both constants are expressed in the same units)

The Freundlich isotherm

This model is based on the same assumptions as the constant K_d model and can be treated in identical way. The only difference is that in the Freundlich model the amount of sorbed metal is proportional to the concentration of metal in solution raised to a power exponent η determined experimentally:

$$C_{XM} = K_L C_M^{\eta} \tag{30}$$

In the case of $\eta = 1$ the Freundlich model is identical to the constant K_d model.

The Langmuir isotherm

It describes the process when the concentration of sorbed solute C_{XM} depends on the concentration in solution C_M and has a limiting value $C_{XM}^{\max}$. This isotherm has the form

$$C_{XM} = C_{XM}^{\max} \frac{K_L C_M}{1 + K_L C_M} \tag{31}$$

where K_L is an experimental coefficient for the sorption reaction.

The Langmuir isotherm is based on the same assumptions as the K_d and Freundlich isotherms, with a significant exception:

- The concentration of surface sorbing sites is limited. However, the competition of the different aqueous species for a particular sorption site is not explicitly treated in Equation (31).
- As with the constant K_d model, the free sorbing sites are not influenced by the nearby sites, i.e., they behave ideally. The standard state is a solid with a concentration of free sites equal to 1 mol/kg water ($a_X = C_X$ in mol/kg water).

Therefore, Equation (29) will in the present case be:

$$K_{ads} = \frac{C_{XM}}{C_X C_M} \tag{32}$$

There is an equivalence between Equations (31) and (32). Let us consider the simple case of adsorption of a cation *M*. Since no other competitive species are considered, the total number of surface sorption sites T_X (mol/kg water) is:

$$T_X = C_X + C_{XM} \tag{33}$$

Replacing C_X in Equation (33) by its value from Equation (32) , the following expression is obtained:

$$C_{XM} = T_X \frac{K_{ads} C_M}{1 + K_{ads} C_M} \tag{34}$$

Equation (34) is equivalent to the Langmuir isotherm (Equation (31)).

2.2.2.2 Surface complexation models

Some minerals such as metal oxides, hydroxides and layered silicates (Al_2O_3, TiO_2, FeOOH, SiO_2, kaolinite, etc.), commonly found as fracture fillings in the geosphere, exhibit electrically charged surfaces in the presence of natural waters. These surfaces contain ionisable functional groups (ex.: silanol groups in hydrated silica: Si-OH), being responsible for chemical reactions at the surface.

The sorption of solutes at the solid surfaces is described as chemical reactions between the aqueous species and specific surface sites. These surface reactions include proton exchange, cation binding and anion binding via ligand exchange at surface hydroxyl sites (represented here as XOH). For example, the sorption of a metal M^{z+} could be represented as:

$$XOH + M^{z_+} = XOM^{z_+ -1} + H^+ \tag{35}$$

Similarly to aqueous complexation, equilibrium for surface complexation reactions can be described by the mass law equation:

$$K_{intr} = \frac{\left[XOM^{z_+ -1}\right] a_{H^+}}{\left[XOH\right] a_{M^{z_+}}} \tag{36}$$

where K_{intr} is the equilibrium constant of the reaction, usually referred to as the intrinsic constant (Dzombak and Morel, 1990), a is the thermodynamic activity of the aqueous species (the product of the concentration in mol/kg water and the activity coefficient γ), and the terms in brackets represent the concentration of surface species (mol/kg water). As a first approach, in Equation (36) it is assumed that the behaviour of surface complexes is ideal, i.e., a particular surface complex is not influenced by the rest of sites (empty or full) in the vicinity. We will discuss the non-ideal behaviour caused by the development of a surface electric potential.

In aqueous complexation reactions, electric charge is distributed homogeneously in the solution. However, surface reactions take place on a fixed and charged surface, and that creates an electrostatic field. An additional energetic term accounting for the work needed for the aqueous species to travel across the surface electric field is required in the energy balance:

$$\begin{aligned} \Delta G^0_{ads} &= \Delta G^0_{\text{int}\,r} + \Delta G^0_{coul} = \\ &= \Delta G^0_{\text{int}\,r} + (\Delta G^0_{\Psi=0} - \Delta G^0_{\Psi=\Psi_0}) = \Delta G^0_{\text{int}\,r} + \Delta z F\,\Psi_0 \end{aligned} \tag{37}$$

where ΔG^0 is the standard Gibbs Free Energy change of the overall adsorption reaction, $\Delta G^0_{\text{int}\,r}$ and ΔG^0_{coul} are the standard Gibbs Free Energy changes due to chemical bonding and to the electrostatic work, respectively, Δz is the change in the charge of the surface species, F is the Faraday's constant (96485 C/mol) and Ψ_0 is the mean surface potential (V). Since

$$\Delta G^0 = -R\,T\,ln K \tag{38}$$

Equation (36) can be rewritten as

$$K_{ads} = K_{intr}\; e^{-\frac{\Delta z F\,\Psi_0}{RT}} \tag{39}$$

where R is the gas constant (8.3144 J/mol/K) , T is the absolute temperature (K), K_{ads} the equilibrium constant of the overall adsorption process and $K_{\text{int}\,r}$ does not depend on the surface charge.

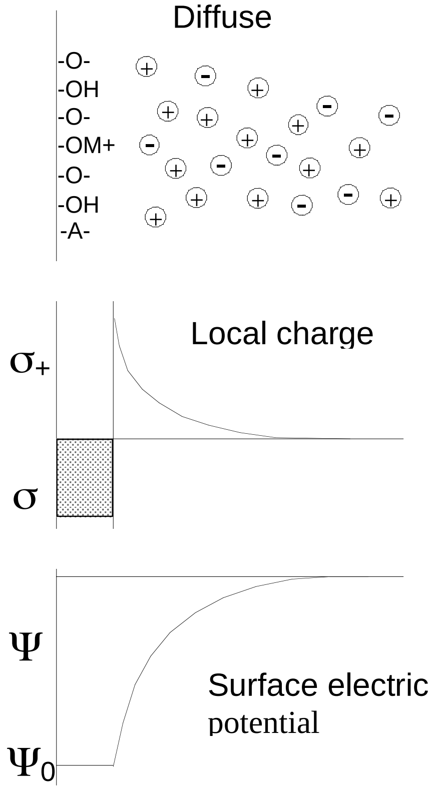

Figure 13. Schematic representation of the Diffuse Double Layer model. A fraction of the permanent negative structural charge of the mineral is compensated by protons, anions and cations attached to the surface as inner-sphere complexes. However, a fraction of the charge is still left uncompensated. The aqueous species in solution are reorganised by increasing the concentration of positive species towards the surface to compensate the excess surface charge. The excess surface charge and the potential changes as aqueous species are attached or detached.

In Equations (36) and (39) the thermodynamic activities of the surface complexes are substituted by their concentrations. This is based on the assumption that all non-ideal behaviour of the surface species is attributed to the mean surface potential and is accounted for by the electrostatic term.

By considering the electrostatic term in the equilibrium formulation a new unknown, the mean surface potential Ψ_0, is introduced. A new equation to find the solution of the problem is, therefore, required.

Several theoretical models describe the value of the capacitance of the surface, i.e., the relationship between the mean surface potential and the charge density. In order of increasing complexity, some of these models are: the constant capacitance model, the diffuse layer model and the triple layer model. The detailed discussion of these models is out of the scope of the present summary. The reader can obtain additional information in Dzombak and Morel (1990) and Davies and Leckie (1978). The option for a particular model depends on the amount of experimental data and degree of difficulty encountered when calculating the equilibrium constant(s) of the set of reactions proposed. In many cases no electrostatic term is assumed in modelling experimental data.

Titration experiments with oxyhydroxides and silicate minerals indicate that surface charge is a function of pH. At low pH surfaces are positively charged and at high pH are negatively charged. There is a pH where the surface charge is zero, the point of zero net proton charge PZNPC, which can be determined experimentally. Since sorption of cations and anions depends on the surface charge, it is important to consider, together with the sorption reaction (35), the protonation and deprotonation equilibria:

$$XOH + H^{+} \Leftrightarrow XOH_2^{+} \; + H^{+} \tag{40}$$

$$XOH \Leftrightarrow XO^{-} + H^{+} \tag{41}$$

As a consequence, sorption of cations increases from essentially zero to nearly 100 percent with increasing pH over a relatively narrow pH range, and sorption of anions typically decreases in a gradual fashion with increasing pH (Figure 14).

The presence of additional dissolved substances may inhibit the sorption of a particular species, due to the formation of more stable aqueous complexes. On the other hand, other dissolved substances may promote the sorption of a particular solute via the formation of new complexes that are easily adsorbed (Figure 15).

The total number of sites T_x involved in surface complexation is a constant and is characteristic of each mineral. It is expressed in mol/kg solid or mol/L, if the solid is of colloidal nature:

$$T_X = \left[XOH\right] + \left[XOH_2^{+}\right] + \left[XO^{-}\right] \quad + \quad \sum_{i=1}^{m} \left[XOM_i^{z_i}\right] \tag{42}$$

Equation (42) indicates that there is competition between the different aqueous species for the available surface sites. Like aqueous speciation, the set of aqueous and surface complexation equilibrium equations and the solute and T_X mass balance equations allow the computation of surface speciation.

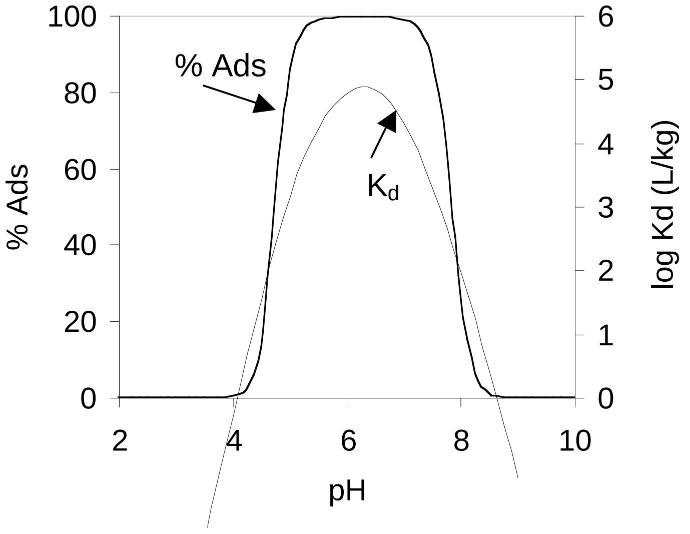

Figure 14. *Sorption of U(VI) on iron hydroxide (PZNPC= 7.8). No sorption takes place at low pH where the surface is positively charged and* UO_2^{2+} *is the predominant aqueous species, and at high pH where the surface is negatively charged and* $UO_2(CO_3)_3^{4-}$ *is the predominant aqueous species. Sorption takes place at neutral pH via the formation of the surface complexes* $(XO)_2UO_2$ *and* $(XO)_2UO_2CO_3^{2-}$*. The figure also shows how the* K_d *values (see below) can vary more than one order of magnitude for a pH unit. Data from Waite et al. (1994) and Grenthe et al. (1992).*

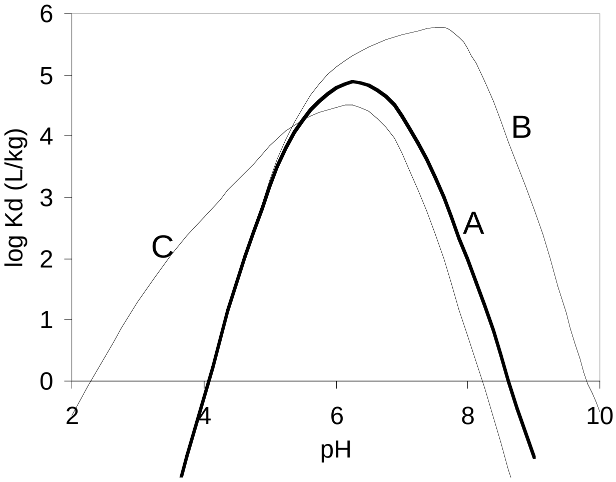

Figure 15. *Sorption of U(VI) on iron hydroxide, expressed as log* K_d*, at pCO2= -2.0 and with no phosphate in solution (case A). Sorption is enhanced at lower pCO2= -3.5 (case B) due to the lower amount of the lower amount of carbonate complexes in solution, and consequently less adsorption as* $(XO)_2UO_2CO_3^{2-}$ *surface complex. On the other hand, the presence of phosphate in solution (*10^{-6} *M) enhances the sorption of uranium at low pH (case C) due to the formation of the* $(XOH_2)_2UO_2(HPO4)_2$ *surface complex. Data from Waite et al. (1994), Payne (1999), and Grenthe et al. (1992).*

2.2.2.3 Ion exchange model

Minerals such as zeolites, smectites and vermiculites, found as fracture fillings, exhibit a fixed charge developed by isomorphic substitutions in the mineral lattice (e.g., substitution of Al^{3+} for Si^{4+}) that is compensated by cations (mainly Na^+, K^+, Ca^{2+}, and Mg^{2+}) in intracrystalline sites.

Cation exchange describes the process when an exchangeable cation located in an intracrystalline site or surface site of a mineral is exchanged with a cation from the solution. The main difference between cation exchange models and the non-electrostatic surface complexation models lays in the fact that no free sorption sites are assumed in cation exchange, and the capture of a cation from the solution is always coupled with the release of a cation from the surface.

Therefore, for monovalent cations the exchange can be described as a reaction:

$$I^+ + (X - J) \Leftrightarrow (X - I) + J^+ \tag{43}$$

where $(X - I)$ and $(X - J)$ denote the exchangeable site occupied by the I and J ions, respectively. As with any reaction, an 'equilibrium constant' can be defined:

$$K_{I/J} = \frac{a_{J^+}\, a_{(X-I)}}{a_{I^+}\, a_{(X-J)}} \tag{44}$$

There is no consensus on how to describe the non-ideal behaviour of the ions attached to the exchangeable sites. Three main different conventions are still in use in current literature: Gaines-Thomas, Vanselow and Gapon. Similarly to the case of solid solutions, the three conventions refer to the activity as a molar or equivalent fraction, and $K_{I/J}$ is considered a partition coefficient rather than a true equilibrium constant. See Appelo and Postma (1994) for further description.

The ability of a mineral to sorb through an ion exchange mechanism is commonly expressed as the cation exchange capacity (CEC). CEC is usually expressed as meq/100 g solid and, as the total number of sorption sites T_X, is characteristic of each mineral.

Sorption of trace metals on clays and zeolites shows behaviour typical of surface complexation. However, sorption shows a constant value at low pH and low ionic strength (Figure 16). Since surface sites are expected to be protonated under these conditions, this constant sorption is attributed to occur by an ion exchange mechanism. Since the CEC is constant, large ionic strengths (of the order of 0.1 M) tend to suppress ion exchange through filling of available sites by competing major components in solution such as Na^+ and Ca^{2+}. Therefore, high ionic strength solutions in pore water relative to fractures may limit radionuclide sorption through ion exchange in the matrix.

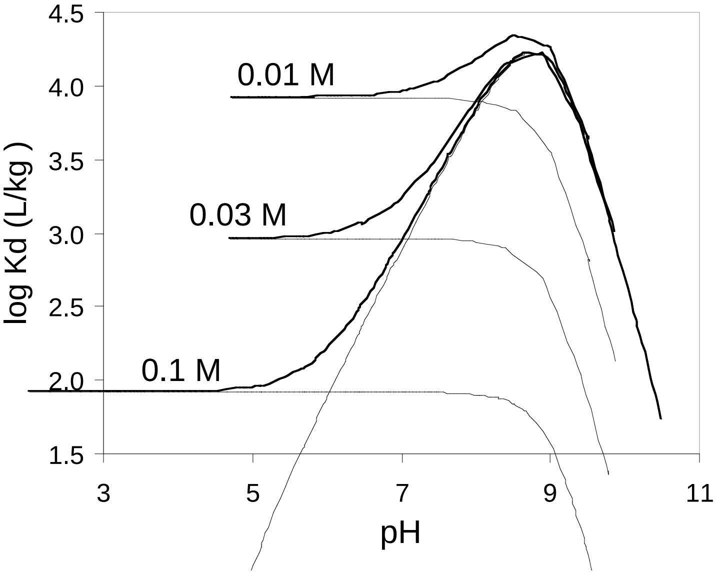

Figure 16. Sorption of Ni in Na-montmorillonite. Ionic exchange is relevant al low pH (horizontal line), whereas surface complexation dominates at neutral and slightly alkaline conditions. Cation exchange is independent of pH except for high pH values due to the formation of the $Ni(OH)_2^0$ *aqueous complex. Cation exchange is drastically reduced as ionic strength increases (from 0.01 to 0.1* $NaClO_4$*) due to the competition of* Na^+ *ions for a finite number of exchange sites. Data from Bradbury and Baeyens (1997).*

2.2.2.4 Measurement and parameterisation of sorption

PA calculations rely on a number of sources of information when selecting the K_d value for a particular radionuclide. The most common source are K_d measurements in batch reactors: a known mass of solid is immersed in a solution containing a known volume of solution with a known concentration of radionuclide. After agitation and a period of time to ensure equilibrium (hours), part of the radionuclide is sorbed on the solid surface. The main experimental parameter is the K_d value, or the ratio between the concentration in the solid, C_{XM} in mol/kg solid (obtained by difference between the initial and final concentration in the liquid) and the final concentration in the liquid, C_M in mol/L.

$$K_d = \frac{C_{XM}}{C_M} \tag{45}$$

The repetition of the experiment for different initial concentration of solute or different solid/liquid ratios enables to obtain a set of values. The empirical function fitting these values are usually called isotherms, and can be linear or not (see Figure 17). Compared to sorption experiments, there is very scarce literature on desorption. They tend to reproduce sorption isotherms, although equilibration times are longer (Comans, 1987).

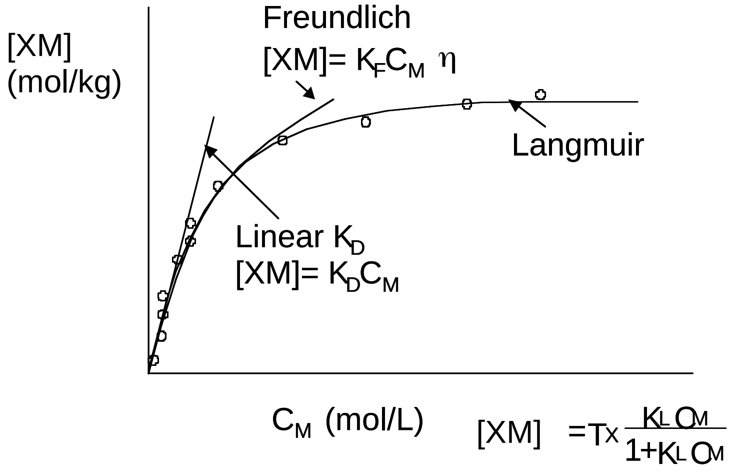

Figure 17. Schematic representation of three isotherm types fitting a set of experimental values. Linear K_d is usually sufficient to describe experiments with diluted concentrations, whereas Freundlich and Langmuir are usually required for more concentrated solutions.

Batch K_d values are frequently validated by interpretation of changes in the transfer of a radionuclide with respect to a conservative tracer in diffusion and advection experiments. These experiments require a large amount of additional information, such as mineralogy, wetted surface areas, porosity, permeability, etc., which introduce a variable degree of uncertainty.

Surface complexation models require a larger set of parameters. The fitting of the set of experimental K_d values for different pH conditions can be used to obtain the equilibrium constants for the sorption complexation, protonation and deprotonation reactions (35), (40) and (41), together with the total number of sorption sites (Equation (42)). The use of some electrostatic models requires, in addition, values of the surface capacitance obtained from data fitting. Since there are many parameters for a reduced set of experimental data, it is also convenient to obtain the protonation and deprotonation equilibrium constants and the total number of sorption sites from independent experiments, such as the potentiometric titration of the surface.

Cation exchange parameterisation is simpler, since no K_d variation with pH is expected. Solid equilibrium with solutions containing different concentrations of a main electrolyte (usually NaCl) is commonly used to obtain the partition coefficients (Equation (44)) and the total exchange capacity. Experiments are performed at low pH to minimise the interference with surface complexation processes (see Figure 16).

2.3 MATRIX DIFFUSION

The chapter also considers surface diffusion and anion exclusion that are often mentioned to influence on matrix diffusion.

2.3.1 Introduction

Rocks, even such as, e.g., dense granite, have a non-zero value for the porosity. On a microscopic scale rocks show an intricate network of micro fractures and connected pores where advective water flow, which may carry radionuclides released from a repository for radioactive waste, is either absent or plays only a minor role. However, dissolved radionuclides may have access to the stagnant water in such pore spaces by molecular diffusion. In the case of sorbing radionuclides the accessible surface for a temporal attachment may be enhanced by orders of magnitudes when compared to the accessible surface in the fractures. Hence, diffusion into the rock matrix and sorption onto the inner pore surfaces results in a temporal immobilisation of dissolved radionuclides drastically reducing their concentration in the flowing groundwater. Matrix diffusion has therefore the potential to increase the transport times of solutes to time scales, which are comparable or even greater than the half-life of the radionuclide under consideration. In such cases, most of the nuclides will decay before reaching the biosphere. For non-sorbing radionuclides this process represents one of the most important retardation mechanisms, because these solutes would otherwise be transported by advection alone; hence, by the speed of the flowing groundwater. Based on these facts, it can be concluded that:

Matrix diffusion is the mechanism by which solutes – being transported in the flowing groundwater within fractures of a porous medium – are transferred to the stagnant water of the rock matrix adjacent to these fractures.

Matrix diffusion as a physical process is based on fundamental principles of thermodynamics and takes place provided that:

- there is a connected porosity in which solutes might be transferred diffusively;
- there are molecules and particles in the water which are small enough to access such a connected porosity and
- the permeability of the matrix is significantly lower than that of the fracture. If the matrix permeability is relatively high, then matrix diffusion still exists but is superseded in importance by matrix advection.

In addition, the effectiveness of matrix diffusion is dependent on

- the geometry of the connected pore space of the rock;
- the area of contact between the mobile water in the fracture and the stagnant water in the porous rock and
- on the solute/rock interaction.

The role of matrix diffusion in sub-surface solute transport was already discussed in the mid twentieth century; a first quantitative investigation was done by Foster (1975), who explained the anomalously low levels of thermonuclear tritium observed in groundwater in chalk by diffusion of tritiated water into the porous rock matrix [1]. Later papers, related to the safe underground disposal of radioactive waste, which considered matrix diffusion to be an important transport mechanism in retarding the migration of dissolved radionuclides are those by Glueckauf (1980) in U.K., Grisak and Pickens (1980a) in Canada and Neretnieks (1980) in Sweden. These authors recognised, as Foster did for tritium, that, even in the absence of any adsorption processes of radionuclides in the rock matrix, the dilution of solutes by the water in the connected micro pores or micro fractures of the rock might still be a significant process. Non-sorbing species may penetrate a few tens of centimetres into the crystalline rock matrix, if the contact time exceeds 1000 years; however, strongly sorbing species only penetrate fractions of millimetres in the same time span.

Many studies of matrix diffusion have been carried out since the initial work in 1975 and 1980 mentioned above. Experimental and modelling work are continuing world-wide, see e.g., Bibby (1981); Maloszewski and Zuber (1990); Haggerty et al. (2000); Ota et al. (2003); Polak et al. (2003). The goal of these investigations is to gain further insight into the nature of the relevant transport processes acting and to obtain reliable values for the transport parameters, which can be used in future performance assessments [2] for the disposal of hazardous waste, e.g. chemical and nuclear waste.

Up until now, there have been numerous experimental results obtained on small samples of rock indicating that indeed a connected porosity exists, even when taking into account the original lithostatic pressure. Some of these investigations clearly showed that the spatial extent of connected pores is limited. However, it is very difficult to specify reliable values for such an extent of and hence, more scientific work will be needed to understand under what condition pores remain open or become closed.

A variety of different experimental techniques have been and is used to investigate the effects of matrix diffusion. Some of them are performed on the laboratory scale with typical length scales in the order of a few centimetres; while field experiments are performed on length scales in the order of a few tens of centimetres up to metres. Typical durations are days to months in the laboratory experiments; but field scale tests need time spans of the order of years.

The laboratory through-diffusion experiments allow a tracer to diffuse from a high-concentration to a low-concentration (normally near zero-concentration) reservoir. Across the sample between the two reservoirs there is no hydraulic gradient, and hence, no additional advective flow takes place. From the experimenter point of view, the breakthrough curve of the tracer into the low-concentration reservoir hence, flux (or alternatively: total diffused mass) versus time is monitored. After a transient phase, a more or less constant mass flux is obtained. When applying a suitable diffusion model,

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[1] Similar work concerning matrix diffusion was performed in parallel in the area of soil science and there might also be some “cross-fertilisation of ideas” between the different communities. However, an exhausting compilation of all the relevant works is definitely beyond the scope of this contribution.

[2] Different waste organisations use different expressions such as “performance assessment”, “safety assessment”, “safety analysis”; they are considered synonymously here. For a tentative definition of each of the terms, see e.g. NEA (1997).

from the steady-state phase a value for the effective diffusion coefficient D_e [3] can be determined, because at steady-state, diffusion is independent on any uptake mechanism such as, e.g., sorption. From the transient phase, values for the sorption capacity (rock capacity factor α) can be derived. In the case of conservative, i.e. non-sorbing species, a value for the connected porosity ε can be deduced. At the end of a through-diffusion phase, the steady-state tracer profile in the sample can be used as the initial condition for a so-called out-diffusion experiment where the traced solution in the high-concentration reservoir is quickly replaced by untraced artificial pore water (Jakob et al., 1999, Tits et al., 2003). This experimental set-up allows measuring independent values for the effective diffusive tracer flux differing at both boundaries. Hence, various independent data can be obtained and used for the inverse modelling in order to extract values for D_e and for a possible tracer's sorption capacity. Values for D_e and α obtained from modelling the out-diffusion phase can then be compared with those from inversely modelling the former through-diffusion phase. Such a procedure is a crucial test of the underlying diffusion/sorption model and of the reversibility of the uptake mechanism(s).

At the end of the through-diffusion phase, where the diffusion process is in steady-state, other procedures are very common. 1) The rock sample can be sliced in order to obtain (steady-state) tracer distribution profiles across the sample. These profiles then reveal further insight into the nature of the uptake mechanism. 2) The rock sample may be leached by placing the loaded rock sample in a known volume of tracer-free artificial pore water. This procedure allows mass-balance considerations and yields further information about the mechanism, especially the kinetics, of the tracer release.

Diffusion can also be studied in the field, hence, on a decimetre to metre scale. Tracer from a packered volume of a borehole may penetrate under more or less virgin conditions the porous rock for months or even years. Through a subsequent over coring and analysis of the tracer distribution in thin slices taken from the bore core, information about the connected porosity, diffusivity, the solute/rock interactions etc. can be gained. Further information can be obtained by evaluating field migration experiments where in addition a pressure gradient pushes the movement of the solutes. With the help of an appropriate model for flow and solute transport and by using supporting information from an extensive laboratory program, especially with regard to diffusion and sorption, as well as from mineralogical and petrophysical investigations, additional details of matrix diffusion can be deduced.

Natural analogue studies might further support investigations on the laboratory and field scale. While the latter methods deal with relatively well-defined systems regarding processes, initial and boundary conditions, for natural analogues they are – although responsible for the actual stage of the natural analogue system – to a high degree unknown and have to be estimated for the interpretation of the long-term development of the natural system. However, the advantage of natural analogues is that the processes have acted under in-situ conditions and over timescales comparable to those used in performance assessments. Although in general the interpretation of observations on natural analogues is not straightforward and it is extremely difficult to draw trustworthy

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[3] For simplicity reason the discussion follows a one-dimensional description and the tensorial properties of certain transport parameters are preliminarily neglected.

conclusions, such studies are indispensable, because they help in recognising the relevant chemico-physical processes affecting the mobility of dissolved radionuclides in the underground and in reducing uncertainties in the values for important transport parameters.

This contribution is organised as follows: In the next section a brief presentation is given of some results from observations of real geological systems on different scales which support the conclusion that matrix diffusion does indeed act and is a key retarding mechanism in sub-surface solute transport. In Section 2.3.3, diffusion in porous media is briefly discussed followed by some considerations concerning the rock porosity.

Due to the fact that geosphere transport calculations for performance assessment purposes are done – as a rule – in the frame of the dual-porosity medium model, key aspects and basic assumptions and approximations of this model are presented. The specific problems of some sub-processes associated with matrix diffusion, such as anion exclusion, surface diffusion, diffusion into stagnant water in the fractures etc. are discussed and open questions are addressed. There is also a compilation of experimental results on the laboratory, as well as on the field scale regarding the extent of the porous rock zone adjacent to fractures, which is accessible by matrix diffusion. The maximum depth for matrix diffusion is one of the most important quantities, especially in the context of performance assessments for the underground disposal of radioactive waste. The lack of reliable data for the extent of the diffusion-accessible zone very often results in over-conservative assumptions in performance assessments; hence, the effects of matrix diffusion are often strongly underestimated. The availability of more realistic values would thus result in more realistic, i.e. lower, calculated doses.

In Section 2.3.4 open issues and unresolved problems regarding matrix diffusion are briefly addressed.

In Section 4.3.1 an overview of how matrix diffusion and related processes were treated in past performance assessments is presented. However, this part is neither comprehensive nor complete and a certain overlap with results from work package 1 cannot be avoided. Finally, some concluding remarks are presented in Section 4.3.2.

2.3.2 Geological evidence for matrix diffusion

From a wealth of observations, the following three examples can be considered as manifestations of effects of matrix diffusion acting on different scales.

1) Clay stones and marls typically act as efficient barriers for dissolved solutes. Consequently they are considered as potential host rocks for the disposal of radioactive or other hazardous wastes in many countries. Their low permeabilities should help to retain such wastes within the disposal site for long time spans and minimise the later contamination of the biosphere. The first example, Figure 18, shows measured δ^2H data from a bore core from a deep drilling at Benken, Northern Switzerland, which is a possible site for a repository for high-level radioactive waste. Relatively highly permeable layers from the partly carstic, partly fractured Malm limestone above, and the Keuper below, sandwich the potential host rock, tight Opalinus clay. In both aquifers the groundwater flows mainly advectively, whereas diffusion is considered to

be the main transport mechanism in the Opalinus clay. Analysing and interpreting measured profiles of stable water isotopes allows past hydraulic processes to be characterised and relevant scales and processes in such formations to be understood. In addition the modelling results allow large-scale transport behaviour to be assessed and the deduced values for the transport parameters in the field to be compared with those from laboratory tests.

The evaluation of the data indicates that δ^2H ratios, which have developed over geological time scales, vary systematically within the pore and groundwater in all of the layers. The deuterium concentration in the Opalinus clay is much lower than that of seawater today and towards the Keuper aquifer the profile falls to values corresponding to those of the meteoric water. Thus, during the last 150 millions of years slow mixing between the original marine water with δ^2H-values around 0 ‰, and younger meteoric water with values around – 65 ‰, leads to a pore water, which is isotopically lighter than that originally present.

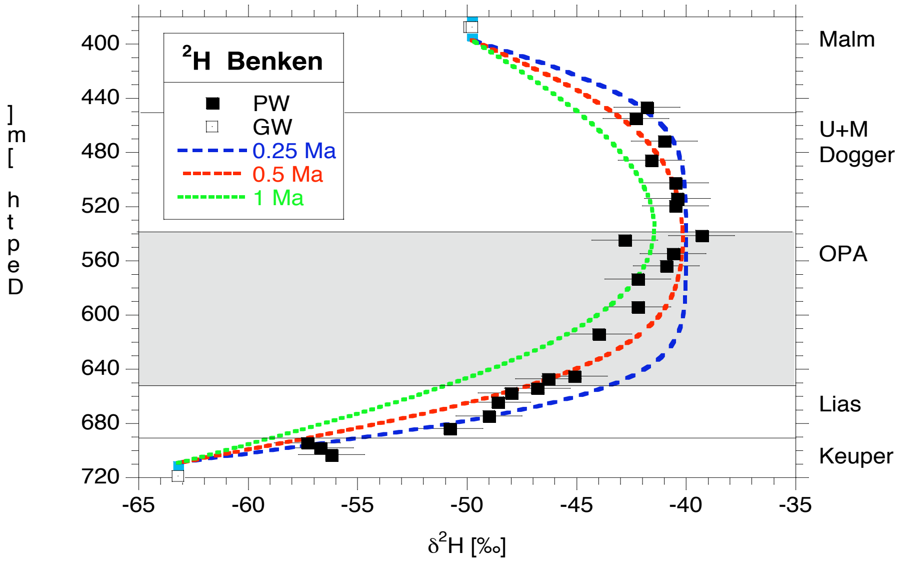

Figure 18. Profile of δ^2H [‰ V-SMOW] across the low permeability units at Benken/Switzerland (PW: pore water, GW: ground water). The lines show simulated diffusion profiles for various evolution times using a laboratory diffusion coefficient for the in-situ temperature. On the right axis, geological units and Malm and Keuper aquifers are indicated (OPA: Opalinus Clay, U+M Dogger: Upper and middle Dogger). Taken from Gimmi et al. (in preparation)

The modelling results indicate that diffusive spreading was predominantly responsible for the development of the observed ^{2}H profile. A slight vertical advective flow through the low permeable layers may have occurred, or is still occurring, but the effects of such low flow rates are masked to a large extent by the considerably faster diffusive transport over the estimated time span of 0.25 to 1 million of years.

While the first example might be indicative of effects of matrix diffusion on the 100 m scale, in the second example matrix diffusion is acting on a scale of a few decimetres.

2) One of the most obvious phenomena at the uranium mine in Osamu Utsumi in Poços de Caldas (Minas Gerais) – South-eastern Brazil is the observation of sharp but irregular redox fronts. Oxidising meteoric water from the surface penetrates the reducing interior of the alkaline volcanic and plutonic rocks – especially along steeply-dipping, active fractures and faults and by molecular diffusion also enters those parts of the rock adjacent to a fracture. These processes result in pronounced fronts between the oxidation- (brownish-red due to the presence of iron oxyhydroxides) and reduction zone, which can be clearly observed in occasional outcrops. Furthermore, the shape of such zones demonstrates that the migration of the solute into the rock matrix is orders of magnitude slower than that in the fracture. Hence, extended oxidised zones within the solid rock are considered indicative of acting matrix diffusion and its potential for efficiently retarding solutes.

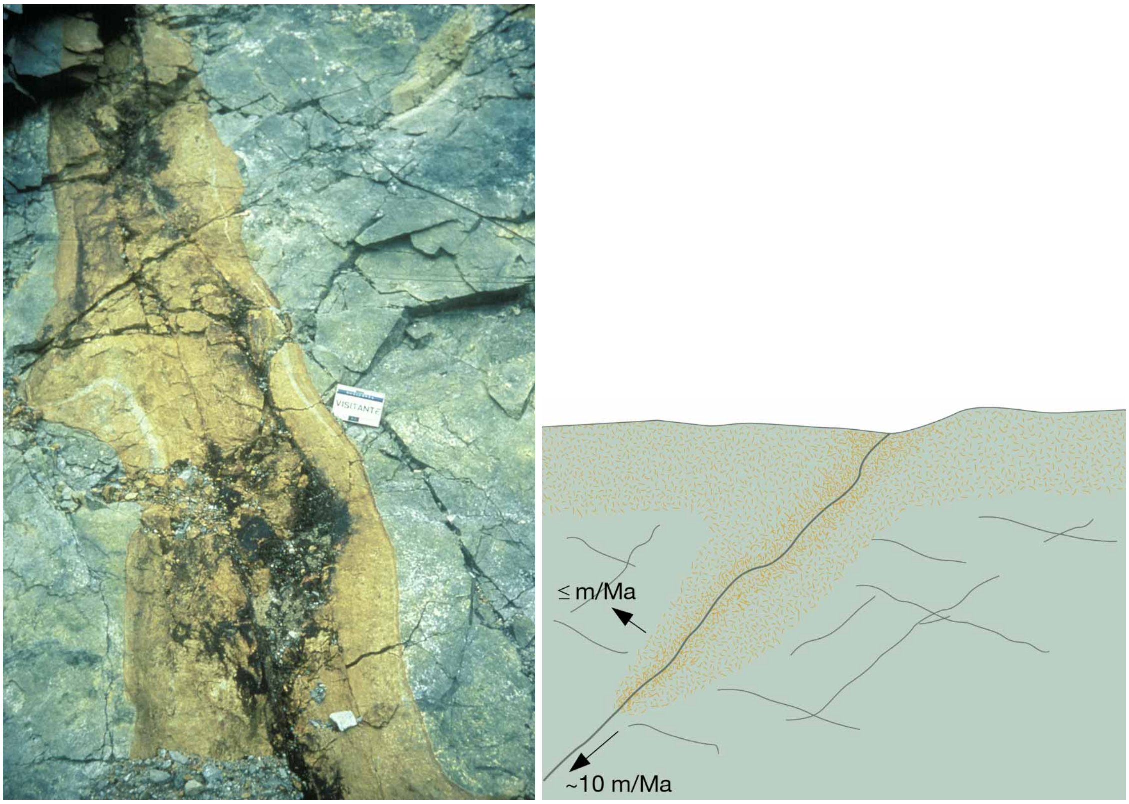

Figure 19. In the photograph (left) the spreading of a marked redox front along a steeply-dipping fracture at the uranium mine Osama Utsumi, Poços de Caldas, South-eastern Brazil, can be clearly recognised. As illustrated in the sketch above, oxygen-rich water from the surface has moved downwards along the fracture resulting in a colour change from greyish-blue to reddish-brown due to oxidation of dispersed pyrite also in the unfractured rock. (Nagra, 1993, p. 38; reproduction by courtesy of Nagra.)

Finally, a third example illustrates that the effects of matrix diffusion can also be seen on the millimetre to centimetre scale.

3) In granitic rock samples from the Äspö site in Sweden, small highly porous zones can be observed, termed by geologists as fault gouge/breccia and embedded in a fine-grained matrix, which is porous as a whole. This fine-grained matrix has apertures on

the sub-micrometer scale only so that advective flow is negligible. Typically the fault gouge/breccia is pervaded by systems of microfractures, often crosscutting the horizons. Hematite colouring impregnates these microfractures and also the adjacent gouge material as well as the porous wallrock. Such a pattern indicates that matrix diffusion is active. Due to this fact, the microfractures must have a natural origin and are not an artefact caused by sample preparation. Furthermore, it is likely that these systems of microfractures in the fault gouge/breccia represent the most dominant flow paths on a microscopic scale.

Figure 20. Indication of effects of matrix diffusion on the millimetre to centimetre scale: Highly porous fault gouge/breccia (upper part) from the Äspö area with hematite impregnation along the contact zone to the wallrock (lower part) and along microfractures crosscutting the gouge/breccia, can be seen. (The sample width of the micrograph is 1.2 mm.) Further details can be found in M. Mazurek et al. (1997). (Reproduction by courtesy of M. Mazurek.)

Many laboratory studies carried out on a broad variety of different rock materials, further support the idea of matrix diffusion. Early experiments were performed by Garrels et al. (1949), later ones by, e.g., Grisak and Pickens (1980b), Skagius and Neretnieks (1983), Hemingway et al. (1983), Johansson et al. (1998) on crystalline rocks.

Small-scale laboratory experiments can be performed in terms of either “infiltration” or diffusion experiments. In the first type of experiment water, chemically the same as that found in the rock naturally, is forced under pressure through a conducting fracture of a core sample stemming from host rock formations relevant for current radioactive waste disposal concepts. After obtaining steady-state flow conditions, a short pulse[4] of the same liquid containing one or more dissolved tracers is then injected into the up-stream section of the equipment; then the temporal evolution of the tracer concentration leaving the down-stream boundary of the sample is monitored. Hence, due to high pressure gradient, advection and dispersion are the main tracer transport mechanisms. By inverse modelling of the tracer breakthrough curve important phenomena in tracer transport through crystalline rocks (and others) can be addressed. These include, beside the above mentioned advection and dispersion, also sorption, possible matrix diffusion, geometry of the water flow paths (e.g. channelling) and effects of stress changes. Such experiments were and are carried out at many places worldwide since they are cost-efficient and well suited for studying complex physico-chemical systems under relatively well-defined conditions (for example INTRAVAL, 1990 and further references therein; Vandergraaf, 1995; Vandergraaf et al., 1997).

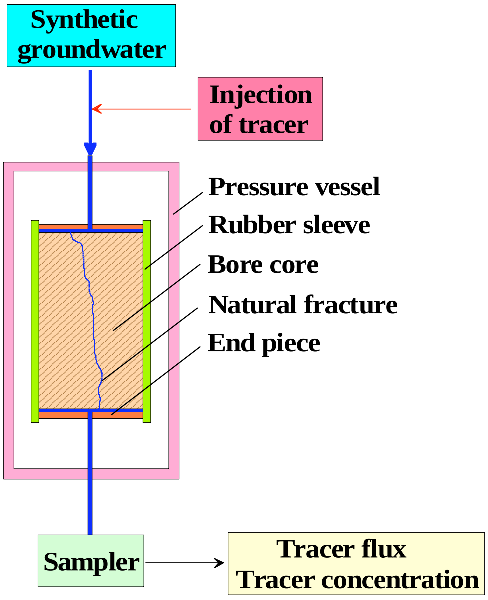

Figure 21. Schematic cross section through a pressure infiltration apparatus. A crystalline core sample with a natural fracture is tightly bound with two end pieces by a flexible rubber sleeve. Both end pieces consist of stainless steel cylinders having a central bore which leads to a spiral groove at the contacting face. The end pieces and the grooves distribute the axial stress and the infiltration fluid, respectively, over the upstream face of the sample. The core assembly is enclosed in a pressure vessel in order to simulate the original lithostatic pressure of the core sample. An additional infiltration pressure pushes a natural or an artificial groundwater with a constant flow rate through the (fractured) sample. After having reached a steady state water flow, a short tracer pulse is injected. At the output of the infiltration line the out-flowing solution is collected drop wise in a fraction sampler and the activity (concentration) of the tracer in each fraction is determined.

A second type of common transport experiments are through-diffusion tests which use a cell divided into two compartments by the rock sample. One compartment contains the

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[4] There are also experiments where the tracer is injected continuously at a constant flow rate.

traced solution and the other natural or synthetic pore water [5]. Typical thicknesses of the cylindrical, disk-like rock samples are millimetres to a few centimetres.

Both cells (for details see Figure 22), the reservoir as well as the measurement cell are filled with natural or artificial pore water. After equilibration the reservoir solution is spiked with the tracers and a gradient in the tracer concentration (strictly spoken: in the activity) pushes the tracer diffusively through the porous rock sample. Hence, such experiments can be carried out in order to determine values for diffusion and sorption for radionuclides which are dose-relevant in forthcoming safety analyses. Alternatively, through diffusion experiments can be performed mainly to gain an improved system understanding. In this case those tracers will be applied which allow the necessary system simplifications neglecting the fact that the chosen radionuclides might not be important in performance assessments [6].

For simplicity reasons a near-zero concentration boundary condition is very often required for modelling purposes in the measurement cell. However, such a restriction requires that the solution in the measurement cell has to be exchanged periodically by fresh pore water. Care has to be taken that such a procedure does not result in an additional driving force due to different heights in the liquid levels in the reservoir and in the measurement cell normally not considered in the modelling.

If the primary compartment, i.e. the reservoir, is small enough, the tracer concentration in solution can decrease significantly during a through-diffusion experiment due to diffusion and tracer uptake by the sample, especially for stronger sorbing substances. In principle, such a tracer reduction allows the deduction of values for the diffusive flux across the upper boundary. Based on that, careful mass-balance considerations also allow to determine time-dependent values for the tracer mass (or activity) taken up by the rock sample. Hence, on one side a small-sized reservoir is highly beneficial in order to gain further information on the diffusion process and the uptake mechanisms. On the other side, again for modelling purposes – which very often require a constant boundary condition – it is also necessary to periodically adjust the tracer concentration in the reservoir. Results for each nuclide are given in form of a time history of $C(t)$ [mole m^{-3}], the tracer concentration in the liquid of the measurement cell, which is

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[5] Very often in the past through-diffusion experiments were performed with distilled water instead of pore water. However, such a system is chemically not in equilibrium. Hence, for the analysis a coupled model for transport and chemical reactions has to be used instead of a simple diffusion model.

[6] Regarding tracers, it is definitely of advantage to perform such experiments by simultaneously applying different tracers; this means, e.g., non-sorbing tracers, i.e. tracers that do not sorb onto the inner surfaces of the rock sample, together with weakly and moderately sorbing tracers. However, a combination of neutral, cationic and anionic species can also be applied in order to study, e.g., exclusion phenomena. Using tracers with different valences may reveal further information about the charge density along preferential diffusion pathways and ion exclusion phenomena.
Simultaneously applying a multi-tracer cocktail guarantees that all the tracers will be transported under the same conditions concerning temperature or the water chemistry of the system. Slow temporal changes of the permeability and/or the chemical conditions may yield results which often cannot be used for trustworthy conclusions. Consequently, performing a series of single tracer tests should not be aspired to. Of course, for a tracer cocktail only those substances that do not interact with each other, neither in solution nor with regard to the inner surfaces of the solid phase, can be used.

$$C(t) = \frac{F}{V}\int_{0}^{t} j(t')\, d\,t' \quad , \tag{46}$$

where F [m^2] is the diffusion-relevant cross-sectional area of the sample, V [m^3] the volume of the liquid in the measurement cell and $j(t)$ [mole m^{-2}s^{-1}] the time-dependent tracer flux into the measurement cell.

Notation is found in APPENDIX 2.

Observing tracer breakthrough is therefore considered a clear indication for a connected porosity permeable for solutes. Solid-state diffusion as an alternative transport process is much less efficient. Bradbury and Green (1986) mention that values for the diffusion coefficient measured in the laboratory on samples in the order of a few centimetres thickness may overestimate the real values by a factor of up to two. According to these authors, such an effect may be caused by the additional contribution of dead-ended pores, i.e. pores which are closed at one end, that are converted to through-transport pores in the small-scale samples. Hence, this is seen as a geometrical effect related to the sample thickness and the internal length of the dead-end pores, which might be in the order of centimetres.

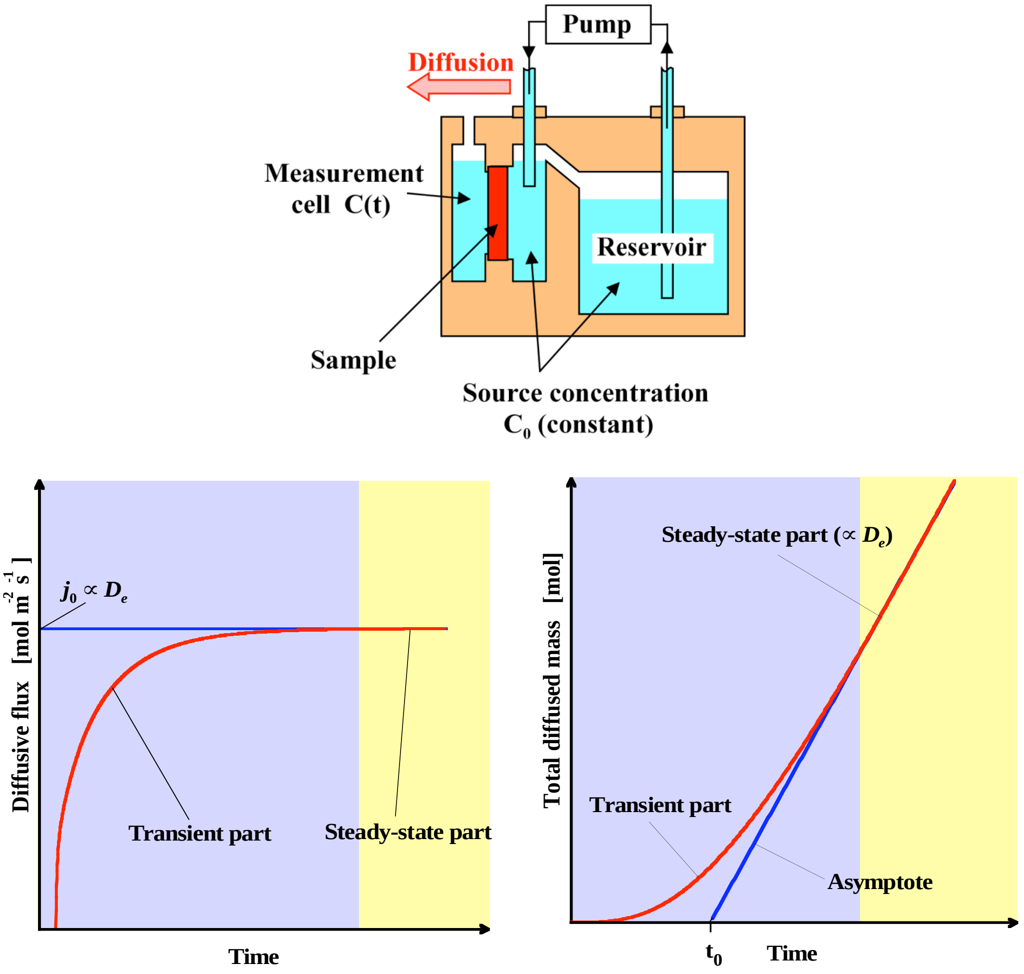

Figure 22. Sketch of cross section through an apparatus for solute through diffusion (upper figure). Tracer diffusion happens from right to left through a porous rock sample; the traced solution in the measurement cell has to be replaced periodically by fresh (artificial) pore water to guarantee a near-zero concentration boundary condition.

In the lower left figure the temporal evolution of the diffusive flux in a log/log or log/lin representation is drawn. After a first transient phase the flux reaches an asymptotic steady-state value (j_0) from which a number for the (constant) effective diffusion coefficient D_e can be extracted. Analysing the transient part of the breakthrough curve with an appropriate transport model reveals further information about solute deposition processes in the sample.

In the lower right figure the typical time history of the total diffused tracer mass in a linear-linear representation is drawn. Indicated is also the asymptotic limit. From the slope of this linear relationship in the frame of a 1D diffusion/sorption model a value for the (constant) effective diffusion coefficient D_e can be deduced, and from the intercept with the time axis (t_0) further information about deposition processes such as, e.g., sorption can be gained. Very often such a procedure results in a value for the rock capacity factor α.

Because diffusion is a slow process its main drawback is the long duration of any experiment. Especially for strongly sorbing tracers there will be no breakthrough in reasonable time spans. However, one can also obtain results concerning diffusion before tracer breakthrough occurs. By grinding or slicing of the sample after a certain time span further information about the radionuclide distribution in the sample can be obtained. By applying an appropriate diffusion model, which – where necessary – also accounts for the deposition process, values for diffusion and sorption can be deduced. However, this is a post-mortem analysis, and consequently additional experiments on the same sample cannot be performed.

To speed up diffusion experiments, more mobile tracers such as gases can be used (Autio et al, 1998). Other methods are based on the measurement of the electrical conductivity, hence the electromigration instead of the traditional tracer diffusion (Ohlsson et al., 2001; Löfgren and Neretnieks, 2003). This method can be applied in the laboratory using stress released water-saturated rock samples or in virgin rock in the field in order to determine in-situ diffusion data. However, whether the electrical conductivity is indeed related to the connected groundwater-filled porosity in the rock matrix or whether this rather reflects domains in the rock which are electrically conductive due to, e.g., present metal oxides, remains unclear.

A non-destructive method was recently applied by Polak et al., 2003 (and further references therein). Using the technique of computed tomography, which employs *x*-rays and mathematical reconstruction algorithms in order to view cross-sectional slices of a rock sample, they could monitor the tracer diffusion from an artificial fracture into the surrounding porous rock matrix unaffected by weathering. Their results indicate that within a few hours NaI penetrates chalk up to at least 2.5 cm and that a Fickian diffusion model could successfully reproduce the concentration profiles in the matrix.

Experiments on a larger scale, field tracer tests, also support the concept of matrix diffusion. Such experiments were performed in the last two decades at many locations in the world, in old mines, tunnels and underground laboratories in crystalline rocks and sediments such as Finnsjön, Stripa and Äspö in Sweden; at Grimsel and Mont Terri in Switzerland; at WIPP in New Mexico, USA, Fanay-Augères and at the Tournemire facility in France; in the research tunnel at Olkiluoto in Finland; in galleries of former mines at Kamaishi and Tono in Japan and in Asse, an old cavern in a former salt and potash mine in Germany.

The goal of field tracer experiments is to test and to enlarge the present understanding of important transport mechanisms on a scale larger than the usual scale for laboratory experiments; i.e. a few metres in the field versus a few centimetres in the laboratory.

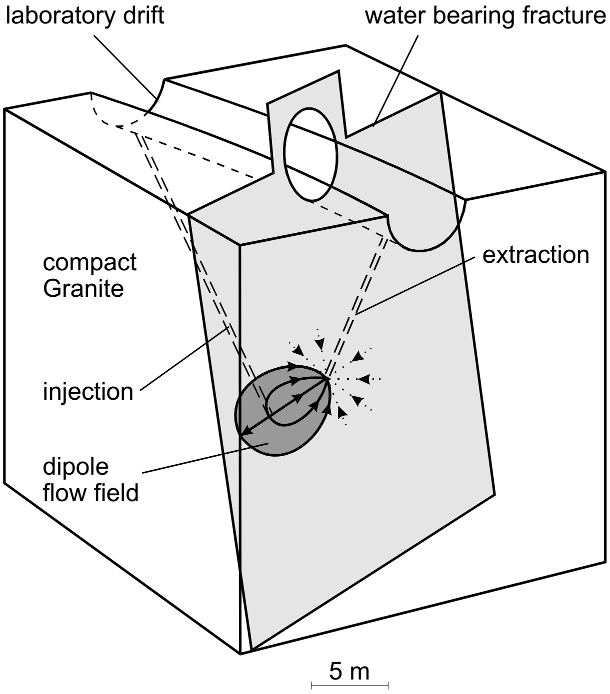

Figure 23. Sketch of a tracer migration experiment under near in-situ condition as performed in underground laboratories such as, e.g., at Äspö (Sweden) or at Grimsel (Switzerland). A highly diluted "cocktail" of inactive and/or radioactive tracers is released from a packered part of the injection borehole into a relatively high-permeable water-bearing fracture. At the withdrawal borehole constant pumping produces a steady-state dipole flow field in a part of the fracture which should guarantee full tracer recovery. By analysing the monitored tracer breakthrough with the help of an appropriate model for flow and transport further information about the rock/tracer interaction, e.g. matrix diffusion and possible tracer sorption onto the inner surfaces of the porous rock etc., can be deduced.

In addition, field tracer tests are performed in, more or less, virgin and – as a rule – heterogeneous rock and allow the build-up of the necessary know-how for methods and instrumentation to be applied in future rock laboratories and disposal sites for radioactive waste. Past evaluation exercises of field experiments have clearly shown that the interpretation of field tracer breakthrough curves are ambiguous (INTRACOIN, 1986). Hence, important components of field tracer tests are extensive, accompanying laboratory investigations, especially on geochemistry and transport mechanisms. Laboratory work includes the physical and mineralogical characterisation of rocks and possible fracture infill material as well as the analysis of groundwater and investigations of water-rock interactions. In addition, static batch sorption and dynamic infiltration and diffusion experiments yield information on deposition processes and on the mobility of the tracers in the rock. Further tasks concern the tracer speciation; the generation and the behaviour of natural colloids in the geosphere, the effects of possible organic complexants on radionuclide transport and the consequences of ubiquitous microbes. The resulting output of all these investigations represents the most rigorous test of competing solute transport models for fractured porous media carried out to date.

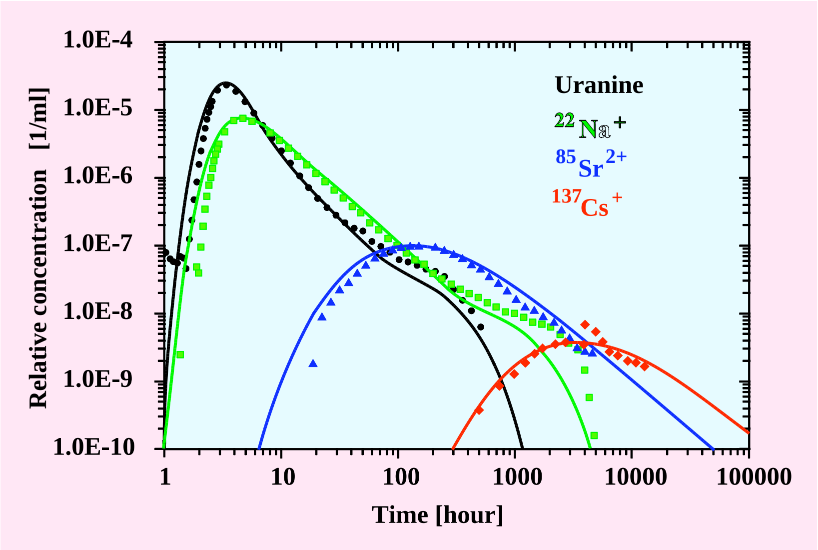

Figure 24. Although the field migration experiments are generally performed over distances of only a few metres, the retardation due to the combined effect of sorption and matrix diffusion of some solutes may be considerable. To illustrate this, a pulse breakthrough migration experiment with non-sorbing uranine as conservative tracer with sorbing $^{22}Na^{+}$, $^{85}Sr^{2+}$ *and* $^{137}Cs^{+}$ *from the Grimsel migration experiment is drawn; the migration distance is approximately 5 m. Shown are calculated (solid lines) and measured (symbols) breakthrough curves for the same transport conditions. The excellent agreement between calculated and measured data strongly supports the applied model. (Note: The disturbance at 4000 hours in the caesium breakthrough was due to a failure of a pumping device.) The strong reduction and delay in the peak maxima compared to non-sorbing uranine demonstrates the effect of the host rock on nuclide transport. The prominent tailing in all the tracer breakthrough curves is caused by matrix diffusion (Figure taken from Heer and Jakob, 1999).*

Many field tracer tests have clearly shown that matrix diffusion indeed acts and is a relevant process which has to be considered in an adequate geosphere transport model.

Both types of experiments, laboratory and field tracer tests, were part of international studies under the aegis of NEA such as HYDROCOIN (1984 – 1987), INTRAVAL (1987 – 1993) and GEOTRAP (1996 – 2001). While HYDROCOIN dealt especially the adequacy of different groundwater flow models, in the subsequent INTRAVAL project several modelling teams from different OECD countries evaluated the usefulness of models for predicting the transport of radioactive substances through the geosphere. Results from selected laboratory and field experiments, as well as from natural analogues, were compared in a systematic way with predictions from transport models. Discrepancies between measurements and predictions were discussed and analysed. In the GEOTRAP workshop (GEOTRAP, 1997) the practise, benefits and limitations of field tracer tests were discussed in detail. The early INTRACOIN project (1981 – 1986), addressed geosphere transport code verification and also the quantitative impact of matrix diffusion on radionuclide transport was modelled [7].

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[7] A short description of the international projects INTRACOIN, HYDROCOIN and INTRAVAL can be found in Larsson (1992).

Experimental investigations on all scales, as well as modelling studies related to matrix diffusion, have always been an intrinsic part of large international conferences such as the annual MRS-meetings and the bi-annual Migration conference.

2.3.3 Basic assumptions for modelling matrix diffusion

The driving force for diffusion[8] of solutes is the thermal movement of small particles such as water molecules, ions, uncharged molecules, suspended particles or colloids in solution (Brownian motion). The thermal kinetic energy of moving particles is of the order of kT, where k is the Boltzmann constant and T the temperature. Hence, the movement of the particles becomes more pronounced with increasing temperature. Due to the random microscopic movement[9] of the particles, which results in increasing entropy of the system, any concentration differences in solution are decreased with time, resulting – in the asymptotic time limit – in a dynamic steady state where the solute concentration is uniform and constant in the whole volume under consideration. On a macroscopic scale, diffusion is driven by a gradient in the chemical potential.

Due to the dipole character of water molecules, there is an electromagnetic interaction with charged particles, and hence, diffusion is dependent on temperature, composition and the concentration of the dissolved or dispersed particles. Furthermore the particle size, charge and hydration energy of the solutes may be of importance.

Diffusion is relatively fast in gases, much slower in liquids and still slower in solids. On a geological time scale, molecular diffusion becomes an important process for the transport of solutes in interstitial water and in reactions between solutes and the solid phases.

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[8] The term “diffusion” means “isotherm diffusion” in order to clearly distinguish this process from “thermal diffusion” which is caused by a temperature difference or advective mass flow due to a pressure difference or other forced diffusion caused by some external forces. (Further information concerning these so-called off-diagonal Onsager processes can be found and in Bear 1972, pp. 85ff.)

[9] Note: Brownian motion is only a random process if the medium is homogeneous and isotropic. If the medium is heterogeneous, it is correlated at the macroscopic scale. This leads to non-Fickian behaviour over the correlation scale. In contrast to ideal systems, the description of diffusion in natural systems is very difficult due to the inherent irregularities of the void space (pores); the shape and the size of grains or minerals and pores may vary greatly. A serious discussion of non-Fickian diffusion however, is definitely beyond the scope of this contribution.

Table 4. Experimental and recommended orders of magnitude of the diffusion coefficient related to different performance assessments. (Note: The values for diffusion through porous media are those in terms of the pore diffusion coefficient D_p. If not declared explicitly the values are valid for all elements, non-sorbing as well as sorbing ones. OPA means Opalinus clay.)
In the lower part, for illustration purposes only, some typical experimental data for the diffusion coefficient for other binary systems are compiled.

Substances, Details	D [m^2 s^{-1}]	Source
Diffusion through-water saturated porous media		
Diffusion through granites (ε_p = 0.005)	$2 \cdot 10^{-11}$	Brandberg and Skagius (1991)
Diffusion through basalt (not site specific value)	$1 \cdot 10^{-11}$	IAEA (1998), p. 116
Anions in OPA (ε_p = 0.06, $\perp$to bedding)	$2 \cdot 10^{-11}$	Nagra (2002a), Table 9.4.-3
Non-anions in OPA (ε_p = 0.12, $\perp$ to bedding)	$8 \cdot 10^{-11}$	
Anions in OPA (ε_p = 0.06, $\parallel$ to bedding)	$8 \cdot 10^{-11}$	
Non-anions in OPA (ε_p = 0.12, $\parallel$ to bedding)	$42 \cdot 10^{-11}$	
Na^+ through hardened cement pastes (ε_p = 0.63)	$25 \cdot 10^{-11}$	Tits et al. (2003)
HTO through hardened cement pastes (ε_p = 0.63)	$46 \cdot 10^{-11}$	
Diffusion in gases		
Highly diluted gases in air (293 K, ca. 10^5 Pa)	$(1 – 7) \cdot 10^{-5}$	Handbook of chemistry and physics
Diffusion in water		
Diluted gases in water	$(1 – 8) \cdot 10^{-9}$	Handbook of chemistry and physics
Cations in water at infinite dilution (at 298 K)	$(0.5 – 9) \cdot 10^{-9}$	Flury and Gimmi (2002), Table 6.2.1
Anions in water at infinite dilution (at 298 K)	$(0.4 – 5) \cdot 10^{-9}$	
Self-diffusion of water (at 298 K)	$2.1 \cdot 10^{-9}$	Wang (1951)
Solid state diffusion		
H_2 in Ni (at 358 K)	$1.2 \cdot 10^{-13}$	Bird et al. (1960), Table 16.2-4
Bi in Pb (at 293 K)	$1.1 \cdot 10^{-20}$	
Sb in Ag (at 293 K)	$3.5 \cdot 10^{-25}$	
Al in Cu (at 293 K)	$1.3 \cdot 10^{-34}$	

2.3.3.1 Diffusion in porous media

Fick (1855), a young German pathologist at the university of Zürich – well trained in physics and mathematics – recognised the analogy between mass diffusion and heat conduction and consequently adopted Fourier’s formalism for heat conduction. Both processes are due to a random molecular motion and hence are based on the same microscopic mechanism. In analogy to Fourier, Fick assumed that the particle current occurs against the concentration gradient. Hence, Fick’s first law giving the mass flux [10] through a porous medium can be written as

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[10] The term “flux” means “rate of solute flow per unit area” with units, e.g. [mol m^{-2} s^{-1}].

$$\vec{j}(\vec{r},t) = -\mathbf{D}_e \cdot \vec{\nabla} C(\vec{r},t) \quad , \tag{47}$$

where j is the mass of solute transferred per unit area accessible for diffusion and unit time, $\boldsymbol{D}_e$ is the effective diffusion tensor [11] and C is the solute concentration, depending on the position vector $\vec{r}$ and time t. (For simplicity reason sink/source terms have been neglected.) The negative sign indicates that the solute is transported in the direction of decreasing concentration. The effective diffusion tensor accounts for the smaller cross-sectional area of a porous medium for diffusion and has a simple relation to the pore diffusion tensor $\boldsymbol{D}_p$:

$$\boldsymbol{D}_e = \varepsilon_p \, \boldsymbol{D}_p \quad , \tag{48}$$

where ε_p denotes the diffusion-accessible porosity [12]. In principle $\boldsymbol{D}_e$ may vary spatially in the porous medium and may be dependent on the solute concentration. The effective diffusion tensor and the diffusion tensor in an unconfined fluid $\boldsymbol{D}_w$ are linked by the so-called geometry factor G or alternatively the formation factor F:

$$\boldsymbol{D}_e = \varepsilon_p \, \boldsymbol{D}_p = \varepsilon_p \, G \, \boldsymbol{D}_w = F \, \boldsymbol{D}_w \quad , \tag{49}$$

hence, $\boldsymbol{D}_e$ accounts for the transport properties of the three-component system: porous solid, solvent and solute.

According to van Brakel and Heertjes (1974) the formation factor is proportional to the ratio of two quantities describing the internal structure of the porous medium according to

$$F = \varepsilon_p \, \frac{\delta}{\tau^2} = \varepsilon_p \, G \quad , \tag{50}$$

where δ represents the constrictivity ($\delta < 1$) and accounts for a varying cross-sectional area for solute diffusion along the transport pathway in the porous medium; the tortuosity τ accounts for the lengthening of the diffusion pathways compared to the straight line distance between two points. Hence, $\tau \geq 1$; $F = \varepsilon_p G$ is the relationship between the porosity ε_p, the geometry factor G and the formation factor F.

Values for the diffusivity of a variety of ions at infinite dilution, which might be reasonable values for dilute solutions, are reported by Lerman (1979) p. 81. In the Swedish SKB 91 study a value of $D_w = 2 \cdot 10^{-9}$ m^2/s was proposed for ions at infinite dilution for both fresh and saline waters (Brandberg and Skagius, 1991, p. 91). Nagra uses values for D_w between $0.5 \cdot 10^{-9}$ m^2/s for larger particles and $2 \cdot 10^{-9}$ m^2/s (Frick, 1992) consistent with Swedish values. Another value for the self-diffusivity of water, i.e. $D_w = 1.9 \cdot 10^{-9}$ m^2/s at 20 °C, is given by Wang (1951). A larger compilation of values for the cationic and anionic diffusion coefficient in water at infinite dilution D_w at 25 °C can be found in Flury and Gimmi (2002).

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[11] Second rank tensors are denoted by bold italic symbols.

[12] There are studies (e.g. Hemingway et al, 1983; Ohlsson and Neretnieks, 1995) where the diffusion-accessible porosity is further sub-divided into the “through-transport porosity” (i.e. the fraction of the total porosity which carries the tracer flux across the sample) and “dead-end (or “storage”) porosity”. However, such a distinction of the diffusion accessible pore space may be questioned, since it is very difficult to specify reliable values for both types of porosities from experiments.

For illustration purposes, in the following table ranges for the porosity, the formation and the geometry factor for Swedish granitic rock from the Finnsjön area and for Grimsel (Switzerland) fault gouge material are compiled. More (species-dependent) values for the formation factor for various types of crystalline rocks can be found in Ohlsson and Neretnieks (1995).

Table 5. Upper and lower limits for measured values for the rock porosity ε_p, deduced formation F and geometry factor G for some Swedish crystalline rocks from the Finnsjön area. For the compilation of F and G a value of $2.0 \cdot 10^{-9}$ m²/s is assumed for D_w. (The values for the porosities are taken from Brandberg and Skagius, 1991.) For comparison purposes, values are also specified for Grimsel (Switzerland) fault gouge material, which is relatively highly porous. (These values are based on the modelling work by Heer and Hadermann, 1994; Table 6, p. 98; and Hadermann and Heer, 1996. For D_w again a value of $2.0 \cdot 10^{-9}$ m²/s was assumed.)

Rock type	$\varepsilon_p \cdot 10^2$	$F \cdot 10^4$	$G \cdot 10^2$
Granite	0.2 – 0.6	0.35 – 2.2	1.8 – 3.7
Granite + fissure coating	1.1 – 7.4	0.15 – 100	0.14 – 14
Granodiorite	0.2 – 3.1	0.014 – 8.5	0.07 – 2.7
Aplite	0.3 – 4.5	0.33 – 12	1.1 – 2.7
Grimsel fault gouge material	$6.2 \pm^{6.8}_{3.2}$	$8 \pm^{35}_{7}$	$1.3 \pm^{5.5}_{1.0}$

For diffusion of spherical particles in a liquid, the diffusion coefficient is related to the temperature, viscosity η [kg m^{-1} s^{-1}] of the liquid and the hydrodynamic radius of the particles r [m] according to the Stokes-Einstein equation

$$D = \frac{kT}{6\pi\eta r} \quad , \tag{51}$$

where k [J K^{-1}] is the Boltzmann constant [13]. Note that the Stokes-Einstein equation for D is dependent neither on the charge nor on the mass of the dissolved particles and does not take into account any interaction between solute and solvent. However, for rough estimations of the diffusion coefficient it might be sufficient. For a fixed particle size and at variable temperature we obtain

$$\frac{D(T_2)}{D(T_1)} = \frac{\eta_1(T_1)/T_1}{\eta_2(T_2)/T_2} \quad , \tag{52}$$

from which a value for D can be extrapolated when the values for the diffusion coefficient and the temperature-dependent viscosity (see e.g. CRC Handbook of chemistry and physics) are known at another temperature. Equation (52) might be of importance when values from laboratory experiments have to be re-scaled to temperatures at performance assessments conditions.

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[13] The friction term $6\pi\eta r v$ [N] related to equation (51) accounts for the irreversibility of the diffusion process, where v [m s^{-1}] means the averaged velocity of the particles.

When combining Fick's first law with mass-balance considerations for a small volume element, Fick's second law results:

$$\frac{\partial C(\vec{r},t)}{\partial t} = \vec{\nabla} \cdot \left(\boldsymbol{D}_a \cdot \vec{\nabla} C(\vec{r},t) \right) \quad . \tag{53}$$

Equation (53) describes the temporal changes of the solute concentration, neglecting sink/source terms. $\boldsymbol{D}_a$ is the apparent diffusion tensor and accounts additionally for possible uptake mechanisms by the porous medium such as sorption. Hence, $\boldsymbol{D}_a$ is specific for each species, the solid phase and the liquid composition. For porous media both diffusion tensors $\boldsymbol{D}_a$ and $\boldsymbol{D}_e$ are linked via the rock capacity factor α according to

$$\boldsymbol{D}_a = \frac{\boldsymbol{D}_e}{\alpha} \quad , \tag{54}$$

where α is

$$\alpha = \varepsilon_p + \left(1 - \varepsilon_p\right) \rho \frac{dS}{dC} \quad . \tag{55}$$

In (55) ε_p is the connected or diffusion-accessible porosity, ρ the (dry) solid phase density and S the amount of solute absorbed onto the solid phase. S might be a given as a function of the solute concentration in solution C. In the case of linear sorption dS/dC is equal to K_d, the linear sorption equilibrium distribution coefficient and hence α reduces to

$$\alpha = \varepsilon_p + \left(1 - \varepsilon_p\right) \rho \; K_d \quad . \tag{56}$$

$\boldsymbol{D}_e$ is often used for describing the boundary conditions where the solute concentration is specified in terms of the pore-water concentration. The apparent diffusivity $\boldsymbol{D}_a$, however, is used together with the total solute concentration in the porous medium.

The main advantage of the diffusion/linear sorption model is its linearity, which allows the use of advanced analytical and numerical methods for obtaining solutions to a broad variety of different transport problems. Preferred methods are based on the Laplace transformed or Green's function.

There is a wealth of small-scale laboratory diffusion experiments with all kind of non-sorbing and sorbing tracers. The aim of these experiments is both to demonstrate that diffusion indeed occurs over distances of at least a few centimetres and to determine values for the porosity, diffusivity and the sorption capacity. From all these investigations it can be concluded that diffusion in homogeneous materials is well understood. However, there are still open questions when dealing with heterogeneous porous media, especially when considering porous media with large inner surfaces, small pores and with view on the interaction of solutes with charged surfaces.

For illustration purposes only a few examples shall be mentioned: Bradbury and Green (1985) measured diffusion through and sorption onto granitic samples from four different regions of the United Kingdom using weakly-sorbing iodide and ^{99}Tc as tracers. Skagius et al. (1982) and Skagius (1986) performed diffusion and sorption measurements on different granite samples from the Finnsjön site and the Stripa mine in Sweden with non-sorbing as well as with strontium and caesium as tracers. A comparison of their laboratory results with data from diffusion experiments on the field scale performed in the Stripa mine (Birgersson and Neretnieks, 1990) showed that the results from laboratory experiments agreed well with those for field conditions. Johansson (2000) measured sorption and diffusion of some selected alkali and alkaline earth metals in laboratory and field experiments. He performed diffusion measurements applying the through-diffusion technique with rock samples from the Swedish Äspö site and compared the parameter values with results from inverse modelling field tracer tests from the TRUE-1 project (Winberg et al., 2000).

If the sample thickness exceeds a few centimetres, through-diffusion experiments are very time consuming. Hence, attempts have been made to speed up through diffusion tests and to analyse the breakthrough curves already in the transient phase before reaching steady state. For example, Skagius and Neretnieks (1986) measured the electrical resistivity [14] of granitic rock under the influence of mechanical stress up to 35 MPa and with a high salinity porewater, and determined values for the formation factor *F*, which can be used to deduce values for the diffusivity. (For the values for the formation factor the applied stress resulted in only a moderate reduction by a factor of four.) Their findings indicate that the electrical resistivity measurement yields result similar to those from through-diffusion experiments because values for the formation factor were in fair agreement in both procedures. New in-situ values for the formation factor by resistivity measurements in boreholes have been reported by Löfgren and Neretnieks (2002).

In many cases the results of performance assessments are very sensitive of the values of the diffusion parameter, and hence, the careful choice of these values is of great importance. Mostly site-specific data and data from field investigations are needed to deduce reliable values for diffusion. For non-sorbing solutes laboratory data may be used directly in performance assessments, but adapting laboratory data for sorbing radionuclides is – as a rule – much less straightforward. However, it can be concluded that our present knowledge provided by small-scale laboratory and field experiments are sufficient for a careful extrapolation in space and time for performance assessment purposes. Studies on natural analogues may help in supporting extrapolated values and reducing uncertainties.

The rock porosity

Crystalline rocks are generally composed of a variety of different minerals with typical sizes of the order of millimetres to centimetres that are bound by electrostatic (surface) forces.

The total volume of a rock may be divided into the volume of the solid and the volume of the void space. The void space arises due to different processes such as crystallisation sequence, brittle or ductile deformation of the fabric, dissolution and precipitation processes as well as alteration of minerals caused by flowing groundwater etc. Pores may be open, closed or isolated from the other void spaces. Although the width of the pores is dependent on pressure, the pores remain open given the mineral fabric of crystalline rocks; mineral deformation is furthermore expected to be small for lithostatic

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[14] The electrical resistivity is the reciprocal to the electrical conductivity.

pressures for planned deep-lying repositories. A given overburden tends to reduce the values of the porosity and the formation factor. Bischoff et al. (1987) investigated the influence of confining pressures up to 600 bars on the hydraulic conductivity and found that the permeability for different granites was reduced by only a factor of 5 – 10.

In the literature, the total porosity ε_{tot} of, crystalline rocks for example, is normally subdivided into the flow porosity ε_f, the diffusion-accessible porosity ε_p and the residual porosity ε_r:

$$\varepsilon_{\text{tot}} = \varepsilon_f + \varepsilon_p + \varepsilon_r \quad . \tag{57}$$

Hence, different terms for the porosity are associated with different objectives and care has to be taken to select the correct one. The flow porosity ε_f accounts for that part of the void space which is affected by flowing groundwater, hence, where advective transport is the dominant process. The diffusion-accessible porosity ε_p means that part of the total porosity where solutes can only have access by pure diffusion, hence, where the water is stagnant and where the effects of a hydraulic pressure gradient are negligible. These parts of the void space are very often dead-ended. Neglecting solid-state diffusion, the residual porosity ε_r finally accounts for the non-accessible, isolated pore space.

The transport-relevant porosity, which is a key issue for describing diffusion, and the internal structure of the rock can be investigated quantitatively by several methods. A common one is the visual method using impregnation, especially with ^{14}C-PMMA-[15] (Hellmuth et al., 1993; Autio et al., 1998) or alternatively, with ^{3}H-PMMA (Siitari-Kauppi et al., 1998). In this procedure a dried rock sample is impregnated with ^{14}C or ^{3}H labelled resin for a certain time span with minimal disruption of the pore structure. During this time span the low viscosity resin, similar to that of water, fills the connected pore space. γ irradiation then causes the resin to solidify due to polymerisation. Subsequently, the sample is sliced into thin sections for autoradiography and the distribution of the solidified resin is evaluated by digital image processing.

There are other methods for evaluating values for the (connected) porosity: e.g. by the gravimetric method with water saturation, the volumetric method with gas pycnometry, or the He-gas or mercury-porosimetry method. Further information on these alternative methods and details about the procedure can be found in Dane and Topp (2002).

By interpreting electrical conductivity measurements a simple empirical relationship between the formation factor F and the porosity ε_p for crystalline rocks (Parkhomenko, 1967, p. 277), also known as Archie’s law, was found

$$F = 0.71\varepsilon_p^{1.58} \quad \text{and} \quad G = 0.71\varepsilon_p^{0.58} \quad . \tag{58}$$

The leading factor (0.71), which is equal to the ratio of the electrical conductivity in a solution saturated porous medium and that in the solution of the same composition, depends on lithology. The exponent is the so-called cementation factor and depends on the crystalline rock structure. This relationship may be appropriate for the average

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[15] PMMA=Polymethyl-methacrylate.

properties of many crystalline rocks, especially for making rough estimates on the formation or geometry factor.

Values for the permeability, porosity and retardation characteristics for Swiss granitic bore cores from the Böttstein deep drilling can be found in Carlson and Platz (1985). Brandberg and Skagius (1991) compiled lots of values for the porosity, sorption and diffusivities based on experimental results on Finnsjön rock for the SKB 91 study. For heterogeneous and fractured rocks, laboratory data for the porosity might be useful for the excavation damage zone, but on a large scale reliable sampling and up-scaling procedure will be needed. For rock under a high lithostatic pressure, corresponding to an overburden of several hundreds of metres, the relevant information, especially the 3D-geometry and its properties, are much less well known.

For host rocks the matrix porosity can be very small. Crystalline rocks show typical values for the porosities of the order of permille to – at most – percents. It is significant that hydrothermally altered rock have porosities approximately an order of magnitude higher than intact crystalline rocks. Porosity values up to 10 % were measured for fracture coating materials; for fracture infill the values may be even higher. From a performance assessment point of view the effects of radionuclide diffusion into fissure coating and infill material are negligible due to their limited extent. Altered zones and – finally – unaltered host rock may be much more of importance as efficient sinks for mobile nuclides. However, whether there is sufficient interconnected porosity to access farther parts of the host rock is still an open question (see below). Nevertheless, the transport properties of the fracture coating and infill material have to be well understood and considered in the modelling of field tracer experiments.

2.3.3.2 Solute transport in the frame of the dual-porosity medium model

A very common approach to modelling transport of solutes in fractured hard rocks is the dual-porosity medium approach. It is based on the assumption that naturally fractured rocks rather behave as two porous media with different values for the porosity of fractures and surrounding matrix, rather than one. The surrounding matrix is considered as the low-conductivity domain, while the fractures are the paths where preferential water flow takes place. Advection within the matrix is usually assumed to be zero, hence, these domains act as sink/source components and in fact the dual-porosity model represents a mobile-immobile model.

Although the dual-porosity medium model is rather a very simplified approach from a scientific point of view, nevertheless it turned out that this model is still used world-wide for modelling both small-scale laboratory but also field experiments. In addition, this model is also extensively used in performance assessment studies. An obvious advantage of the model is that the underlying physics and chemistry are relatively easy to understand. Past experience has shown it to be a versatile, efficient and also appropriate tool for modelling because it covers the most important transport processes such as advection, dispersion, matrix diffusion, sorption, etc. It is also flexible enough to take into consideration various flow geometries such as the planar fracture (parallel plate representation), tube-like vein geometry and superposition of flow paths in terms of the streamtube/streamline formalism. It is the simplicity of this concept, its versatility and applicability to a broad variety of real-world observations in the context of solute transport in geological media, which has established the usefulness of the dual-porosity medium model. The underlying formalism of the dual-porosity medium model, its approximations and most common simplifications are briefly addressed in this section.

Solute [16] transport in a dual-porosity medium can be formulated in terms of a system of two coupled partial differential equations. This formalism is based on mass-balance considerations for carefully chosen representative elementary volumes (REV's – Bear, 1979, p. 29ff) in the fracture and in the porous rock matrix.

In the frame of this model, the transport equation for a dissolved species for a volume element of a water-conducting feature is given by:

$$\frac{\partial}{\partial t}\left[\varepsilon_f\, C_f^i + \delta_f\, S_f^i\right] = \vec{\nabla}\cdot\varepsilon_f\left[\boldsymbol{D}\cdot\vec{\nabla} - \vec{v}_f\right]\; C_f^i + \varepsilon_f\left[\frac{d\vec{F}}{dV_f}\cdot\varepsilon_p^i\boldsymbol{D}_p^i\cdot\vec{\nabla}C_p^i\right]_{\text{interface}} + Q_f^{i,i-1}. \tag{59}$$

The transport equation for a volume element of the porous rock matrix is:

$$\frac{\partial}{\partial t}\left[\varepsilon_p^i C_p^i + \left(1-\varepsilon_p^i\right)\rho\, S_p^i\right] = \vec{\nabla}\cdot\varepsilon_p^i\boldsymbol{D}_p^i\cdot\vec{\nabla}C_p^i + Q_p^{i,i-1} \quad . \tag{60}$$

The left-hand side of Equation (59) describes the variations with time t of the total concentration of the species i in the liquid phase C_f^i and on the solid phase S_f^i of a water-conducting feature. ε_f is the solute independent flow porosity (the ratio of the water-carrying fracture volume and total volume [17]) and δ_f denotes the sorbing surface per total volume.

The right-hand side is equal to minus the divergence of a total flux and net source/sink terms. In the water-conducting zone the total flux is composed of

- a flux term for the hydrodynamic dispersion $\vec{j}_{\text{disp.}}^{\,i} = -\varepsilon_f\boldsymbol{D}\cdot\vec{\nabla}C_f^i$, where $\boldsymbol{D}$ is a second-rank tensor taking into account molecular diffusion and the fact that the direction of the dispersive flux is not only determined by the concentration gradient, but also by the geometry of a possible fracture infill, and
- a flux term representing advection $\vec{j}_{\text{adv.}}^{\,i} = +\varepsilon_f\vec{v}_f C_f^i$, where $\vec{v}_f$ is the velocity vector of the liquid flow field.

A sink/source term describing the diffusive mass transfer of nuclide i across the interface between the water-conducting zone and the porous rock matrix is given by the term $-\varepsilon_f\left[\frac{d\vec{F}}{dV_f}\cdot\varepsilon_p^i\boldsymbol{D}_p^i\cdot\vec{\nabla}C_p^i\right]_{\text{interface}}$, with second-rank diffusion tensor $\boldsymbol{D}_p^i$ considering species dependent diffusion and taking into account that the direction of the diffusive flux is not only given by the concentration gradient, but also by the rock pore geometry. In this expression $d\vec{F}/dV_f$ is a vector representing the ratio of the surface area of the

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[16] The terms "solute", "species", and "(radio-)nuclide" are used synonymously.

[17] The total volume is composed of the volume of the water-saturated void space and the volume of the solid phase.

interface between water-conducting zone and porous rock matrix to the volume element of flowing water. Its orientation is perpendicular to the surface element and points towards the altered rock zone. This term links the transport equation for advection and dispersion (59) with that for matrix diffusion (60). In the case of an open planar fracture (i.e. no fracture infill present) the ratio $d\vec{F}/dV_f$ is equal to $1/b$, where b [m] is half of the fracture aperture. The leading factor ε_f takes into account that due to partial coverage of the interface surface by a possible fracture infill [18] only the fraction ε_f [19] of the porous rock zone is accessible to diffusion [20]. ε_p^i [-] is the species dependent matrix porosity and is the ratio of volume of stagnant liquid to total rock volume. C_p^i [mol/m^3] is the amount of dissolved radionuclide per unit volume of stagnant liquid.

Equations (59) and (60) are three-dimensional equations for solute transport. However, very often it is not necessary or useless, due to the lack of appropriate data, to attempt to develop a full three-dimensional formalism. In such a case a two- or even one-dimensional description may be sufficient to encompass the most relevant mechanisms and processes [21]. Necessary simplifications are typically based on one or more of the following arguments:

- Since the model is based only on mass-balance considerations, any force, pressure, friction etc. is not included in the transport model.
- The volume of the solute is negligible when compared with that of the liquid in the fractures and in the porous rock.
- It is assumed that advective transport in the water-conducting features may be one-dimensional along a trajectory given by the hydrology. The underlying assumption is that the fracture aperture is much smaller than its length, hence providing the basis for a one-dimensional description. Thus the water velocity vector is reduced to a single component v_f along the flow path.
- Molecular diffusion is assumed to be negligible compared to the effect of mechanical dispersion, and transverse dispersion is also neglected [22]. (The effects of molecular diffusion are small and can be incorporated into the coefficient for mechanical dispersion whose value is uncertain anyway.) Consequently, the second-rank tensor for the hydrodynamic dispersion simplifies to

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[18] For simplicity reasons the fracture infill is considered as being not porous. Otherwise a third type of porosity has to be taken into account and a third transport equation would be necessary to describe contaminant transport from the flowing water into the fracture infill.

[19] The term ε_f represents the ratio of uncovered fracture surface accessible to matrix diffusion and total fracture surface and is approximated – again for simplicity – by the flow porosity.

[20] This may be a reasonable assumption if pores, which are blocked by a fracture infill to diffusion from the fracture interface, cannot be reached by diffusing solute via unblocked pores. However, if pore interconnections and fast diffusion in the flow direction allow such blocked pores to be reached, the factor ε_f has to be omitted.

[21] In principle, such conceptual restrictions and approximations have to be estimated quantitatively or, at least, qualitatively assessed. This means, in a rigid sense, that results from, for example, a one-dimensional model have to be compared with results from a two- or even three-dimensional model.

[22] Transverse dispersion, represented by a_T, will certainly play a minor role if

$$b \ll a_T \approx a_L/10$$

holds. According to de Marsily (1986), p. 238, values for a_T are between $a_L/5$ and $a_L/100$.

the mechanical dispersion only, which is represented finally by a single scalar quantity

$$\boldsymbol{D} \approx a_L v_f \tag{61}$$

where a_L [m] is the longitudinal dispersion length.

- Since in crystalline rocks the width of the pores in the rock matrix are much smaller than the fracture apertures, different solutes may have access to different parts of the connected porosity. Therefore the rock porosity ε_p^i is assumed to be a species dependent quantity.
- In the rock matrix diffusive processes occurring perpendicularly to the fracture are only considered. This approximation is surely reasonable, if transport in the fracture is much faster than in the matrix because of the much lower hydraulic conductivity. The thickness of the porous rock matrix accessible to diffusion will be limited to a finite value.
- Since only small values for the fracture aperture are mostly considered, molecular diffusion results – in reality – in fast equilibration of the solute concentration across the fracture width (“fast” here means with regard to typical transport times along the fracture). Hence, an averaged (constant) solute concentration across the fracture width is assumed and replaces the parabolic concentration profiles.

  $$C_f^i(z,x,t) = \text{const.}\ ;\ x \in [0, \pm b]\ ;\ t > 0\ \ . \tag{62}$$

  Such a consideration is equivalent to averaging the solute concentration over the fracture REV.

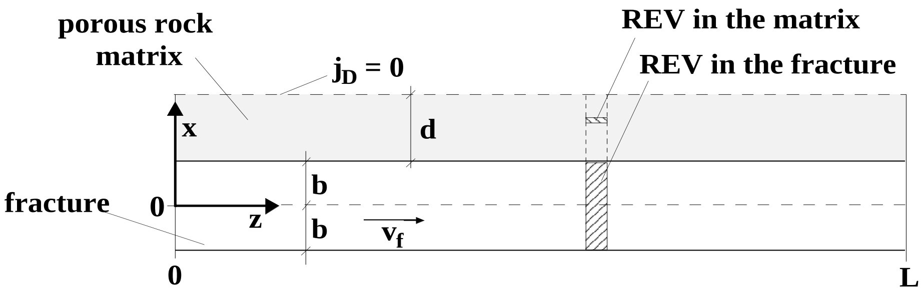

Figure 25. Schematic sketch of the simplified transport domain in the frame of the dual-porosity medium model and the co-ordinate system used in the formalism. The planar fracture extends from z = 0 to z = L*, the migration distance, and has a constant aperture of 2b. The direction of the advective/dispersive flow is from left to right, and across the fracture width instantaneous equilibration of the nuclide concentration is assumed. Matrix diffusion occurs only perpendicularly to the fracture, in the x-direction, and is limited by a zero-diffusive flux boundary condition at distance x = (b + d) measured from the symmetry axis. In the model the rock matrix beyond this boundary is considered inaccessible to diffusing nuclides.*
In the sketch both representative elementary volumes (REV) are drawn. The size of the REV in the water-conducting fracture is selected in such a way that all the microscopic space-dependent values within the REV can be replaced by their averaged and constant (macroscopic) continuum values. The REV spreads over the whole cross section of the fracture. In direction of the water flow, however, it has to be sufficiently narrow to represent the temporal variations of the solute concentration along the fracture with the required precision. A second REV extends into the matrix diffusion zone parallel to the interface area fracture/porous rock matrix. Its extent in the water-flow direction corresponds to that of the former REV in order to guarantee mass flow across the fracture/matrix interface (see below). In the direction of matrix diffusion (x-direction), the REV has to be sufficiently small to represent the temporal variations of the solute concentration in the porous rock matrix with sufficient precision [23].

The terms $Q_f^{i,i-1}$ and $Q_p^{i,i-1}$ in Equations (59) and (60) denote general net source/sink terms describing radioactive decay and ingrowth in the case of nuclide chains with nuclide members …→ *i*–1 → *i* . Thus, the source terms become

$$Q_f^{i,i-1} = -\lambda^i(\varepsilon_f\, C_f^i + \delta_f\, S_f^i) + \lambda^{i-1}(\varepsilon_f\, C_f^{i-1} + \delta_f\, S_f^{i-1}) \qquad (63)$$

and

$$Q_p^{i,i-1} = -\lambda^i[\varepsilon_p^i\, C_p^i + (1-\varepsilon_p^i)\,\rho\, S_p^i] + \lambda^{i-1}[\varepsilon_p^{i-1}\, C_p^{i-1} + (1-\varepsilon_p^{i-1})\,\rho\, S_p^{i-1}] \quad . \qquad (64)$$

In order to calculate the time- and space-dependent concentration in the flowing water C_f^i and in the stagnant pore water of the rock matrix C_p^i, reasonable assumptions about the relationship between the concentrations in the aqueous phase *C* and on the solid phase *S* have to be made. For host rocks considered in a safety assessment of a repository for radioactive waste, water velocities are on the order of a few meters per

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[23] The requirements for the REV's may result in sophisticated spatial discretisation schemes for the transport domain and advanced numerical algorithms for solving the system of coupled partial differential equations.

year, hence very small. Thus, typical transport times (neglecting all retarding mechanisms) are of the order of – at least – hundreds of years. In such a case sorption kinetics play only a minor role; kinetics may become important, however, when modelling laboratory and field experiments on a much smaller time scale. Accounting for a possible influence of kinetic speciation in the liquid and solid phase would result in a further differential equation.

Therefore it is assumed, for the sake of simplicity, that sorption kinetics play no role, i.e. instantaneous sorption equilibrium with a sorption isotherm of the form

$$S^i_{f,p} = f(C^i_{f,p}) \quad , \tag{65}$$

is assumed where $f(C)$ may be any function which in general has different forms for the fracture and the matrix. Applying this relationship we get for the temporal variation of the total solute concentration in the fracture

$$\frac{\partial}{\partial t}\left[\varepsilon_f C^i_f + \delta_f\, f(C^i_f)\right] = \varepsilon_f \left[1 + \frac{\delta_f}{\varepsilon_f}\frac{d f(C^i_f)}{dC^i_f}\right]\frac{\partial C^i_f}{\partial t} = \varepsilon_f R^i_f \frac{\partial C^i_f}{\partial t} \tag{66}$$

and for that in the matrix

$$\frac{\partial}{\partial t}\left[\varepsilon^i_p C^i_p + \left(1-\varepsilon^i_p\right)\rho\, f(C^i_p)\right] = \varepsilon^i_p \left[1 + \frac{\left(1-\varepsilon^i_p\right)}{\varepsilon^i_p}\rho\frac{d\, f(C^i_p)}{d\, C^i_p}\right]\frac{\partial\, C^i_p}{\partial\, t} = \varepsilon^i_p R^i_p \frac{\partial\, C^i_p}{\partial\, t} . \tag{67}$$

In Equations (66) and (67) the following abbreviations for the (concentration dependent) retardation functions $R^i_f(C^i_f)$ and $R^i_p(C^i_p)$ were introduced:

$$R^i_f = 1 + \frac{\delta_f}{\varepsilon_f}\frac{d\, f(C^i_f)}{d\, C^i_f} \qquad \text{(in the fracture),} \tag{68}$$

$$R^i_p = 1 + \frac{(1-\varepsilon^i_p)}{\varepsilon^i_p}\rho\frac{d\, f(C^i_p)}{d\, C^i_p} \qquad \text{(in the matrix)} \quad . \tag{69}$$

Evaluating the source/sink terms (63) and (64) results in two further retardation functions:

$$\tilde{R}^i_f = 1 + \frac{\delta_f}{\varepsilon_f}\frac{f(C^i_f)}{C^i_f} \qquad \text{(in the fracture),} \tag{70}$$

$$\tilde{R}^i_p = 1 + \frac{(1-\varepsilon^i_p)}{\varepsilon^i_p}\rho\,\frac{f(C^i_p)}{C^i_p} \qquad \text{(in the matrix)} \quad . \tag{71}$$

In the case of a linear sorption isotherm of the form $S(C) = K \cdot C$ the following constants are obtained:

$$R^i_f = 1 + \frac{\delta_f}{\varepsilon_f}K^i_a \equiv \tilde{R}^i_f \qquad \text{(in the fracture),} \tag{72}$$

$$R^i_p = 1 + \frac{(1-\varepsilon^i_p)}{\varepsilon^i_p}\rho\, K^i_d \equiv \tilde{R}^i_p \qquad \text{(in the matrix),} \tag{73}$$

where δ_f / ε_f [m^{-1}] is the sorbing surface of the water conducting zone per unit volume of flowing water[24] In the case of an open planar fracture this ratio is assumed to be $\delta_f / \varepsilon_f = 1/b$.

For more complicated isotherms such as, e.g. the Freundlich isotherm, one must use concentration-dependent retardation functions, hence different parts of a migrating solute plume will move with different rates, and the shape of the plume will change with time, even when neglecting dispersive effects and matrix diffusion. Some radionuclides may have a finite natural (stable) background concentration in the transport domain, which is assumed to be constant in time and space. Therefore, the cumulative element concentration $C^i_{f,p,\text{total}} = C^i_{f,p} + C^i_{\text{background}}$ enters the equations for the retardation functions, thereby avoiding the unrealistic special feature of the Freundlich isotherm that $R(C)$ becomes infinitely large for concentrations approaching zero. Hence, for non-linear isotherms of the Freundlich type the concentration-dependent retardation functions are as follows:

$$R^i_f(C^i_{f,\text{total}}) = 1 + \frac{1}{b} K^i_f N^i_f (C^i_f + C^i_{\text{background}})^{N^i_f - 1} \qquad \text{(in a planar fracture)}, \qquad (74)$$

$$R^i_p(C^i_{p,\text{total}}) = 1 + \frac{(1-\varepsilon^i_p)}{\varepsilon^i_p} \rho\, K^i_p N^i_p (C^i_p + C^i_{\text{background}})^{N^i_p - 1} \qquad \text{(in the matrix)} \quad . \qquad (75)$$

$$\tilde{R}^i_f(C^i_{f,\text{total}}) = 1 + \frac{1}{b} K^i_f (C^i_f + C^i_{\text{background}})^{N^i_f - 1} \qquad \text{(in a planar fracture)}, \qquad (76)$$

$$\tilde{R}^i_p(C^i_{p,\text{total}}) = 1 + \frac{(1-\varepsilon^i_p)}{\varepsilon^i_p} \rho\, K^i_p (C^i_p + C^i_{\text{background}})^{N^i_p - 1} \qquad \text{(in the matrix)} \quad . \qquad (77)$$

With these expressions the sink/source terms Q^i_f / ε_f and Q^i_p / ε^i_p can be written as

$$Q^i_f / \varepsilon^i_f = -\lambda^i \tilde{R}^i_f C^i_f + \lambda^{i-1} \tilde{R}^{i-1}_f C^{i-1}_f \qquad (78)$$

and

$$Q^i_p / \varepsilon^i_p = -\lambda^i \tilde{R}^i_p C^i_p + \lambda^{i-1} \frac{\varepsilon^{i-1}_p}{\varepsilon^i_p} \tilde{R}^{i-1}_p C^{i-1}_p \quad . \qquad (79)$$

Considering all these simplifications and approximations the set of coupled transport equations for solute transport in an open planer fracture is:

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[24] In the transport model the interface area for matrix diffusion $d\vec{F} / dV_f$ needs not necessarily be the same as for the sorption of solute onto the surface of the water-conducting feature, which is denoted by δ_f / ε_f. Such a distinction is important in the case of a fracture infill.

$$\frac{\partial}{\partial t}C_f^i = \frac{1}{R_f^i(C_f^i)}\left[a_L v_f \frac{\partial^2 C_f^i}{\partial z^2} - v_f \frac{\partial C_f^i}{\partial z} + \frac{1}{b}\varepsilon_p^i D_p^i \left.\frac{\partial C_p^i}{\partial x}\right|_{x=b} - \lambda^i \tilde{R}_f^i C_f^i + \lambda^{i-1}\tilde{R}_f^{i-1} C_f^{i-1}\right] \tag{80}$$

$$\frac{\partial}{\partial t}C_p^i = \frac{1}{R_p^i(C_p^i)}\left[D_p^i \frac{\partial^2 C_p^i}{\partial x^2} - \lambda^i \tilde{R}_p^i C_p^i + \lambda^{i-1}\frac{\varepsilon_p^{i-1}}{\varepsilon_p^i}\tilde{R}_p^{i-1} C_p^{i-1}\right] \quad . \tag{81}$$

Because both transport equations are first order in time and second order in space, one has to specify one initial and two boundary conditions for each differential equation depending – of course – on the physical problem at hand.

The following relationships are used as initial conditions for the differential equations:

a) $C_f^i\left(z,t\right) = C_{\text{background}}^i\left(z,t\right) \quad ; \; t \le 0 \;\; \text{and} \;\; z \in [0,L] \quad ,$ (82)

b) $C_p^i\left(z,x,t\right) = C_{\text{background}}^i\left(z,x,t\right) \quad ; \; t \le 0 \;\; \text{and} \;\; z \in [0,L]; \;\; x \in [\pm b, \pm(b+d)]$ (83)

meaning that the whole domain of interest has a certain (space-dependent) initial background concentration [25]. However, for most solutes the background concentration is zero.

At the interface fracture/porous (altered) rock matrix, continuity in the concentration is assumed. This is given by:

c) $C_f^i\left(z,t\right) = C_p^i\left(z,\pm b,t\right) \quad ; \quad \forall z \quad ; t > 0 \quad ,$ (84)

and continuity in mass flow (but not in the flux!) [26] is implicitly included in Equations (80) and (81), respectively.

The boundary conditions are as follows: In the porous rock matrix a zero diffusive-flux boundary condition at a certain distance ± (*b* + *d*) [m] is chosen; *d* being the maximum depth for matrix diffusion:

d) $j_D^i = -D_p^i \left.\frac{\partial C_p^i}{\partial x}\right|_{|x| = b+d} = 0 \quad ; \quad \forall t \quad .$ (85)

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[25] Examples of a non-zero initial condition are, for example, the natural ^{235}U and ^{238}U content of crystalline granitic rocks.

[26] The diffusive solute out-flux across the fracture/matrix interface [mol m^2 s^{-1}] is $\vec{j}_f^i = +\varepsilon_f \, \varepsilon_p^i D_p^i \left.\frac{\partial C_p^i}{\partial x}\right|_{x=\pm b}$ and the diffusive in-flux into the matrix is $\vec{j}_p^i = -\varepsilon_p^i D_p^i \left.\frac{\partial C_p^i}{\partial x}\right|_{x=\pm b}$, hence $-j_f^i \neq j_p^i$.

Although the flux is not continuous at the interface, mass is conserved, since the flow per unit volume of flowing water [mol m^{-3} s^{-1}] leaving the fracture is equal to that entering the porous rock zone according to: $-\frac{dJ_f^i}{dV_f} = -\frac{d\vec{F}}{dV_f}\vec{j}_f^i = \varepsilon_f \frac{d\vec{F}}{dV_f}\vec{j}_p^i = \frac{dJ_p^i}{dV_f}$. The term $\varepsilon_f \frac{d\vec{F}}{dV_f}$ takes into account the restricted volume of porous rock matrix available by diffusion.

With the conditions (82) - (85) the second transport equation, the diffusion Equation (81), can be solved; the corresponding boundary conditions for the transport equation in the fracture also have to be fixed: At the inlet, i.e. at the upstream boundary, the following form of the mixed von Neumann/Dirichlet (also called Fourier type) boundary condition [27] is applied specifying the solute flow:

$$\text{e)} \quad \varepsilon_f \, v_f \, F \left(C_f^i - a_L \frac{\partial C_f^i}{\partial z} \right) \Bigg|_{z=0} = f^i(t) \cdot \text{È} \left(T_L^i - t \right) \quad ; \quad t > 0 \quad . \tag{86}$$

In this expression $\Theta(w)$

$$\Theta(w) = \begin{cases} 0 & ; \quad w < 0 \\ 1 & ; \quad w \geq 0 \end{cases} \tag{87}$$

is the Heaviside step function and $f^i(t)$ is a time-dependent input function with units of $[\,\text{mol/m}^3\,]$ describing the release of the solute i. T_L^i [s] is the release time for the species i. The Heaviside step function switches on the release function $f^i(t)$ during the period $[0, T_L^i]$.

$\varepsilon_f \, v_f \, F$ is the total water flow rate Q [m^3/y] with cross-sectional area F for the water flow and corresponding flow porosity ε_f averaged over the transport domain.

Equation (86) may also be applied for the downstream boundary at $z = L$. But, very often, a zero concentration boundary condition is assumed:

$$\text{f)} \quad C_f^i \left(z = L, t \right) = 0 \quad ; \quad \forall t > 0 \quad , \tag{88}$$

and the nuclide flow across the boundary consists of the dispersive flow part only. This boundary condition may also be used for the solute breakthrough in performance assessments or for the analysis of field experiments where at $z = L$ (L finite) the solute becomes strongly and instantaneously diluted by uncontaminated groundwater.

In most cases it is not possible to obtain an analytical solution of the coupled system of partial differential Equations (80) and (81), especially when they are non-linear. Therefore it is necessary to solve the system of equations numerically. In principle it is possible to obtain solutions with the help of a variety of numerical methods such as finite differences (Smith, 1985), finite elements (Lapidus and Pinder, 1982), spectral method (Canuto et al, 1988), method of line approximations (Schiesser, 1991) and random walk (Weiss, 1994).

Further details about the dual-porosity medium model and the effects of matrix diffusion on radionuclide transport through fractured porous media, can be found in Neretnieks (1993); Jakob (1997) and Carrera et al. (1998).

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[27] A boundary condition is of the von Neumann type if the flux in the direction normal to the bounding surface of the physical system is known. If the value of the quantity (i.e. concentration) on the boundary is specified, we have a boundary condition of the Dirichlet type. However, a mixture of both types of boundary conditions is also possible.

The flow-wetted surface

$d\vec{F}/dV_f$ in Equation (59) is a crucial quantity in radionuclide transport modelling and is either addressed as "specific interface area" or also as "flow-wetted surface area per unit volume of mobile water". However, both expressions mean the same, i.e. that part of the fracture surface that stays in contact with mobile water and where mass transfer may occur between the fracture and the immobile water of the rock matrix. The larger this value is, the larger is also the diffusive mass transfer of solute into or out of the porous rock matrix. For a simplified system where flow takes place through an open planar fracture with aperture $2b$ the value for the specific interface area is $1/b$.

Ohlsson and Neretnieks (1995) confirmed the results by Bradbury and Green (1986) that a possible fracture coating, which can cover the interface surface partially or might even be many millimetres thick, may not essentially hinder the diffusion of the solute into the rock matrix because it often has a considerably higher porosity than the host rock.

Very often the flow-wetted surface is defined with regard to unit volume of (total) rock and not to unit volume of mobile water in the fracture, as above. This is because the flow-wetted surface per unit volume of rock is primarily estimated from observations on bore cores. However, both quantities are related to each other by the flow porosity ε_f

$$\frac{d\vec{F}}{dV_{\text{total}}} = \frac{d\vec{F}}{dV_f}\frac{dV_f}{dV_{\text{total}}} = \frac{d\vec{F}}{dV_f}\varepsilon_f \quad . \tag{89}$$

By measuring – in samples from borecores – the fracture surface in contact with flowing groundwater, i.e. by assessing the conductive fracture frequency, information on the flow-wetted surface in the transport domain can be obtained. However, such values have to be carefully interpreted if the water-conducting features are made up of a network of micro fractures and/or in the case when fracture infill material is present. In addition, a few – or only parts of a few – of the fractures may carry the major amount of water (channelling – see below).

Analysing complex tracer experiments can also provide values for the flow-wetted surface. However, additional information concerning other transport parameters, such as the diffusivity and the sorption capacity, is needed as further constraints in order to reduce the fit-parameter space. Such values for the specific interface area are therefore difficult to deduce and are strongly model-dependent. However, these values represent rather "integral numbers" across the transport-relevant domain.

Evaluating resin-impregnated micrographs of thin sections of borecores may yield further information on the flow-wetted surface which can be applied for modelling purposes and in performance assessments.

As already mentioned, matrix diffusion may cause a pronounced retardation in the migration of solutes, even in the absence of other interactions of the solute with the solid phases, e.g. sorption. In the frame of the dual-porosity medium model, a measure of the additional delay due to matrix diffusion is the so-called "matrix diffusion time" τ_0^i [s] (Jakob, 1997) which is a lumped parameter of the following form:

$$\tau_0^i = \left(\varepsilon_p^i \, \delta_p\right)^2 \left(\frac{L}{v_f}\right)^2 \frac{D_p^i \, R_p^i}{4} \quad , \tag{90}$$

where $\delta_p \equiv d\vec{F} / dV_f$ [m^2 / m^3] is the specific interface area [28]. If, within the framework of the dual-porosity medium model, dispersion in the fracture as well as radioactive decay are neglected for simplicity reasons, there is an analytical 1D-solution for two-fold a semi-infinite medium along the flow path and in matrix diffusion direction. Initially, the whole transport domain is assumed to be free of solutes. At time equal to zero a constant concentration C_0 of the solute is considered as the up-stream boundary condition; down-stream a zero-concentration boundary condition for $z \rightarrow \infty$ is assumed. The time- and space-dependent solution of the transport problem is as follows:

$$\frac{C^i(z,t)}{C_0^i} = \begin{cases} 0 & ; \text{ for } \; 0 \le t \le t_{\text{adv}}^i \\ \operatorname{erfc}\left(\sqrt{\dfrac{\tau_0^i}{t - t_{\text{adv}}^i}}\right) & ; \text{ for } \qquad t_{\text{adv}}^i < t \end{cases} \quad , \tag{91}$$

where

$$t_{\text{adv}}^i = \frac{R_f^i}{v_f} z \tag{92}$$

is the nuclide-dependent advection time [s], possibly retarded due to fracture surface sorption resulting in $R_f^i > 1$ [29]. As can be seen from Equation (91) the effects of matrix diffusion on solute transport are described completely by the lumped parameter τ_0^i.

In the literature, for the special case of an open planar fracture with aperture 2*b* and width *W* [m] (in *y*-direction), an alternative expression for Equation (91), shown below, is often given (see also Chapter 2.1 for further details):

$$\frac{C^i(z,t)}{C_0^i} = \begin{cases} 0 & ; \text{ for } \; 0 \le t \le t_{\text{adv}}^i \\ \operatorname{erfc}\left(\varepsilon_p^i \sqrt{\dfrac{D_p^i \, R_p^i}{t - t_{\text{adv}}^i}} \left(\dfrac{zW}{Q}\right)\right) & ; \text{ for } \qquad t_{\text{adv}}^i < t \end{cases} \quad , \tag{93}$$

where $Q = 2bWv_f$ [m^3/s] is the water flow-rate in the open fracture and the flow-wetted surface area is $2zW$. Equations (91) and (93) implies that decreasing the value for the flow-wetted surface (which is difficult to estimate) by a factor of two will result in a – roughly – four times earlier solute breakthrough. The term $D_p^i \, R_p^i$, however, which characterises sorption and diffusion, and the values of which can be assessed much better in appropriate laboratory and field experiments, only affects the solute arrival time linearly. Hence, $2zW$ or alternatively, $\delta_p \equiv d\vec{F} / dV_f$ is a critical quantity in the dual-porosity medium model.

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[28] Normally the temporal evolution of the solute concentration is calculated or measured at the down-stream boundary at $z = L$, where L [m] means the migration distance.

[29] Concerning the conditions for a repository for radioactive waste where long transport times and small water flow rates prevail, the advection time is negligible compared to the nuclide transport time *t*, even if there is no further interaction of the nuclides with the solid phases, e.g., sorption.

Regarding performance assessments, the specific interface area is often estimated based on the frequency and the geometry of fractures in the host rock due to the lack of site-specific data or due to other – rather technical – restrictions. Such a procedure is certainly an oversimplification since the transport properties may vary strongly along the flow paths and in the rock matrix. As will be outlined below, today’s (process) models are very well able to account for locally varying properties – provided the necessary data concerning diffusion and sorption properties as well as the penetration depth are available.

Channelling

Another phenomenon, which may strongly affect matrix diffusion, is channelling. Early work on flow and transport was done within the framework of the parallel-plate formalism. Witherspoon et al. (1980) found that the cubic law was appropriate for a closed fracture under the influence of external stress. However, experimental and theoretical investigations of solute transport indicate that the parallel plate model with a constant aperture might be inadequate and the fluid might flow preferentially through channels (Moreno and Neretnieks, 1985; Rasmuson and Neretnieks, 1986; Johns and Roberts, 1991).

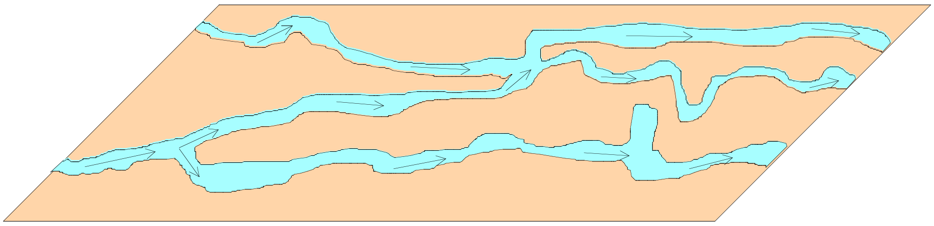

Figure 26. Sketch of channelling in a hypothetical fracture plane. (The arrows indicate the flow direction.)

According to their investigations groundwater flow is unevenly distributed in the fracture plane (Bourke, 1987; Neretnieks, 1987; Tsang and Tsang, 1987). Observations indicate that a few pathways may transport the major part of the solute much faster than the mean. Based on this, only a limited part of the fracture surface is in contact with the liquid. Therefore the specific-interface area (flow-wetted surface) for matrix diffusion and any other uptake mechanism of the solid phase, such as sorption, might be strongly reduced. The influence of irregular flow pattern due to sealed areas in the fracture plane might be of special importance with regard to performance assessments because the effectiveness of matrix diffusion may be strongly reduced.

Numerical investigations in the frame of a statistical aperture model show that solute transport is mainly determined by the mean of the fracture apertures. However, if the variance of the fracture apertures becomes too large, fracture flow will be increasingly dominated by channelling (Wendland and Himmelsbach, 2002).

Time-dependent transport parameters

Certain problems associated with the disposal of hazardous waste in the subsurface can never be addressed only by laboratory or field investigations; other sources of information about the system are required. For example, due to the very long time scales involved, it is nearly impossible to demonstrate that today's groundwater flow field is indeed in steady-state with regard to boundary conditions or rather whether it is slowly transient responding to natural geological changes. One can imagine scenarios where geological changes will definitely occur but the magnitudes of the changes and their effects on the efficiency of the geosphere barrier are highly unknown. For example, presumably there will be future glaciations, which will then strongly affect – inter alia – groundwater flow. Changes in the air temperature, annual rain- and snowfall, evaporation etc. will subsequently also alter the regional fluid flow regime. In addition, water-saturated parts of the sub-surface may become unsaturated. Varying ice overburden causes subsidence and uplift of whole areas generating chemical gradients in the underground due to mixing of different types of water, as presently observed in Äspö (Sweden). Especially for sedimentary rocks such as clay or shale, compaction of the host rock will furthermore result in long-term transients of the water flow (Horseman et al., 1991). An uplift of the area hosting the radioactive waste repository combined with erosion in an inter-glacial period will also result in slow temporal changes of the conditions for the geology, groundwater hydraulic and chemical conditions of the domain. Analogous changes will happen during a new subsidence.

Fortunately very unlikely events, which can cause profound changes in the flow and chemical conditions, are heavy earthquakes and major rock displacements especially when these displacements intersect the repository domain. However, it is extremely difficult to quantify their effects.

A post-closure chemical evolution can also affect the geosphere barrier system: a slow change from oxidising to reducing conditions in the vicinity of the repository; slow degradation of the repository construction materials, e.g., cementitious materials, will generate chemical gradients in the domain of interest.

Time dependencies of all the parameters are generally not taken into account, neither in the modelling of laboratory and field experiments, nor in performance assessments. For example, when analysing field tracer tests fluctuations in the hydraulic head are taken into account by averaging on a daily, weekly etc. basis. Such a procedure – averaging – is the most common approach to time-dependencies and is very often done without any further comment. Averaging, or neglecting time dependencies at all, is therefore, in view of the long time scales to be considered in performance assessments, a gross oversimplification of most of the parameters; the decay constants are an exception. In performance assessments the inevitable uncertainties concerning the temporal evolution of the repository domain are normally covered by a large numbers of different scenarios, each using time-invariant parameters often resulting in series of very pessimistic assumptions and hence, over conservatism. To reduce them in future assessments, and since little is known on the possible time evolution of the transport-relevant parameters such as, e.g. effective diffusion coefficients, parameters for describing sorption, spatial extent of altered zones adjacent to water conducting features, etc., further work on this topic is required. (See also Annex 6 in this context – Conclusions of working group D, in: GEOTRAP, 1998.)

Variability of rock properties – space-dependent transport parameters

If more detailed structural information on rock properties such as mineralogy, porosity etc. is available, the effects of a more realistic description of radionuclide transport have to be assessed quantitatively in order to motivate necessary model simplifications for performance assessment purposes and to reduce over-conservatisms in the geosphere transport modelling. A possible space dependence of the transport properties [30] along the water conducting feature might be modelled by piecewise constant parameters (Hadermann, 1980). Such a procedure defines a series of N segments with lengths l_k, $k = 1, 2, \ldots, N$, along the migration pathway.

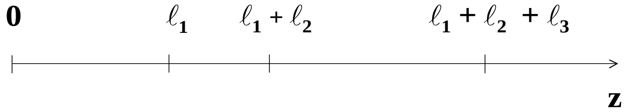

Figure 27. Definition of the co-ordinates for the migration in a piecewise homogeneous porous medium.

Radionuclide mass conservation at the segment's interfaces requires continuity in the solute concentration

$$C_k(0,t) = C_{k-1}(l_{k-1},t) \quad , \quad 2 \le k \le N \quad , \tag{94}$$

and in the flow according to

$$\varepsilon_{f,k}\, F_k\, v_{f,k} \left(C^i_{f,k} - a_{L,k} \frac{\partial\, C^i_{f,k}}{\partial\, z} \right)\Bigg|_{z\,=\,0} = \varepsilon_{f,k-1}\, F_{k-1}\, v_{f,k-1} \left(C^i_{f,k-1} - a_{L,k-1} \frac{\partial\, C^i_{f,k-1}}{\partial\, z} \right)\Bigg|_{z\,=\,l_{k-1}} \quad . \quad , \; 2 \le k \le N \tag{95}$$

F_k [m^2] is the cross-sectional area for the water flow in the k-th segment. Provided that the water flow $\varepsilon_{f,k}\, F_k\, v_{f,k}\ ; 2 \le k \le N$, is unsteady at a segment interface, the ratio of the water flows of the two segments defines a dilution factor.

In performance assessments the different diffusion and sorption properties of different rock materials in the vicinity of water-conducting features representing small-scale heterogeneities are normally neglected. However, first attempts have already been made to account in more detail for the heterogeneities of a possible host rock on different scales (Nagra, 2000). One of Nagra's transport models (Barten, 1996; Barten and Robinson, 2001) accounts for both, the larger scale heterogeneities represented by a network of water-conducting conduits and the multiple porous layers which can be addressed by matrix diffusion. From a performance assessment point of view, considering further rock formation features which act as additional sinks for diffusing radionuclides is highly beneficial with regard to total doses to men.

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[30] One may think of different geological layers such as altered and unaltered rock in the vicinity of a water conducting feature, or of a single layer with piecewise different physicochemical properties representing different mineralogy, porosity etc.

Spatially dependent transport parameters in the matrix diffusion direction can be taken into account by treating the rock as a multi-layered matrix where each layer is characterised by constant parameters. The mathematical/numerical procedure is similar to that outlined above where a migration pathway is divided into segments. At the layer's interfaces continuity of the solute concentration and of the diffusive flow has to be ensured.

Limited extent for matrix diffusion

While the theoretical basis for matrix diffusion is well accepted by the experts, there are still different opinions regarding the volume of porous rocks which can be accessed by matrix diffusion. In early performance assessments such as the Swedish KBS-3 (1983), matrix diffusion was assumed to be limited to 100 m for the zero-diffusive flux boundary. In contrast to this, in the Swiss Project Gewähr (Nagra,1985) it was assumed that the lateral extent of the diffusion-accessible zone in the base case was only 1 mm, hence, a very conservative value [31]. In the last Finnish safety assessment TILA-99 (Vieno and Nordman, 1999) the maximum penetration depth for matrix diffusion was limited to 10 cm.

Because a possible limitation is a critical issue, considerable efforts have been made in laboratory and field investigations to determine reliable values for the depth of the connected porosity. There are clear indications that connected porosity exists at distances up to decimetres in the field and, at least, a few centimetres in laboratory experiments. However, most of the measurements were not performed under virgin conditions. Rock samples were cored and therefore the original lithostatic pressure was released. Applying the original pressure does not guarantee that the former in-situ conditions can be reached again (Ohlsson and Neretnieks, 1995). Excavation damage zones around the boreholes, too, disturb larger-scale field experiments. Only at some distance away from such disturbances may the rock still be in its virgin conditions. Consequently, one has to accept the need for much longer transport distances. However, such experiments are very difficult to perform and, last but not least, extremely expensive.

In general, all sampling procedures tend to result in too high values for the porosity, which is – from a performance assessment point of view – non-conservative because it results in an over-estimation of the efficiency of radionuclide immobilisation in the rock matrix. Our present knowledge indicates that the connected porosity is limited [32]. Such a picture is also based on measurements and observations of natural analogues as already outlined in Section 2.3.2. Under in-situ conditions, due to compression and the

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[31] In Project Gewähr (Nagra, 1985), alternatively also nuclide transport in kakirites was considered where for the water flow-paths a tube like vein geometry was assumed. The penetration depth for matrix diffusion in the kakirites was varied between 0.1 and 0.5 m resulting in a change of the nuclide release rates up to seven orders of magnitude (Hadermann et al., 1985). Such sensitivity studies clearly demonstrate the capacity of limited matrix diffusion for an efficient retardation and dilution of migrating radionuclides.

[32] According to Birgersson and Neretnieks (1990) there are indications for rock domains with closed pores which are surrounded in 3D by other domains with open pores so that solutes may – in principle – diffuse around closed regions into further parts of the porous rock.

subsequent closing of pores, the depth of the interconnected porosity is finite. Attempts were made to measure radionuclide transport under high pressure, but very low values for the hydraulic conductivity required extremely high pressure gradients to detect any tracer breakthrough in a reasonable time span. Such experiments were performed, for example, by Bischoff et al. (1987) on small pieces of granite. Gureghian et al. (1990), Vandergraaf (1995), Vandergraaf et al. (1997) performed similar experiments on a larger block of crystalline rock containing a single natural fracture. Both experiments were part of the INTRAVAL project (INTRAVAL, 1990) and thereby carefully analysed by different modelling teams. Valkiainen (1992) compiled much laboratory and field data on matrix diffusion for various crystalline rocks. His data reveal that within the first few centimetres from a water-bearing fracture the porosity is greater by a factor of 2 to 3 compared with the rock farther away. These first few centimetres adjacent to a fracture are considered the zone where matrix diffusion of solutes will occur. However, due to the heterogeneity of the crystalline rocks such values for the extent may scatter considerably. Due to the higher porosity, the altered wall rock has the greater potential for solute uptake than fresh rock, and consequently matrix diffusion affects mainly these zones and not the entire rock volume before the radionuclides have decayed. Furthermore, it should be mentioned that relatively large faults often contain clay minerals (fault gouge) and fault breccia in the fault crushed zone. However, hydrogeological data on such features at relevant depths are very sparse. In fractures with fault gouge, diffusion into and sorption onto this material can be expected. This might be of importance when analysing field tracer tests, but for performance assessment purposes fault gouge is not the relevant material with respect to matrix diffusion.

The extent of the connected porosity can also be assessed by analysing complex field tracer tests such as those carried out in Stripa (Abelin et al., 1985) and Äspö (Winberg et al., 2000), at Grimsel (Frick et al., 1992) and at the El Berrocal site in an uranium mine in Spain. By a strongly model-dependent interpretation of breakthrough curves for various tracers and considering additional system information (e.g. structural geological information from bore core investigations, mineralogy etc.), rough values for the penetration depth of a diffusion-accessible zone can be deduced (Mazurek et al., 2003 and Jakob et al., 2003). Such values, however, reflect only those parts of the connected porosity which were accessed within the experimental time span and hence, do not represent the whole available depth. However, it is exactly this part – not investigated by short-term field experiments – which is important in the frame of long-term performance assessments. Finally, it should be mentioned that different models might fit the measured breakthrough curves more or less equally well when focussing on different aspects of the experiments (Elert and Svensson, 2001). Therefore, the interpretation of in-situ migration experiments is still an area for future investigations.

Electrical conductivity measurements performed either in the laboratory on rock samples of bore cores or under in-situ conditions in the field provide a new technique to investigate the extent of a porous rock matrix. The method is based on electro migration instead of solute diffusion as in “traditional” transport experiments. First results are encouraging and indicate that the pore system might be connected over distances of at least 0.5 m up to several metres (Löfgren and Neretnieks, 2003). However, the method must be further tested, especially also on other field sites and for other than granitic host rocks in order to get information on the variability of the values for the extent of the connected porosity and for the diffusivity.

Supporting information about the possible extent of the connected porosity can also be obtained by studies on natural analogues; see the overview by Neretnieks (1996). However, the details which led to the observed profiles of decay series, rare-earth elements or redox sensitive tracer distributions in the rock are, to a high degree, unknown, making the interpretation of such observations very difficult. Nevertheless, such studies are indicative of pore connectivities on a scale of up to one metre. Other observations on natural systems led to the conclusion that matrix diffusion is limited to weathered (altered) zones adjacent to fractures where groundwater was, or still is, flowing. The typical extent of such zones is in the order of a few centimetres to a few decimetres, depending on the degree of weathering or hydrothermal activity (Alexander et al., 1990).

In the following compilation some typical values for the extent of the connected porosity are presented as deduced from laboratory and field investigations. For illustrative purposes, values from natural analogues are also included.

Table 6. Compilation of typical values for the depth of the connected porosity based on experimental investigations in the laboratory and in the field. In addition, some values from natural analogue studies are also included. Especially the natural analogue data indicate that the pore system has been open over very long time spans and hence, matrix diffusion was acting for thousands to million of years in altered crystalline rocks.

Examples	Typical distances	References (examples)
Field-diffusion experiments	5 – 40 cm	Birgersson and Neretnieks (1990)
Resin impregnation	1 – 2 cm	Autio et al. (1998)
Leach tests	3 – 14 cm	Ohlsson and Neretnieks (1995)
Electrical conductivity (lab. experiments)	2 – 125 cm	Atkinson and Titchell (1985)
(laboratory / field experiments)	50 cm – m	Löfgren and Neretnieks (2003)
Uranium-series disequilibria	3 – 4 cm	Smellie et al. (1986)
Redox front in unfractured rock	40 cm	See the example in Section 2.3.2.
Alteration zones with higher porosity	50 cm	Alexander et al. (1990)

Anion exclusion

The classical matrix diffusion formalism, such as that in the framework of the dual-porosity medium model, does not account for the different charges of solutes. In addition, the broad variety of complex interactions between dissolved species and solid phase are very often merged into a simple value for the distribution ratio K_d. The idea of anion exclusion is that anions – when compared with cations or neutral solutes – only have access to a limited part of the connected porosity. This is due to a net-negative electrical charge of mineral surfaces resulting in a certain repulsion of anions close to the surfaces while cations and neutral solutes may be attached to the surfaces. Anion exclusion thus promotes the transport of anions through the geosphere. With regard to matrix diffusion, anion exclusion will result in less retardation for dissolved, negatively charged particles, because the narrowest pores are less accessible.

In the dual-porosity model, the consideration of anion exclusion would result – from a very purist point of view – also in ion-dependent values for the flow porosities, for the flow-wetted surface, for the nuclide velocity in the flowing water and for the sorbing surface (see Equations (59) and (60)). However, it might be very challenging to determine reasonable values for all these parameters. Particle exclusion can also be seen in colloid transport, where, for example, the flow porosity and particle arrival times are indeed size- (and surface charge-) dependent. In experiments using columns filled with a dual-porous medium, the colloids show significantly shorter transport times and are less influenced by matrix diffusion than dissolved conservative tracers (Niehren and Kinzelbach, 1998).

However, it should be mentioned that the effects of anion exclusion for dissolved radionuclides are much less prominent in crystalline rocks compared to sedimentary rocks, e.g., argillaceous rocks. In these cases, anion exclusion affects more strongly a number of diagonal and off-diagonal Onsager transport processes, such as Fickian diffusion, chemical osmosis or hyperfiltration. In crystalline rocks, however, where a pressure gradient is the main driving force for fracture flow, apertures are many orders of magnitude larger than openings in clay materials, the latter with typical widths of the order of nanometres. If the values for fracture apertures are in such a range, advective flow certainly plays a negligible role and diffusion is the relevant transport process in the system. Consequently, anion exclusion is only related to solute diffusion in the bulk where it affects the retardation of different species. It is also the reason why a species-dependent porosity ε_p^i was introduced in the transport Equations (59) and (60).

Most of the radioactive waste organisations consider anion exclusion as a relevant process in the porous rock which has to be taken into account in performance assessments. In previous assessments such as, e.g., the Finish TILA-99 safety assessment, effects of anion exclusion were indeed considered in the matrix. Values for the porosity and the diffusivity were applied which are different for anions and non-anions.

Diffusion into stagnant water

The zone with immobile water accessible by matrix diffusion may be augmented by domains with stagnant water within the fracture. Radionuclides in zones with mobile water in the fracture may diffuse into pools of stagnant water and therefore be withdrawn temporarily from the flowing groundwater.

Diffusion of radionuclides into stagnant water was invoked in order to explain the observed pronounced tailing in tracer breakthrough curves where the effects of matrix diffusion into a limited zone of altered rock adjacent to a fracture were believed to be insufficient (Johansson, 2000). In performance assessments diffusion into stagnant water is mostly neglected due to the lack of appropriate data and for conservatism reasons.

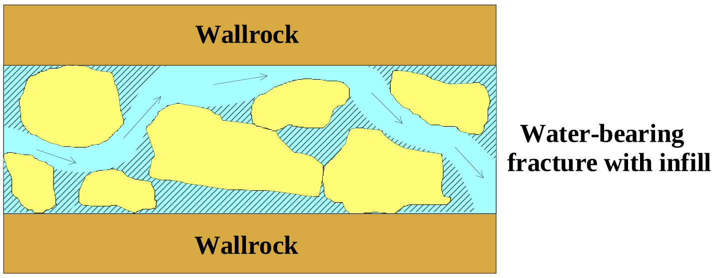

Figure 28. Sketch of a cross-section through a hypothetical planar fracture with fracture infill. Advective water flow takes place in an intricate channel with mobile water. Solutes may have access to pools of stagnant water, depicted in the sketch by the shaded areas, by molecular diffusion only.

Surface diffusion

Surface diffusion postulates that, in contrast to the classical diffusion theory, a fraction of the adsorbed nuclides is mobile and that they might diffuse along the solid surfaces and contribute to the total diffusive flux in the rock matrix. The flux rate is controlled by a specific surface diffusion tensor $\boldsymbol{D_s}$. Such an ad-hoc assumption results from the observation of increased diffusion rates for some cations in compacted bentonite systems (Torstenfelt et al., 1983) and was subsequently also applied to heterogeneous crystalline rocks (Rasmuson and Neretnieks, 1983; Ohlsson and Neretnieks, 1998).

If surface diffusion does occur, the diffusion Equation (53) would be written, e.g., in the one-dimensional form (neglecting sink/source terms such as radioactive decay) and including linear sorption of the solute on the solid phase, according to Rasilainen (1997) as

$$\frac{\partial C}{\partial t} = \left(\frac{D_e + (1-\varepsilon_p)\,\rho\, K_d\, D_s}{\alpha} \right) \frac{\partial^2 C}{\partial x^2} \quad . \tag{96}$$

In this relationship the effective diffusivity is increased by the term $(1-\varepsilon_p)\,\rho\, K_d\, D_s$ accounting for the observed increased mobility of the radionuclides due to migration along the surfaces. From a computational point of view surface diffusion could – according to Equation (96) – be easily taken into account by a simple re-definition of the value for the diffusion coefficient. In the formulation above it is assumed that surface diffusion is uniform in the diffusion domain and D_S was introduced as an averaged empirical parameter; the driving force would be a concentration gradient of the sorbed species on the surface. So far, the proposed mechanism has not yet been accepted for heterogeneous porous media such as crystalline rocks and highly diluted solutes. Conca et al. (1993), p. 399 state, " *… for systems with mineral surfaces that do not maintain a high electrostatic potential, D_S could not be an important contributor to the overall diffusion coefficient.*" Due to the lack of reliable data, surface diffusion has been consequently neglected in performance assessments. Such a procedure is certainly conservative because it reduces the efficiency for matrix diffusion as a temporal sink for solutes.

Pore plugging – reactive transport

Transient flow fields with changing chemical conditions may occur – as already outlined – due to geological events such as, e.g., periodic uplifts and subsidences of larger areas – especially at coastal sites – or heavy earthquakes. Other phenomena, which may result in chemical gradients, are high pH-plumes migrating from the repository domain [33], because the disposal of radioactive waste – especially for long-lived intermediate level waste – requires the use of large amounts of cementitious material. Formation water rich in carbonate will lead to calcite precipitation in the water-conducting zones but also in the porous rock adjacent to fractures in the vicinity of the waste repository caused by the increase in the pH [34]. Thus, a high pH solution emerging from the repository can have a significant effect upon the performance of this repository regarding the ability of the host rock to retard efficiently the migration of radionuclides to the biosphere. The bentonite buffer, too, may affect the chemical stability of the groundwater on a local scale. Notably, the excavation of shafts and tunnels during construction, but also the operation phase of a repository, may further change the original geochemical conditions in a complex way. All of these events and processes will have an impact on the mobility and the transport behaviour of dissolved radionuclides.

Precipitation and dissolution of mineral phases may occur in response to geochemical gradients, e.g. due to changes in the water composition. These processes could affect the available transport porosity in both the fracture and in the matrix. Porosity changes may be beneficial or detrimental to radionuclide transport through the geosphere. Mineral precipitation will increase the potential for fractures clogging – especially for those with small apertures; plugging however, can also seal pores in the rock, thereby reducing the efficiency of matrix diffusion – an effect which is certainly not desirable for the performance of a planned repository for radioactive waste. Calcite and other mineral precipitation, with subsequent clogging of the transport-relevant porosity, has been observed in small-scale diffusion experiments with hardened cement paste samples by Sarott et al., (1992) but also in theoretical studies (Lichtner and Eikenberg, 1995; Steefel and Lichtner, 1994, Soler and Mäder, 2004). Similar effects could be recognized on “old concrete structures” exposed to the atmosphere and to drinking or lake water (Lagerblad, 2001). A theoretical study has recently shown the beneficial aspects of self-sealing of a repository domain by calcite precipitation applying a coupled model for flow, transport and chemical reactions (Pfingsten, 2001; 2002). There are many reactive transport models existing and a growing application of these models in analysis of experiments on all scales. Van der Lee and De Windt (2001) recently gave an overview about the present state of geochemical models.

From a scientific point of view, dissolution and precipitation are well understood for a few pure phases such as calcite. Hence, such reactions could – in principle – be considered in performance assessments, provided the thermodynamic data are available. However, dissolution and precipitation reactions were – in general – not modelled in past performance assessments specifically due to the lack of appropriate data and for

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[33] Note: Neither the far-field/biosphere interface nor near-field disturbances from the disposal facility are considered in RETROCK.

[34] The pH in crystalline rock is in the order of pH ≈ 8 – 9, whereas that of a calcium-rich groundwater released from a cementitious near field is in the order of pH ≈ 12 – 13.5.

conservatism reasons [35]. Consequently, pore plugging in the matrix was not explicitly considered, although by applying a conservative limitation on the matrix diffusion depth such a process can be taken into account, too.

Clogging can also be caused by mobile colloids. Colloids are ubiquitous in the flowing or pore water of fractured crystalline rocks. In addition, the bentonite buffer of the near field may be seen as a further source of colloids. The bentonite consists of very small particles, which – being in contact with groundwater – can produce colloids. Small particles may have access by molecular diffusion to pores with sufficiently large openings and hence, colloids could seal a part of the connected porosity in the matrix, reducing the efficiency of matrix diffusion. However, it is very difficult to estimate whether small colloids may block a certain part of the diffusion-accessible zone. Therefore this problem deserves further investigations. In all performance assessments clogging of fractures having large apertures (compared to the averaged colloid size) is not considered to be a significant process.

2.3.4 Open issues and unresolved problems

Matrix diffusion undoubtedly occurs and is one of the most important retardation processes in geosphere transport of solutes, but it depends in a complex way on various properties of the solution/rock system. It is obvious that matrix diffusion can only play a critical role if the value for the diffusivity is sufficiently large. Solid diffusion with extremely small values for diffusion can be neglected for performance assessment purposes. As outlined above, there still remains a catalogue of open questions. Knowledge gained in these questions can help to reduce conservatisms in performance assessments thereby reducing calculated doses.

- A key issue is certainly the **flow-wetted surface**, which may be affected additionally by channelling and by diffusion into pools of stagnant water within the water-bearing fracture. There are, in principle, several possibilities to determine values for the specific interface area. Assessing the conducting fracture frequency, or evaluating resin-impregnated thin sections of borecores, may yield values for the flow-wetted surface. However, both methods have shortcomings, especially when regarding complex geometries of the water-bearing features such as, e.g., 3D-network of micro fractures. In addition, both procedures represent point measurements and the determination of values which can be used in performance assessments is not straightforward. Analysing migration experiments in the laboratory, or on the field scale, can also provide values for the flow-wetted surface. Since this quantity is only part of a lumped parameter in the model formalism, further information on other transport parameters such as diffusivity (values, or at least a range, has to be specified) is needed as

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[35] A further potentially beneficial process not considered in performance assessment is co-precipitation through which radionuclides in solution are trapped in the precipitating mineral phase limiting the radionuclide solution concentration. According to Curti (1997; 1999) there are clear indications that metals are incorporated into precipitating solid alteration products following well-defined and predictable geochemical rules confirming the large potential of co-precipitation as a solubility-limiting process for many radionuclides. Lacking appropriate laboratory data on co-precipitation with calcite for many safety-relevant radionuclides, there are also open questions regarding the effects of pH and complexation on co-precipitation. The latter investigations would be particularly important for the performance assessment of a waste repository containing large amount of cementitious materials and organic substances.

constraints for the analysis. Finally, at the present time it is still unclear, how to discriminate between different processes and geometries, which can limit the specific interface area for the exchange of solute between water-carrying fractures and porous rock.

- There are indications from a wealth of experiments on different scales and from “real world observations” for a **limited extent of the porous matrix** for diffusion to values of the order of centimetres or even decimetres. However, the value assigned to the penetration depth has a profound effect on the release rates to the biosphere. Hence, site-specific data at the repository depth are needed. Care has to be taken to address the relevant material for long-term predictions. For example, highly porous fault gouge might be important in short-term migration experiments where it can account for the pronounced tailing in the tracer breakthrough curve, but dense mylonite might be the relevant sink for diffusing radionuclides which has to be considered in the long-term predictions for a radioactive waste repository. Furthermore, it should be investigated whether fresh rock, too, may act as a diffusion-accessible domain for the radionuclides. However, considerations more in detail are strongly dependent also on the nuclide/rock interaction and on the half-life of the nuclide.

  New experimental techniques for investigating the connected pore space under in-situ conditions, such as electrical conductivity measurements are very promising and they will certainly yield more and – especially important – also site-specific data that can be applied in future performance assessments.

- **Surface diffusion** was introduced as an ad-hoc mechanism to explain differences in values for the diffusivities in two kinds of experiments. Values for the apparent diffusion coefficient based on results from batch sorption experiments were much smaller than those from through diffusion experiments. Effects of surface diffusion were observed for adsorbed gases on metal surfaces and here the process, as such, is well established. However, whether surface diffusion is also relevant for highly diluted radionuclides and heterogeneous porous materials such as crystalline rocks is still an open question. The discrepancies in the values for the diffusivity mentioned could also be an artefact in the experiments. Hence, further experimental investigation on this topic is urgently needed. Furthermore, a mathematical description of the process starting from basic principles, such as mass-balance considerations, is still missing and would have to be developed.

- **Anion exclusion** is a process that can – in principle – reduce the beneficial effects of matrix diffusion for negatively charged particles, especially when pore space with small openings can be excluded for the diffusion of such species. Anion exclusion is also dependent on the ionic strength, hence on the composition of the groundwater. In low ionic strength waters the effects of anion exclusion are more pronounced than in highly saline waters. However, few data are available which can shed light on this issue. Although anion exclusion is presumably not so important when considering crystalline as a potential host rock, having more reliable data available, which could be used in performance assessments, would further reduce conservatism.

- There is more and more work which deals with **chemical reactions** combined with models for flow and transport. Some of these works predict pore plugging in the rock matrix. Reactive transport modelling is especially needed to predict the evolution of the transport relevant porosity, the permeability, constrictivity and diffusivity of the rock over geological periods of time. Hence, this coupling is a very complex subject, and many aspects of solution interactions with minerals are only very poorly understood. In performance assessments, chemical reactions coupled with flow and transport and consequently pore plugging are typically excluded due to the lack of suitable data and missing system understanding. Having recognised this problem, research is increasing in this area worldwide. However, important thermodynamic and kinetic data that are required for the calculations are still missing. Such a lack of fundamental data requires new and elaborate laboratory as well as in-situ measurements of the mineral surfaces in contact with the solution and investigations on mineral dissolution and the formation of secondary minerals. Especially sorption of radionuclides on secondary minerals deserves scientific attention. In performance assessments radionuclide sorption on these phases are taken into account – at the best – by an appropriate K_d-variation. Having reliable data available would result in an improved and more realistic description of chemical processes in geosphere transport.

- Crystalline rocks are heterogeneous on a variety of scales resulting in large natural **variabilities of the rock properties**. The models and big computation facilities are, in principle, available and there is also a fast-growing amount of generic and also site-specific data, which can be considered in forthcoming performance assessments. The stochastic modelling, too, has developed in the last couple of decades considerably and profound knowledge has accumulated. The smallest heterogeneities for crystalline rocks, which are relevant for geosphere transport, are of the order of 10^{-5} to 10^{-3} metres, such as the mineral grain size or the pore scale. Crystalline formations are heterogeneous at much larger scales, too. There are also heterogeneities at a scale of 10^2 to 10^3 metres, which have to be considered in performance assessments. Hence, these scales differ by five to eight orders of magnitude and make the up scaling of values for the transport parameters obtained in small-scale (short-term) laboratory investigations and field tracer tests very difficult because they address heterogeneities on scales other than those which are relevant in performance assessments.

  Considering matrix diffusion, the variability concerning porosity, diffusivity and the extent of the connected porosity is much less (see values of Table 4 and Table 5). Consequently the extrapolation to performance assessment is more straightforward. In the future a more realistic description of the pore space geometry accounting for detailed 2D or even 3D structures in order to reduce (over-) conservatisms of the more simplified 1D transport models should be aspired. In addition, the variability of sorption of solutes due to the different mineralogy in the host rock resulting in space-dependent values for the apparent diffusion coefficient will have to be considered. Such a detailed description of the solute/rock interaction on a mesoscopic scale [36] will support the K_d concept,

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[36] The mesoscopic scale consists of an intermediary scale between the macroscopic (where processes are described, as a rule, by partial differential equations in terms of macroscopic variables), and the microscopic scale of molecular dynamics (typically in the order of nm's).

The "particles" in a mesoscopic simulation are mathematical abstractions and do not correspond to individual atoms or molecules of the actual system under consideration. The number of particles is large enough to make statistical concepts meaningful, but is still many orders of magnitude smaller however, based on less conservative assumptions and will provide the implementers with more realistic databases for performance assessment purposes.

- In research but also in performance assessments the formalism for matrix diffusion is mostly based on Fick’s first and second law and the diffusion domain is assumed to be homogeneous and isotropic. However, there are indications that either some or all of these basic assumptions might be violated for certain rock types and at some scales (Meigs et al., 1997). The spatial variability in the rock porosity, the tortuous nature of the pore space and the variability in the sorption capacity due to variations in the mineralogy will result in significant variations of the diffusivity over small rock volumes. **Non-Fickian diffusion**, as well as heterogeneous and anisotropic matrix properties may result in non-conservative estimates of radionuclide retention. Field diffusion experiments but also electrical conductivity studies however indicate that diffusion might indeed be Fickian over larger scales. Hence, there is serious lack of understanding on a fundamental level. Presently, many researchers are investigating these open questions and their results and conclusions will certainly be considered in future performance assessments.
- Matrix diffusion is affected by processes and geometrical aspects of the immobile phase that are **dependent on both time and space**. Unfortunately these changes are very slow with regard to time, and the spatial heterogeneity is large; i.e., parameter values very often covers several orders of magnitude. Furthermore, all parameters are burdened with uncertainties. In performance assessments, time dependencies are mostly neglected due to the lack of data, and instead, averaged and time-independent values are applied. The spatial variability can be taken into account by sensitivity analyses, i.e., by varying the parameter values within certain limits. Uncertainties are often handled by determining a realistic and a pessimistic value; those effects are quantified by evaluating the radionuclide release rates to the biosphere.

  Time and space-dependent quantities that affect matrix diffusion directly are:

  - Groundwater pressure and flow conditions in the fracture system;
  - Groundwater composition including parameters such as pH, Eh, gas content, natural element content, radionuclide content;
  - Rock stress including information concerning the extent of the connected porosity in the matrix;
  - The rock fabric and fracture systems on various scales (e.g. brittle micro fractures, secondary fractures adjacent to main fractures etc.)
  - Mineralogical composition of a possible fracture coating and infill material including information concerning flow porosity;
  - Mineralogical composition of the rock matrix including information concerning matrix porosity and diffusivity;

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than the real number of particles (atoms or molecules) involved. Hence, a mesoscopic approach accounts for those elements of the microscopic reality (e.g. statistical fluctuations) that are likely to play a role at the macroscopic level; it further models physicochemical processes at a sufficiently elementary level to make the implementation of various reaction schemes and boundary conditions, as well as their re-adjustment as the system evolves, intuitively transparent.

  - Temperature in the geosphere.

  In the future more attention will have to be paid to all of these issues in order to reduce conservatism and to achieve a more realistic description of geosphere transport.

- Laboratory diffusion experiments suffer from relatively short time-scales and problems due to sample preparation (pressure release resulting in irreversible distortion of the geometrical structure, etc.). Field experiments are more realistic because tracer migration occurs, after a certain distance from the borehole, in a more or less virgin environment. However, the depth of tracer penetration is still small because of the short time-scales, even when such experiments are conducted over years. Hence, for both types of quantitative investigations there remain shortcomings which are related to **up scaling** in space and time in performance assessments. As already outlined, natural analogues are widely used to assess matrix diffusion on all scales. There, results have proved to be useful but they are not conclusive due to the lack of information concerning processes acting over long time scales and the initial and boundary conditions.

- Another problem arises when comparing **laboratory data with in-situ values**. For example: values for K_d measured in laboratory batch experiments may differ significantly from those determined under in-situ conditions in field tracer tests or in laboratory diffusion experiments. Mostly, batch values are larger and one can apply the more conservative matrix values from field investigations in performance assessments. However, especially field data are scarce and therefore it is hard to justify batch K_d-values. It is still an open question whether these differences are caused by the sample preparation in the batch sorption experiments due to crushing of the rock material. The discrepancies can also be due to the changed solid/liquid ratio that is lower by orders of magnitude in the batch experiments. However, one should keep in mind that for the majority of the radionuclides such a comparison cannot be made due to the lack of data. It is further worth mentioning that there are also a few cases where K_d values originating from batch sorption experiments are in good agreement with values from tracer tests performed either in the field or in the laboratory. Good agreement was obtained for the Grimsel migration experiment (Hadermann and Heer, 1996) for tracers such as Sodium and Strontium; or for the Äspö TRUE-1 field tracer test for various tracers (Johansson, 2000 – Paper V; Widestrand et al., 2001 – p. 85ff) and for compacted bentonite (Bradbury and Baeyens, 2003a). However, further work is required for this issue, too.

- Finally, an important issue concerns data and data collection methods suitable for performance assessment purposes. Performance assessments often use bounding analysis covering wide ranges of different scenarios and of parameter values. The efforts spent on data acquisition strongly depend on the stage of a given waste disposal program. At an early stage, a limited effort acquiring generic data may be sufficient, whereas at a later and more mature stage, the requirements are more towards a well-supported, site-specific database to reduce conservatisms applied in former stages. However, more efforts should be made for an integration of available data from different investigation methods. An excellent example of the derivation of input data for geosphere transport models which can be applied in performance assessments is the methodology reported by Mazurek (1998). The following figure illustrates the use of different characterisation methods, supporting hypotheses and interpretative models to provide the necessary input data for geosphere transport models that can be used either in the evaluation of (field) experiments or in performance assessments.

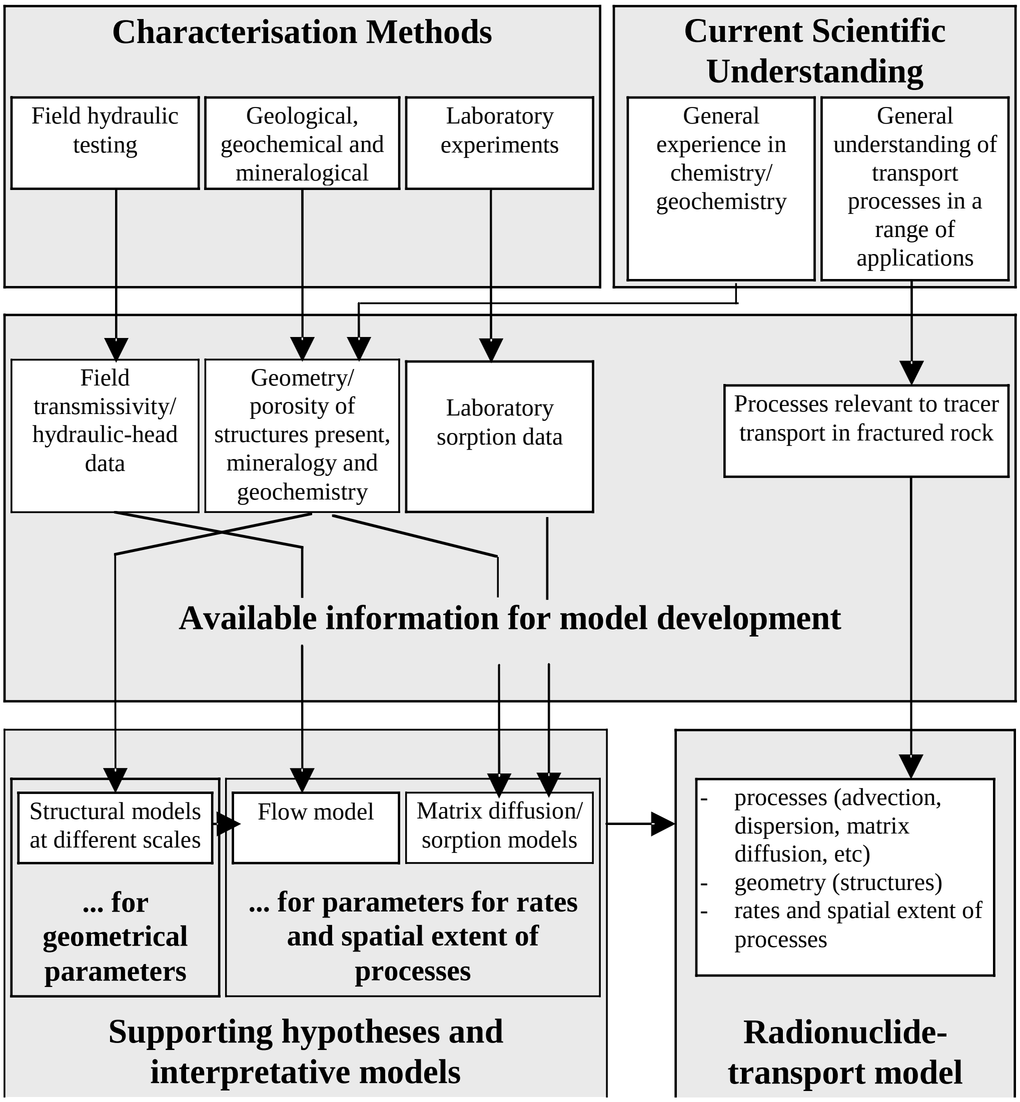

Figure 29. Different characterisation methods, the use of supporting hypotheses and interpretative models and their inter-relationships to ascertain the values for geosphere transport parameters that can be applied either in the evaluation of (field) experiments or in performance assessments. (Figure taken from Smith et al. 2001; reproduction by courtesy of P. Smith.)

On one side new experimental techniques such as, e.g., neutron diffraction; *x*-ray absorption spectroscopy; time-resolved laser-induced fluorescence-spectroscopy; atomic force microscopy etc., will yield new and fundamental insights into physical/chemical processes acting and into geometrical structures of the solid phase on a microscopic scale, i.e., down to the scale of nanometres. On the other side – as an example – molecular modelling techniques will allow to elucidate on an atomic scale the mechanisms of radionuclide sorption onto clay minerals and to explore the migration behaviour of solutes through expandable clays. All these new methods will result in an improved system understanding and help to further reduce conservatisms in transport models. However, the problem of up scaling of those results to scales in space and time relevant in performance assessments will be a very challenging task.

2.4 RADIOACTIVE DECAY INCL. DECAY CHAINS

A distinguishing feature of radioactive waste is radioactive decay, which leads to a gradual decrease in radiotoxicity of the waste as a function of time. The radioactive components do not need to be isolated or retarded forever but only for the time period necessary to reduce their concentrations to insignificant levels.

In a stable nucleus, neutrons act to separate the positively charged protons and keep the nucleus together. However, an unstable nucleus undergoes spontaneous decay when a neutron disintegrates to a proton, an electron (negatively charged beta particle) and an antineutrino, or alternatively a proton disintegrates to a neutron, a positron (a positively charged beta particle) and a neutrino. Most of the energy is emitted in terms of kinetic energy of the beta particles. In another kind of reaction, an unstable isotope can emit an alpha particle (2 neutrons and 2 protons). In the mentioned reactions elements are converted to other elements with different chemical properties. In gamma decay a nucleus changes from a higher energy state to a lower one through the emission of electromagnetic radiation (photons) so that the number of protons and neutrons in the nucleus does not change; nor do the chemical properties.

Each disintegration of the nucleus implies a change of the charge of the nucleus and, thus, a successive transformation of the mother isotopes into a series of daughter isotopes with consistently lower atom number in a finite series of decay. The radioactive decay of heavier elements is dominated by four chains named the uranium, the thorium, the actinium and the neptunium series of which the first three are naturally occuring. For instance, the uranium decay chain starts with emission of an alfa particle, whereby ^{238}U is transformed into ^{234}Th. Next step is a beta emission, whereby ^{234}Th is transformed into ^{234}Pa and so on.

The significance of radioactive decay varies tremendously between different nuclides. Its importance in performance assessment is mainly determined by the time-scale of decay in relation to the time-scales of radionuclide transport or radionuclide isolation. There are nuclides that can probably be ruled out as potential dose contributors, since they are likely to almost completely decay before they reach the biosphere (e.g. Cs-137, Sr-90). Conversely, there are also nuclides that can significantly contribute to dose, since they have long half-lives in relation to an expected travel-time from the repository to the biosphere (e.g. I-129).

3 PROCESSES DISCUSSED IN PA'S

3.1 COLLOIDS

3.1.1 Generation and sources of colloids

Colloids are minute particles in the size range 1 nm to 1 μm that can remain suspended in water. Larger solids are classified as suspended particles and anything smaller is considered to be in true aqueous solution. Colloids can be of both organic and inorganic origin. Inorganic colloids are formed by alteration or physical erosion of minerals, or by direct precipitation from groundwater, and typically comprise silica, clay minerals, calcite or Fe-oxyhydroxides. Organic colloids may comprise fragments of degrading organic material, or they may be organic macromolecules, such as humic or fulvic acids. Organic materials may form coatings on inorganic colloids, increasing their stability.

Colloids can be classified in various ways, including:

- By origin. Colloids may be distinguished as natural groundwater colloids or anthropogenic colloids (e.g. Triay et al., 1995). Groundwater colloids occur in many aquatic systems and consist of inorganic and/or organic molecular constituents or micro-organisms. Anthropogenic colloids are produced by physical, chemical and/or biological processes acting on materials created by humans. In the context of radioactive waste disposal, anthropogenic colloids may be derived from the waste form itself, or from the repository construction and sealing materials.
- By composition. Two types of colloids are distinguished in this way (e.g. van der Lee et al., 1994). Type I (intrinsic) colloids consist essentially of polymerised complexes of a particular element. Type II (carrier) colloids comprise compounds of other elements to which a particular element may be attached.
- By type. A possible classification scheme is summarised below (US DOE, 1996):
    - Mineral fragments consisting of crystalline or amorphous solids.
    - Actinide intrinsic colloids, such as the Pu(IV)-polymer, formed by condensation of hydrolysed actinide ions and consisting of actinide cations linked by anions.
    - Humic and fulvic acids consisting of high-molecular-weight organic compounds that may be present in natural waters as negatively charged macromolecules.
    - Microbes, stabilised by hydrophilic coatings on their surfaces.

3.1.2 Concentrations of colloids

Natural colloids are present in all groundwaters with concentrations typically ranging from 0.1 ng ml^{-1} to 100 μg ml^{-1}. Based on sampling and characterisation of colloids in natural groundwaters from a wide range of localities world-wide, Degueldre et al. (1996; 2000) demonstrated that there is a simple relationship between colloid concentration and groundwater ionic strength. This relationship can be used to predict the colloid concentration in a groundwater of known chemical composition. The analytical data defining the relationship is illustrated in Figure 30.

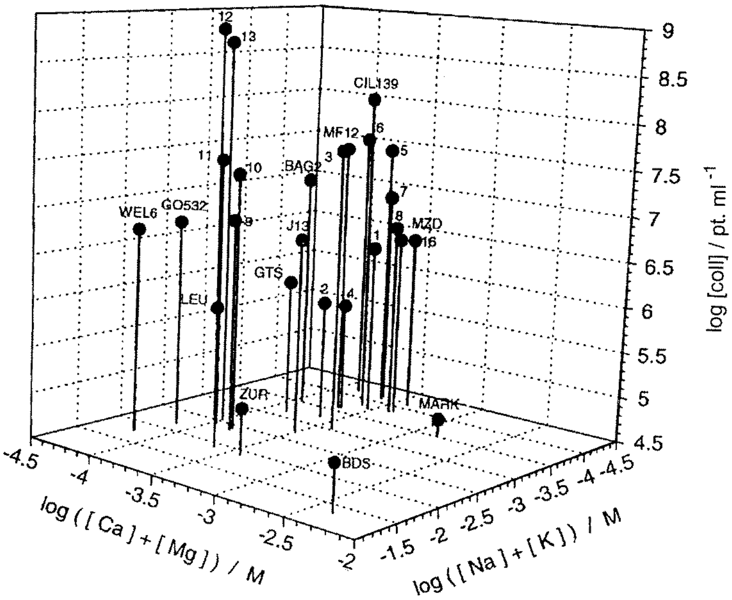

Figure 30. Relationship between colloid concentration and ionic strength for groundwaters sampled from a variety of locations world-wide, after Degueldre (1996; 2000).

The colloid concentration in a given aquifer depends on colloid stability, and is a function of the chemical composition of the water, as well as of the hydrogeochemical steady state of the aquifer. For an aquifer in a steady state, colloids are stabilised by alkaline elements having a concentration below 10^{-2} M and alkaline earth elements below 10^{-4} M. In general, transient conditions, such as changes in temperature, flow rate, pH and Eh enhance colloid stability, as do high concentrations of organic molecules.

The relationship between colloid concentration ([*coll*] in particles per litre) and colloid size (*d*) may be expressed mathematically by a Pareto power law relationship as follows (Degueldre et al., 1996; 2000):

$$\frac{\delta[coll]}{\delta d} = Ad^{-b} \quad \text{with} \quad [coll] = \frac{A}{(1-b)} d^{1-b} \qquad (97)$$

The parameters *A* and *b* are constant for a given colloid size range, and *b* may be obtained by plotting the log of the normalised colloid concentration as a function of the log of the colloid size.

The presence of a repository is likely to increase the concentration and range of colloids present in groundwater. This is due to the excavation carried out during repository construction, and post-closure degradation of the waste form and engineered barrier system materials. Colloids formed in the near-field could be transported to the far-field by advecting groundwater, where they would add to the natural groundwater colloid population. Colloids may also be transported, albeit slowly, by diffusion.

3.1.3 Carrying capacity of radionuclides in and on colloids

In radioactive waste disposal systems, natural colloids and waste- and repository-derived colloids may strongly enhance the migration of radionuclides (Kim 1994; McCarthy and Zachara, 1989). Highly charged metal ions, such as polyvalent actinide ions, with low thermodynamic solubility and strong sorption tendencies, may interact strongly with natural colloids present in groundwater, or may themselves form a colloidal solid phase. The radionuclides may therefore become fixed to a solid phase, which is mobile and may be transported without retardation at or close to the speed of the groundwater. In some cases, electrostatic effects may keep colloids in the central parts of channels where flow velocities are higher than average.

Aquatic colloids are chemically surface active and therefore highly charged radionuclides are readily sorbed to them. The radionuclide-colloid interaction may vary from weak (e.g. ion exchange within clay interlayers), to moderate (e.g. complexation with surface sites or with functional groups of humic substances) to strong (e.g. incorporation into the bulk colloid by phase alteration). Similarly, the desorption reaction and the leaching rate of the radionuclides from the colloids will exhibit a broad distribution range.

Depending on the nature of the sorption process and the data available to quantify its effects, sorption processes can be modelled in a number of different ways. Where little or no mechanistic information is available, empirical distribution coefficients or isotherms may be used to estimate the distribution of radionuclides within a given system. Alternatively, distribution coefficients or isotherms can be derived from the results of mechanistic chemical speciation modelling for use in more simplified assessment models. Where detailed information is available, a range of different process models and codes may be applied (e.g., PHREEQE, Parkhurst et al., 1980; CHEMTARD, Bennett et al., 1992).

All of the methods for quantifying sorption noted above assume chemical equilibrium. Further complexity is introduced where sorption is kinetically controlled. Although it is quite possible to extend chemical speciation / sorption models to consider reaction kinetics (e.g., EQ3/6, Wolery and Daveler, 1992; the k1D model, Warwick et al., 2000), few data are available with which to quantify kinetically controlled sorption processes. Because of the lack of kinetic data, it is often only possible to assume that the net rate of sorption of radionuclides on colloids will lie in between the two theoretical end member cases of reversible (equilibrium) sorption and instantaneous irreversible sorption. For saturated systems, a conservative approach is to assume that radionuclides are irreversibly bound to colloids.

3.1.4 Filtration of colloids

Colloids may be filtered during transport through low-permeability media such as clay. For example, bentonite is widely considered to be an excellent filter of colloids. Where it is used as a buffer in waste repository designs, it is considered unlikely that near-field generated colloids would escape into far-field groundwaters (Kurosawa *et al.*, 1997).

3.1.5 Microbes as colloids

Microbes, or microorganisms, are a large and diverse group of microscopic organisms that exist as single cells or cell clusters, and may behave as relatively large colloids (Keith-Roach and Livens, 2002). Potentially important colloid-sized micro-organisms include bacteria, fungi, yeast, and protozoa. Microbes are known to actively bioaccumulate actinides within their cells, as well as to act as substrates for passive extracellular sorption.

Because radionuclides may become bound to microbes of natural origin, as with other types of colloid, they may be stabilised in the mobile phase at concentrations far above the solubility limit. As found in column experiments, radionuclides attached to micro-organisms may be transported faster than conservative tracers owing to pore-size exclusion and electrostatic effects. Some of the most important mechanisms by which bacteria can transform and influence the mobilisation and/or immobilisation of metals and radionuclides are (Selenska-Pobell, 2002):

- Direct oxidation and/or reduction of metals, thereby influencing solubility.
- Direct or indirect oxidation of metal sulphides and associated dissolution of some elements.
- Indirect alteration of speciation by microbially-induced pH and Eh changes.
- Bioaccumulation and/or uptake of metals inside cells.
- Biomineralisation and the promotion of metal precipitation.
- Release of biosorbed metals by chelation, alkylation or decomposition.

3.1.6 Recent Observations of Colloids and Radionuclide Migration

Recent observations made at the Nevada Test Site (NTS) in the United States have demonstrated migration of Pu 1.3 km from the site of the BENHAM underground nuclear test. It has been suggested that the migration may have occurred as a result of the attachment of the Pu to colloids (Kersting et al., 1999).

Groundwaters sampled at the NTS ERDA 12 well cluster contain radioactive isotopes of Pu, Am, Cs, Co and Eu. The isotopic composition of the Pu observed at the ERDA 12 well cluster matches the composition of Pu from the BENHAM underground nuclear test, implying that the Pu has migrated 1.3 km in ~30 years. At the sampling point, the radionuclides are associated with colloidal material in the groundwater.

It is not clear whether the Pu has been transported by colloids the entire distance from the BENHAM detonation point to the observation point. The radionuclides may have been transported some of the distance from the detonation point by a mechanism known as “prompt injection”, whereby vapourised or molten material is advected rapidly along fractures. However, prompt injection has never been observed to operate on a scale greater than 300 metres. The high permeability of some volcanic units such as lava flows, and the perturbations to the regional hydrologic system caused by repeated underground testing, may also be responsible for enhanced transport.

In the European Commission/EURATOM Fifth Framework project BORIS, colloids associated with radionuclides, including actinides, were observed in groundwater sampled from monitoring wells at the Tomsk-7 borehole injection site. At this location, liquid radioactive waste has been disposed by injection into confined aquifers at 300-400 metres depth. However, these results do not prove that colloid-facilitated transport is important in the groundwater system, because it is not certain whether the colloids sampled originate from the groundwater or are artefacts due to the sampling. It will therefore be important to verify the results by using other sampling techniques.

3.1.7 Models of Colloid Transport

Mechanistic models of colloid-related transport processes that aim at realism include diffusion-limited aggregation, and models for colloid transport with exchange of radionuclides between dissolved, mobile sorbed and immobile sorbed phases, governed by reaction rate constants.

For example, SKI's colloid transport code, COLLAGE II, considers radionuclide transport in a one-dimensional planar fracture and represents radionuclide–colloid sorption and desorption assuming first-order, linear kinetics (Klos et al., 2002). Radionuclides in solution travel with the groundwater flow within the fracture but interact with the rock matrix or the fracture walls, as illustrated in Figure 31. If suspended colloidal material is present in the fracture, radionuclides can sorb onto the colloids and desorb back into solution. Some of the colloids may be captured by the walls of the fracture and some may be released.

The one-dimensional approach used in COLLAGE II to characterise fracture properties, with matrix sorption into the wall rock perpendicular to the direction of flow has been used in many cases (e.g., Nagra, 1994; US DOE, 1998; JNC, 2000). A similar approach is currently also used in the US Yucca Mountain programme (Wolfsberg and Reimus, 2000).

Mechanistic models of colloid transport are not used directly for PA transport modelling, due mainly to their high data requirements, and the fact that, in their current form, they are suitable only for simple systems (1-D simple fractures with uniform transport properties). The modelling of filtration in fractured rock systems (as opposed to idealised filters) presents particular difficulties. Some respondents to the RETROCK questionnaire noted that studies to enhance mechanistic models, and to improve the realism of PA models with respect to colloid-related processes, are currently underway.

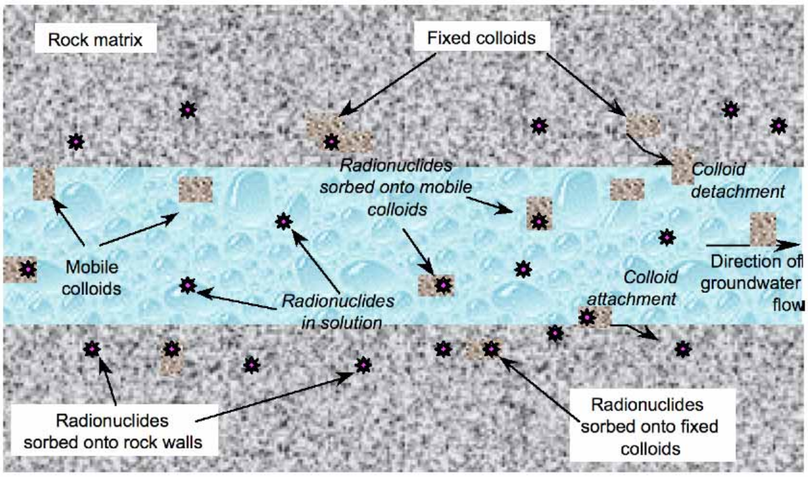

Figure 31. Illustration of the COLLAGE II conceptual model for colloid transport in a thin planar fracture.

3.2 PRECIPITATION AND COPRECIPITATION

3.2.1 Precipitation

3.2.1.1 Conceptualisation of the process

Precipitation can be considered as a further step of surface sorption. The aqueous complexes can be incorporated to the surface of a solid substrate by losing the hydration water dipoles and establishing chemical bonds with atoms of the crystalline structure of the solid. This mechanism leads to the accretion of the solid structure (Figure 32). Dissolution can also be understood as the reverse process.

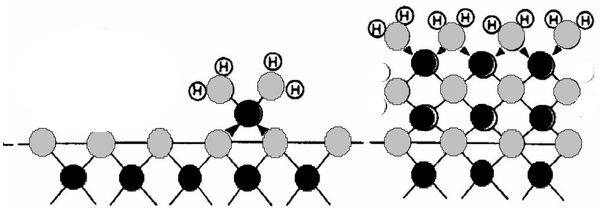

Figure 32. Structural arrangement of precipitation as a continuum from sorption of aqueous complexes on an oxide surface (see Figure 12). The shaded circles represent oxygens and the small solid circles represent metal ions. The initial solid is located below the horizontal line (modified from Brown, 1990).

3.2.1.2 Precipitation-dissolution in equilibrium

From the thermodynamic point of view, the amount of mass involved in precipitation-dissolution reactions is larger than that related to surface sorption. Moreover, thermodynamics is not linked to the surface of the solid (unlike kinetics, as we shall see below), but only to the concentration of aqueous species and to the energy of the chemical bonds in the solid phase. Therefore, the thermodynamics of precipitation-dissolution are described by a formulation simpler than that of sorption. Once equilibrium between solid and solution is reached, dissolution-precipitation reactions can be described by the Law of Mass Action. The dissolution reaction of a mineral can be written as

$$\text{Mineral}\, m \Leftrightarrow \sum_{i=1}^{N_c} \nu_{mi} A_i \tag{98}$$

where N_c is the number of chemical components of the system (for each given reaction it can be thought of as the number of species participating in the reaction besides the mineral), ν_{mi} is the stoichiometric coefficient of species i and A_i is the chemical formula of species i. The Law of Mass Action states that

$$K_m = \prod_{i=1}^{N_c} \left(c_i \gamma_i\right)^{\nu_{mi}} \tag{99}$$

where K_m is the equilibrium constant of the reaction, and c_i and γ_i are the concentration and activity coefficient of species i, respectively. Notice that the activity of pure solid phases is equal to unity, but that is not the case for the components of a solid solution, as we shall see in Section 3.2.2 (coprecipitation).

The description of the chemical system requires knowing the number of phases present. Some minerals are initially present in the system. Others, however, may form during its hydrochemical evolution. The formation of all minerals must obey the principle of minimum Gibbs Free Energy. The change of the Gibbs Free Energy of the reaction (ΔG) is related to the saturation ratio Ω_m through

$$\Delta G = RT \ln \Omega_m = 2.303\, RT \log \Omega_m \tag{100}$$

where the saturation ratio is the ratio between the ion activity product and the equilibrium constant of the reaction.

$$\Omega_m = \frac{1}{K_m} \prod_{i=1}^{N_c} \left(c_i \gamma_i\right)^{\nu_{mi}} \tag{101}$$

The value of log Ω_m is known as the saturation index SI_m of the solution with respect to a mineral.

The system reaches the minimum Gibbs Free Energy at equilibrium ($\Omega_m = 1$ or $SI_m = 0$). Saturation ratios Ω_m greater than 1 ($SI_m > 0$) indicate that the system will evolve so that the m-th mineral precipitates. On the contrary, when $\Omega_m < 1 (SI_m < 0)$ the mineral will tend to dissolve. This means that the mineral phases that can participate are those initially present plus other potential minerals corresponding to Ω_m values greater than 1. However, the phase rule states that at given pressure and temperature the number of phases cannot exceed the number of components N_c. In such cases, only the minerals having the largest Ω_m values will remain.

3.2.1.3 The kinetics of dissolution-precipitation

Thermodynamic chemical equilibrium states only the minimum energy state of the system, but says nothing about the progress of the reactions. Kinetics offers a way to analyse the chemical evolution of a reaction and allows the incorporation of time, in an explicit manner, in the calculations.

Some geochemical processes (such as the dissolution and precipitation of many minerals) are known to progress so slowly that they may never reach equilibrium. This is especially true if the water moves fast and remains in a given volume of rock less time than needed. In these cases kinetic rate laws are required. Quantitative data on mineral dissolution have been accumulated during the last decades. Very few data, however, are known on precipitation kinetics. It is usual practice to assume equilibrium (or equivalently very fast reaction rates) in the calculation of mineral precipitation.

For mineral dissolution, the following general expression, based on Lasaga et al., (1994), can incorporate most of experimental rates reported in the literature.

$$r_m = \varsigma_m e^{-\frac{Ea_m}{RT}} \sum_{k=1}^{N_k} k_{mk} \prod_{i=1}^{N_c+N_x} a_i^{p_{mki}} \left|\Omega_m^{\theta_{mk}} - 1\right|^{\eta_{mk}} \qquad (102)$$

r_m is the mineral dissolution rate (moles of mineral per unit mineral surface area per unit time), N_k is the number of experimental terms required (usually different terms for low, neutral and high pH), k_{mk} is the experimental rate constant (same units as r_m), Ea_m is the apparent activation energy of the overall reaction process, R is the gas constant ($\mathrm{Jmol^{-1}K^{-1}}$) and T is temperature (K). The term $a_i^{p_{mki}}$ accounts for the catalytic effect of any species in solution, N_c is the number of components or aqueous primary species (H^+ is usually included here) and N_x is the number of secondary species or aqueous complexes. Ω_m is the saturation ratio as calculated according to Equation (100), and the parameters p_{mki}, θ and η are determined experimentally. Usually, but not always, θ and η are assumed to be equal to 1. The last term of the equation describes the dependence of the rate on solution saturation state. Dissolution rates decrease non-linearly in magnitude as the solution approaches equilibrium (Figure 33). The factor $\boldsymbol{\zeta_m}$ takes on values of +1 or -1 depending on whether Ω_m is larger or smaller than 1 (precipitation or dissolution). At equilibrium $\Omega_m = 1$ and therefore $r_m = 0$**.**

Contrary to the assumption of equilibrium, kinetics provides an explicit expression of the rate of change of concentrations linked to reaction progress. The rate of change of the concentration of the i-th solute, R_i (moles of solute per unit of mass of water and unit of time) is calculated according to

$$R_i = -\sum_{m=1}^{N_p} \nu_{mi} A_m r_m \qquad (103)$$

where ν_{mi} is the stoichiometric coefficient of the i-th solute in the dissolution reaction of the m-th mineral, and A_m is a surface area term (units of mineral surface per kg of water).

Precipitation can be thought of as the addition of three subsequent processes: nucleation, Ostwald ripening and growth. Nucleation takes place when supersaturation reaches a critical value, sufficiently high to compensate the excess surface Free Energy caused by the presence of many small nuclei. This is the reason why many groundwaters are supersaturated with respect to certain minerals and they do not precipitate. Once nucleation takes place and a large number of nuclei are available, the smaller ones have a larger excess surface energy and tend to redissolve, transferring the mass to the larger ones. Finally, only a small fraction of the initial nuclei reach the stage of growth and become independently growing solids. All these processes can be quantified and modelled (Steefel and Van Cappellen, 1990). However, many parameters are required to model nucleation. These parameters are usually not available. Besides, the process of nucleation is highly non-linear. Therefore, the inclusion of detailed precipitation kinetics equations in PA modelling is not realistic.

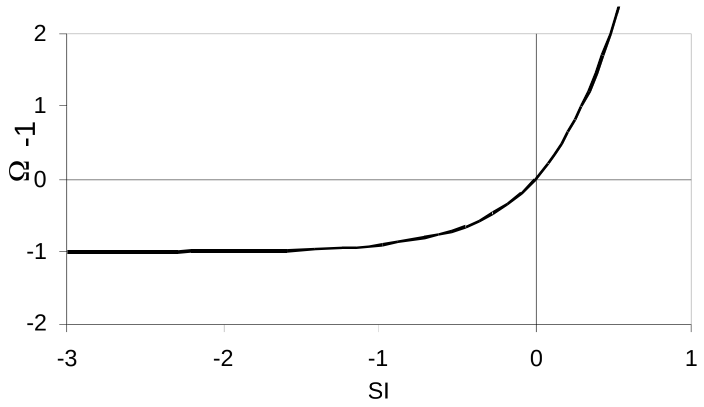

Figure 33. Non-linear dependence of reaction rate on saturation index (SI), given by the term describing the effect of solution saturation state (last term of Equation (102)).

There are two more realistic alternatives: 1) to calculate the precipitation in equilibrium according to Section 3.2.1.2, and 2) to take precipitation kinetics into account, following experimental expressions such as Equation (101) and Figure 33. These rate laws have been proved to match experimental data for some minerals, such as calcite (Inskeep and Bloom, 1985). When using this kinetic formulation, it is possible to define a threshold supersaturation value that has to be reached before precipitation starts.

3.2.2 Coprecipitation

3.2.2.1 Conceptualisation of the process

Coprecipitation is the removal of a trace element from solution as an impurity or minor component in secondary phases formed from the major components of the system, so that the remaining concentration of the trace element in solution is smaller than the one that would be predicted from the solubilities of solids containing that trace element as a major component (Kolthoff and Sandell, 1952; Bruno and Sandino, 1988; Curti, 1997, 1999).

3.2.2.2 Coprecipitation in equilibrium

The formal treatment of coprecipitation starts from considerations on the thermodynamics of solid solutions and the law of mass action (Stumm and Morgan, 1996). Thus, for example, if the incorporation of Sr into calcite is considered, the equilibrium between the two end-members of the solid solution can be formulated as

$$\mathrm{CaCO_3(s)} + \mathrm{Sr^{2+}} \Leftrightarrow \mathrm{SrCO_3(s)} + \mathrm{Ca^{2+}} \tag{104}$$

and the equilibrium constant K will be defined by

$$K = \frac{\mathrm{X_{SrCO3}}\Gamma_{\mathrm{SrCO3}}c_{\mathrm{Ca}^{2+}}\gamma_{\mathrm{Ca}^{2+}}}{\mathrm{X_{CaCO3}}\Gamma_{\mathrm{CaCO3}}c_{\mathrm{Sr}^{2+}}\gamma_{\mathrm{Sr}^{2+}}} = \frac{K_{\mathrm{CaCO3}}}{K_{\mathrm{SrCO3}}} \tag{105}$$

where the c and γ terms are concentrations and activity coefficients of the aqueous species in solution, the X and Γ terms are molar fractions and activity coefficients of the components of the solid phase, and K_{CaCO3} and K_{SrCO3} are the equilibrium constants for the dissolution reactions of the two solid end-members.

3.2.2.3 Phenomenological partition coefficients

In most cases, the lack of knowledge of the detailed chemistry of the system and/or the fact of not considering non-idealities (activity coefficients), especially regarding the solid end-members, leads to the use of phenomenological partition coefficients, where activity coefficients are not taken into account and total concentrations in solution (e.g. C_{CaTOT}) are frequently used instead of the concentrations of the relevant species (e.g. $c_{\mathrm{Ca2+}}$). Note that we use c for concentrations of species and C for total concentrations of solute, as in Equation (24). For the example given above, the phenomenological partition coefficient would be given by

$$Ph.Part.Coeff. = \frac{\mathrm{X_{SrCO3}}C_{\mathrm{Ca_{TOT}}}}{\mathrm{X_{CaCO3}}C_{\mathrm{Sr_{TOT}}}} \tag{106}$$

Although the phenomenological partition coefficients are more commonly used, their applicability is restricted to the range of conditions under which the experimental work has been performed. There are two types of phenomenological partition coefficients: heterogeneous and homogeneous.

Heterogeneous partition coefficients (λ) refer to the case when the partitioning of the tracer between solid and solution affects only the surface of the precipitating solid, leading, for instance, to the zonation of a growing crystal. Following the terminology used by Curti (1999), if T refers to a trace element (e.g. Sr in the example given above) and C refers to a carrier element (e.g. Ca in the example given above), λ is defined as

$$\lambda = \frac{\mathrm{X_{T,\,surface}}C_{\mathrm{C}}}{\mathrm{X_{C,surface}}C_{\mathrm{T}}} \tag{107}$$

where the X terms refer to the molar fractions at the surface of the solid, and C refers to total concentration in solution. This type of partition coefficient has been found to apply to many solids precipitating in low-temperature (< 100 °C) geologic environments.

Doerner and Hoskins (1925) developed a relationship for closed systems that allows the determination of the partition coefficient λ from solution data alone. This relationship is known as the logarithmic law and is given by

$$\ln\frac{C_{\mathrm{T}}}{C_{\mathrm{T}_0}} = \lambda \ln\frac{C_{\mathrm{C}}}{C_{\mathrm{C}_0}} \qquad (108)$$

where C_{T0} and C_{C0} refer to the initial concentrations in solution in a closed system experiment (no tracer or carrier is added after the beginning of the coprecipitation experiment).

Homogeneous partition coefficients (*D*) refer to the case when the partitioning of the tracer between solid and solution affects the bulk of the solid, i.e., there is a continuous re-equilibration between the surface and the bulk of the solid. This partition coefficient is given by

$$D = \frac{\mathrm{X}_{\mathrm{T,\,bulk}} C_{\mathrm{C}}}{\mathrm{X}_{\mathrm{C,\,bulk}} C_{\mathrm{T}}} \qquad (109)$$

and the logarithmic law (Doerner and Hoskins, 1925) does not apply. Bruno and Sandino (1988) suggested that this was the case for the hydrothermal aging (temperature between 110 and 120°C) of La(III), Th(IV) and Ba(II) previously coprecipitated with UO_2.

3.2.2.4 Conditional solubility constants

An alternative way to treat coprecipitation is by means of conditional solubility constants. This concept is based on the assumption that the activity of the minor component in a binary solid solution is equal to its molar fraction in the bulk solid. Bruno et al. (1995) applied this concept to the interpretation of coprecipitation experiments where U(VI) was coprecipitated with $Fe(OH)_3$. Following their example, the dissolution reaction for schoepite is written as

$$UO_2(OH)_2(s) + H^+ \Leftrightarrow UO_2(OH)^+ + H_2O \qquad (110)$$

with an associated equilibrium constant

$$K = \frac{a_{\mathrm{UO_2(OH)^+}}}{a_{\mathrm{H^+}}\, a_{\mathrm{UO_2(OH)_2(s)}}} \qquad (111)$$

The *a* terms refer to activities. Substituting the molar fraction of $UO_2(OH)_2(s)$ in the $Fe(OH)_3$ precipitate ($X^{S}_{\mathrm{UO_2(OH)_2}}$) for the activity of the $UO_2(OH)_2(s)$ and rearranging, the following expression for the conditional solubility constant (K*) is obtained

$$K^{*} = K \cdot X^{S}_{\mathrm{UO_2(OH)_2}} = \frac{a_{\mathrm{UO_2(OH)_2^+}}}{a_{\mathrm{H^+}}} \qquad (112)$$

Bruno et al. (1995) successfully applied this approach to the interpretation of their coprecipitation experiments and to the field cases at Poços de Caldas and El Berrocal. However, their experimental results (uranium solubilities vs. pH) could also be interpreted using a surface complexation model, although it required the use of many more parameters (surface charge, acid/base properties of the solids, numbers of available sites, surface areas).

3.2.2.5 Experimental and modelling support

Besides the examples mentioned above, coprecipitation has been extensively applied in analytical chemistry for the separation of trace elements, enrichment processes and mixed-oxide fuel production (Bruno and Sandino, 1988, and references within). There are also extensive data on the coprecipitation of radionuclides with calcite (Curti, 1999). Bruno et al. (2002) presented a compilation of studies in natural analogues regarding the mechanisms controlling the aqueous concentrations and speciation of several elements. It has been shown that under reducing conditions, the solubility of U(IV) is controlled by equilibrium with uraninites (UO2+x) or coffinite (USiO4), i.e., dissolution/-precipitation reactions (Figure 34). However, under oxidizing conditions, the concentrations of U(VI) are frequently controlled by coprecipitation with Fe(III) oxyhydroxides (Figure 35), although equilibrium with U(VI) silicates has also been reported. Regarding other elements, Sr is usually controlled by equilibrium with Ca-containing phases (calcite, fluorite), Zn is controlled by calcite and Fe(III) oxy-hydroxides and REEs are controlled by incorporation into phosphates, i.e., coprecipitation/codissolution reactions.

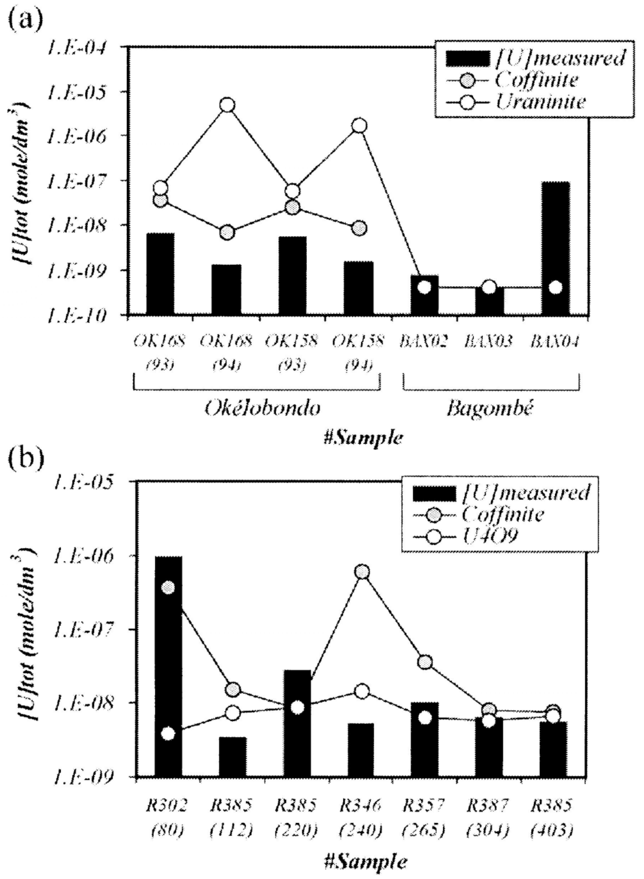

Figure 34. *Comparison between the actual U concentrations measured in the reducing groundwater samples of Oklo (a) and Palmottu (b) and the calculated solubility for uraninite and coffinite (Bruno et al., 2002).*

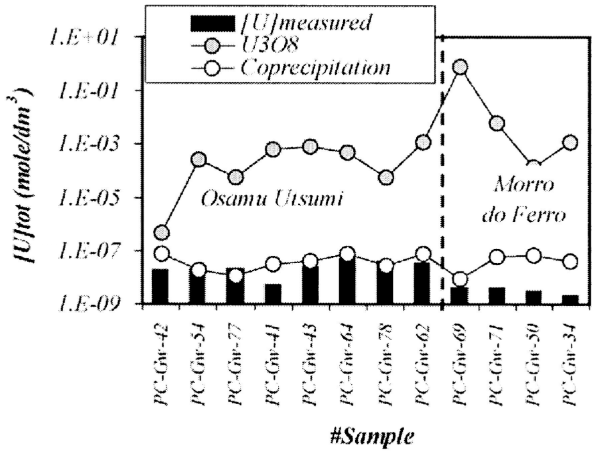

Figure 35. *Comparison of the agreement reached between the actual U concentrations measured in the groundwater samples of Poços de Caldas, the calculated solubility for U3O8 and the solubility of U calculated by assuming coprecipitation of U(VI) with iron (III) oxyhydroxides (Bruno et al., 2002).*

There is little doubt that coprecipitation will play an important role in the retention of radionuclides migrating from a repository. From a modelling point of view, the approaches are mostly empirical, and work concerning the thermodynamics of solid solution formation and the influence of nucleation and reaction rates on coprecipitation phenomena would be needed for a better understanding and description of the processes.

3.3 MICROBIOLOGICALLY MEDIATED PROCESSES

3.3.1 About the microbes

A microbe is an organism that has all it needs for a complete life cycle in one single cell. Many microbial species may under appropriate circumstances form multi-cellular structures, sometimes with morphological and metabolic differentiations between the different cells making up a bio-structure. Growth by cell division is the most common way of microbe propagation. The microbes outnumber multi-cellular organisms on our planet. They are characterised by their almost infinite ability to bio-degrade and bio-synthesize naturally occurring compounds in the environment. Microbial reactions control, partly or fully, the chemical composition of many, very different environments such as sediments, soils, lakes and groundwater.

Microbes occur either as unattached, planktonic cells passively floating or actively swimming in the free water phase, or are attached to solid surfaces. Any solid surface, living or dead, immersed in a water phase with living microbes is predestined to develop biofilms i.e. films of life that cover the surface. Microbes from the water phase become attached to the surface and, if growth conditions are appropriate, they start to grow and divide, in an attached mode.

All microbial life is based on metabolic processes driven by chemical energy extracted from the oxidation of inorganic or organic compounds. The oxidative harvesting of energy requires an electron acceptor that is concomitantly reduced. This process is called respiration when a reducible external electron acceptor is used (e.g. oxygen, nitrogen, sulphur, iron or manganese), and fermentation when the electrons are shuffled around between the degradation products of the original energy source (e.g. sugar to alcohol and carbon dioxide). The microbes certainly must obey the laws of thermodynamics, but they are utterly sophisticated lawyers that understand to use every single, constructive combination of those laws for making a good living of all or almost nothing. There are many basic textbooks on the microbes. “Brock Biology of Microorganisms” (*Madigan et al.* 2002) is a good source on microbes.

3.3.2 Microbial processes and radionuclides

Microbial processes can significantly alter the mobility of radionuclides in the environment. Multi-disciplinary research combining microbial physiology, ecology and molecular biology with nuclear chemistry, geochemistry and geology plays an important role in the exploration of the processes described in this chapter.

Table 7 summarises microbial processes that can influence radionuclide speciation and thereby their migration behaviour. Microbial processes will act immobilising or mobilising, depending on the type of process and the state of the microbes. Microbes in biofilms will, with exception for those who produce complexing agents, be immobilising. Planktonic cells, that bio-sorb or bio-accumulate radionuclides, will act mobilising on radionuclides. The processes can have a direct or indirect action on radionuclide transport in the geosphere. A direct action involves contact between a microbe and the radionuclide with a resulting change in its speciation. Indirect action is caused by changes in the environment generated by microbial metabolism, which in turn influences radionuclide behaviour. Finally, all microbial processes except bio-sorption require an active, energy driven metabolism. The modelling of microbial processes, therefore, must include a proper understanding of microbial energy turnover rates in deep rock aquifers. Each process in Table 7 is discussed in some detail below, with emphasis on their importance for understanding geosphere retention phenomena in the safety assessments of radioactive waste disposal.

Table 7. Microbial processes can influence retention of radionuclides directly or indirectly in several different ways. The most important variables for such processes are the state of attachment, are the microbes attached or unattached, and whether the microbes are active with a metabolism that turns over energy, or dormant and inactive.

Microbial processes that influence radionuclide migration	**Microbes in this process are in the following state(s):**		**This action of this microbial process on radionuclides is:**		**This process requires an active microbial energy driven metabolism:**	
	planktonic	**biofilm**	**direct**	**Indirect**	**yes**	**no**
Immobilisation processes						
Bio-sorption		x	x			x
Bio-accumulation		x	x		x	
Bio-transformation	x	x	x		x	
Bio-mineralisation	x	x		X	x	
Metabolic red-ox reactions	x	x		X	x	
Mobilisation processes						
Bio-sorption	x		x			x
Bio-accumulation	x		x		x	
Production of complexing agents	x	x	x		x	

3.3.2.1 Bio-sorption

The term bio-sorption is used to describe the metabolism-independent sorption of heavy metals and radionuclides to biomass, i.e. microbial cells. Bio-sorption can be summarized as the sorption and accumulation of trace elements to the surface of microbial cells. Both living and dead biomass are capable of bio-sorption and ligands involved in metal binding include carboxyl, amine, hydroxyl, phosphate and sulfhydryl reactive groups on the cell wall (*Lloyd and Macaskie,* 2002).

Microbes have the largest surface area to volume ratio of any independent life form due to their extremely small size, typically centring around 1 μm^3. Fitting of experimental data to Langmuir sorption isotherms gives information on the sorption capacity of microbes that can be cultured on the laboratory. Values for equilibrium sorption constants and sorption capacity have been established for the two major types of bacterial cells, those with Gram-positive and Gram-negative cell walls (*Kulczycki et al.* 2002). Distribution ratios at varying pH, cell number and concentration of the lanthanide Promethium have also been determined (*Pedersen and Albinsson,* 1991).

The typical volume of a groundwater bacterium is in the range of a part of one μm^3 up to a couple of μm^3. Numbers of planktonic microbes in deep groundwater vary in the range of 10^6 to 10^9 cells L^{-1} of groundwater (*Pedersen,* 1993, 2001). Bio-sorbing planktonic microbes can be regarded as large colloidal particles and are dealt with elsewhere in this report. However, microbes in biofilms are different. They have been reported to reach 10^{11} cells m^2 in Fennoscandian shield rock groundwater (*Pedersen,* 2001). Biofilm microorganisms commonly excrete extra-cellular material supporting attachment and also the three dimensional shape of a growing biofilm. As this extra-cellular material is organic in its nature, it will add a bio-sorption capacity to the cell's surfaces. In conclusion, bio-sorption to planktonic microbes will act mobilising on radionuclides, while bio-sorption to biofilms will act immobilising Table 7).

Up to date, no, or very little *in situ* experimental data exist on the importance of bio-sorption processes for understanding geosphere retention phenomena in the safety assessments of radioactive waste disposal. Laboratory data are available for planktonic cells though, and may be used in first approximations.

3.3.2.2 Bio-accumulation

Metals catalyse many metabolic reactions in the microbial cell. Microbes, therefore, have evolved energy dependent uptake systems for physiologically important metals. The import mechanisms of metals and other elements into the cells relate to size and charge of the element in focus. For example, the close similarity of the Cs^+ and K^+ cations dictates that the broad-specificity alkali metal uptake transporters take up both those cations in all microbial groups. The specific mechanisms by which Cs^+ is transported into the cell have been reviewed by *Lloyd and Macaskie* (2000).

As concluded for bio-sorption, bio-accumulation will have a very different effect on radionuclide retention in planktonic versus biofilm microbes (Table 7). In the planktonic state, the microbe can be regards as a large, living colloid, while the biofilm microbes relate to solid phase retention models. Although some microbes may alter between unattached and attached modes, many may become trapped and fossilised over time (*Pedersen et al.* 1997). As bio-accumulation is a process that requires energy, it can be expected that this process is biased towards biofilm microbes, because microbial biofilm populations have been found much more metabolically active relative to planktonic microbes (*Pedersen,* 2001).

Up to date, *in situ* experimental data does not exist on the importance of bio-accumulation processes for understanding geosphere retention phenomena in the safety assessments of radioactive waste disposal. The potential of this process is linked to metabolism, and therefore also to the availability of sources of energy for microbial metabolic reactions in deep groundwater, further discussed below.

3.3.2.3 Metabolic red-ox reactions

Microbial energy metabolism requires a reduced electron and energy donor and an oxidised electron acceptor (Table 8). The energy donor can be an organic or an inorganic compound. The electron acceptor is generally an inorganic compound, with exception for fermentation, where the electron donor and electron acceptor is the same organic compound. Electron donors and acceptors can be combined in redox couples according to the difference in free energy. Any redox couple that releases energy via a reaction is a possible source of energy for microbes. (*Madigan et al.* 2002, *Pedersen and Karlsson,* 1995, *Stumm and Morgan,* 1996). The result from microbial harvesting of energy from redox couples is an oxidised donor and a reduced acceptor. Important to notice here is that microbial metabolism generally lowers the redox potential in the environment. Further, some of the reduced electron acceptors (e.g. sulphide), may result in bio-mineralisation processes, as discussed under next heading.

Table 8. The most common energy and electron donors and electron acceptors in microbial metabolism. The respective atom that donates or accepts one or several electrons is underlined.

Organic energy sources and electron donors		**Inorganic energy sources and electron donors**		**Electron acceptors**	
Reduced	**Oxidised**	**Reduced**	**Oxidised**	**Oxidised**	**Reduced**
Carbo-hydrates	$\underline{C}O_2$			$\underline{O}_2$	$H_2\underline{O}$
Amino acids	$\underline{C}O_2$	$\underline{N}H_4^+$	$\underline{N}O_3$	$\underline{N}O_3$	$\underline{N}_2$
Organic acids	$\underline{C}O_2$	$\underline{Mn}^{2+}$	$\underline{Mn}^{4+}$	$\underline{Mn}^{4+}$	$\underline{Mn}^{2+}$
Fat	$\underline{C}O_2$	$\underline{Fe}^{2+}$	$\underline{Fe}^{3+}$	$\underline{Fe}^{3+}$	$\underline{Fe}^{2+}$
		$H_2\underline{S}$	$\underline{S}O_4^{2-}$	$\underline{S}O_4^{2-}$	$H_2\underline{S}$
		$\underline{C}H_4$	$\underline{C}O_2$	$\underline{S}^0$	$H_2\underline{S}$
		$\underline{C}O$	$\underline{C}O_2$	$\underline{U}^{6+}$	$\underline{U}^{4+}$
		$\underline{H}_2$	$\underline{H}_2O$	$\underline{C}O_2$	$\underline{C}H_4$

A case of special importance is the reduction of oxygen in microbial metabolism. Oxygen is the preferred electron acceptor by many microorganisms, because the free energy available in oxidation of an electron/energy donor is largest when oxygen is used, compared to other acceptors (Table 8). A first indication that microbial oxygen reduction may be of considerable proportions in granitic environments was published after a series of full scale oxygen intrusion experiments into a 70 m deep vertical fracture zone at the Äspö Hard Rock Laboratory (HRL), Sweden (*Banwart et al.* 1996). Later, the Michaeles-Menten kinetics was successfully used to model oxygen reduction during a series of field (also at Äspö HRL) and replica laboratory experiments in a detailed scale called REX aiming at the study of O_2 depletion in granitic media (*Puigdomenech et al.* 2001). This model describes the effect of the initial oxygen concentration on the oxygen reduction rate. Over a wide range of O_2 concentrations tested *in situ*, the variation of (ν) with respect to [O_2] followed the empirical Monod equation (Michaelis-Menten kinetic used for microbial growth):

$$\nu = V_{\max} \frac{[O_2]}{Km_0 + [O_2]} \tag{113}$$

where ν is O_2 reduction velocity at a specific O_2 concentration, V_{max} is the maximum rate when the organism is O_2 saturated and Km_0 is the O_2 concentration when the O_2 reduction rate is ½ of the maximum. This model was further developed and adapted to experimental data during the REX-project. For details, see *Kotelnikova and Pedersen* (1999) and *Puigdomenech et al*. (2001).

The most important conclusions from the REX experiments were (*Puigdomenech et al.* 2001):

- Microbes play a substantial role in O_2 reduction in granitic media, and microbial processes implicate a significant added reducing capacity in a repository environment.
- When a surface water containing O_2 encounters the "stationary" groundwater system at depth, there is an important increase in microbiological activities, resulting in O_2 depletion, transformation of organic material to CO_2 and formation of biofilms.
- The time scale for microbial oxygen reduction to nought in typical fractures was estimated to be in the order of a few days.

3.3.2.4 Bio-mineralisation

Radionuclides can precipitate with microbially generated ligands, e.g. phosphate, sulphide or carbonate. The concentration of free radionuclide (metals) at equilibrium is governed by the solubility product of the metal complex (typically 10^{-20} to 10^{-30}). Most of the metal or radionuclide should therefore be removed from solution if an excess of ligand is supplied. Phosphate concentration in deep groundwater is very low, and this compound is an indispensable and central metabolic energy transport entity. Therefore, it is not likely that microbes excrete phosphate to the environment. Sulphide is the respiration waste product from sulphate reduction, and is commonly found in deep groundwater. With exception for volcanic and hydrothermal areas, it can be safely assumed that dissolved sulphide to a large part is the result of microbial sulphate reduction. Sulphate reducers have been demonstrated common in Fennoscandian groundwater (*Pedersen,* 2001), which support the assumption that sulphate reduction is an important retention factor for radionuclides prone to form solid sulphide compounds. Microbial metabolism results in the production of carbon dioxide from degradation of organic carbon. Locally, such production may give rise to carbonate precipitates, e.g. calcite, with a concomitant co-precipitation of radionuclides (*Ferris et al.* 1995).

Organic surfaces and iron oxides have been identified as important factors in radionuclide transport modelling. Several microorganisms oxidise ferrous iron to ferric iron resulting in a mix of organic material (microbes) and iron oxides, here denoted BIOS (Biological Iron Oxide Systems). Such biological iron oxide systems will have a retardation effect on many radionuclides. Typically, the microbes form stalks and sheaths that increase the volume of the iron oxides from densely packed inorganic oxides to a fluffy rust-like material with water contents of up to 99 % or more. The microbes contribute to the exposure of a large oxide area to trace elements flowing by and the organic biological material adds a strong retention capacity in addition to iron oxides. BIOS can be found everywhere along the Äspö Hard Rock Laboratory tunnel system. This BIOS is mainly produced by the stalk-forming bacterium *Gallionella ferruginea* (*Hallbeck and Pedersen* 1990, 1991). BIOS from different sites and with varying age were analysed for the content of rare earth elements (REE). The results showed that the REE concentration analysed in the inflow and outflow of the experimental artificial ditches were more than 1000 times lower compared to a chondrite standard. Ten to twelve weeks old BIOS that had developed in artificial ditches at tunnel length 2200 m adsorbed three orders of magnitude more REE compared to the groundwater. Very old BIOS (4 – 6 years), collected at 1127B m tunnel length had a REE concentration that were about one million times higher compared to the groundwater and 10 to 100 times higher than what is found in typical Äspö/Ävrö rock material. The obtained data clearly demonstrates the excellent REE sorption capacity of BIOS, as first suggested by *Ferris et al.* (1999, 2000).

Microbial BIOS and carbonate mineralisation processes will have the largest retention impact on radionuclides at sites where there is an outflow of anoxic groundwater to an aerobic environment. This is because the gradients formed when the anoxic groundwater is oxygenised offer an excellent environment for microbial proliferation resulting in development of BIOS and carbonates that co-precipitate and sorb radionuclides. In opposite, sulphide bio-mineralisation will occur along the transport routs up to the ground surface.

3.3.2.5 Bio-transformation

Microbes can catalyse the direct transformation of some radionuclides to less soluble forms via metabolic processes. The most studied process is how sulphate and iron reducing bacteria can use U^{6+} as a surrogate for sulphate (*Lovley and Phillips* 1992) and Fe^{3+} (*Lovley*, 2000), respectively, as electron acceptors (Table 8). It is not known if this process is of significant importance for the safety in radioactive waste. The concentrations of SO_4^{2-} and solid Fe^{3+} phases in most repository environments will be much higher that possibly occurring U^{6+}. Therefore, bio-transformation of radionuclides escaping from a waste repository may not be significant, but this remains to be demonstrated under *in situ* conditions.

3.3.2.6 Production of chelating compounds

Microbes need metals for their metabolism, just as all multi-cellular living organisms. Such metals are often available only in small quantities or, as in the case of iron in surface waters, are not bioavailable at all due to low solubility under aerobic conditions. Therefore microbes produce various kinds of chelating compounds to increase the bioavailability of essential elements, needed for metabolism. These ligands are not always highly specific, and several of them will also mobilize other elements such as heavy metals and radionuclides. In the process of capturing the metal-ligand complex, microbes sort toxic metals from essential ones and expel the toxic elements back to the environment. The potential for mobilization of radionuclides from repository environments by bacterially produced ligands is unknown and, therefore, a concerning possibility in the safety analysis that should be explored.

If ligands are produced in a repository environment, it is crucial to study whether the postulated rock-retardation mechanism of released radionuclides can be impaired by microbial ligands. Three bacterial species (*Shewanella putrefaciens, Pseudomonas fluorescens* and *Pseudomonas stutzeri)*, isolated from the deep subsurface, and four radionuclides (^{59}Fe(III), ^{147}Pm(III), ^{234}Th(IV) and ^{241}Am(III)) were selected for a recent laboratory study. The microbes were cultured in the laboratory, separated from dissolved compounds that were produced by the microbes and expelled into solution. The separation was performed by centrifugation, and the supernatants were collected. The supernatants were mixed with radionuclide and solid phase (TiO_2 or SiO_2). The pH ranged between 7.5-9.0, which is an interval, within which all investigated radionuclides should adsorb to the added solid mineral phase, provided the system is free from ligands. All three bacterial species produced ligands that were able to complex the radionuclides at various degrees in competition with the solid phase (Figure 36).

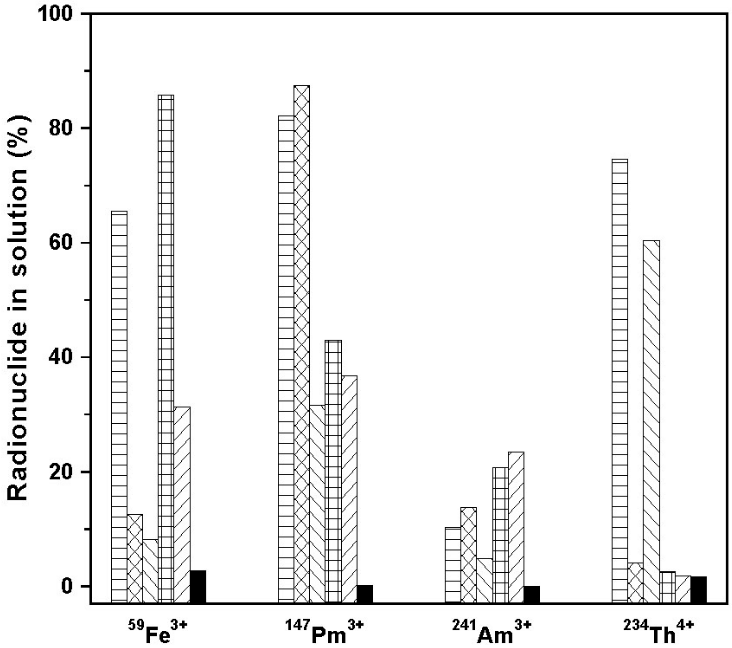

Figure 36. Mobilisation of radionuclides by three different mixes of dissolved compounds that were produced by the microbes and expelled into solution, and two known chelating compounds (Hydroxamate and Catechol) in competition with solid phase SiO_2 at around neutral pH. Bars are, from left to right: Pseudomonas fluorescens (pH 8.9); Pseudomonas stuzeri (Ph 7.6); Shewanella putrefaciens (pH 7.3); Hydroxamate (pH 6.1); Catechol (pH 6.2); Culturing medium (pH 8.4).

Further investigations were accomplished to identify the complexing agents that caused the obtained mobilization. High performance liquid chromatography (HPLC) was used to separate substances in the microbial supernatant for further characterization. Prior to injection into the HPLC the bacterial supernatants were purified and mixed with $^{59}FeCl_3$. The eluate was measured with UV (435 nm) and scintillation detector in series.

The ^{59}Fe identified the retention times for metal complexed substances, which had correlating peaks in the UV-chromatogram. Four Fe-complexing substances were detected in the supernatant from the *P. fluorescens* culture. The results of HPLC analysis with *P. stutzeri* and *S. putrefaciens* showed two peaks and one peak respectively. All substances eluted from the column varied in retention times, indicating that the microbes studied produced several metabolites that have different chelating abilities. Detailed identification of those and other complexing agents will facilitate the search for presence or absence of identified complexing agents in natural repository environments.

In another study, the action of the chelating compounds described above on solid phase material was investigated (Kalinowski et al., 2004). A uranium mine shale material for the former uranium mine Ranstad was chosen for this study. The three species described above were incubated in a chemically defined medium supplemented with tailings material that had been exposed to natural weathering conditions for 30 years having a content of 0.0013 % U by weight. Non-leached uranium ore (0.61 % U by weight) from the same area were also incubated. *Pseudomonas fluorescens* managed to mobilize 0.001 – 0.005 % of uranium from the two ores. This release of U was attributed to the production of species specific pyoverdine chelators, as U could not be detected in either sterile controls or in the experiments with the other two bacteria. *P. fluorescens* also doubles the Cr concentration in solution as compared to the sterile controls whereas *P. stutzeri* and *S. putrefaciens* result in a 5 to6 fold increase in Cr concentration. The difference in leaching behaviour between the bacteria used in this study is likely to be explained by the production of different chelators, found to be four using HPLC, as described above.

The possible production of chelating compounds in deep repository environments is unknown. Therefore, investigations are being launched during 2003 at the MICROBE site 450 m underground at Äspö Hard Rock Laboratory, Sweden (*Pedersen,* 2000). Microbial biofilms and planktonic microbes are being grown under anaerobic and reduced *in situ* conditions, including pressure, temperature, geochemistry and flow rate. Their possible production of chelating agents will be investigated on solid and dissolved phases of selected radionuclides.

3.3.2.7 Research needs

The literature database on the microbial processes described here is extensive for laboratory research, but sparse when it comes to in situ experiments, performed under repository conditions. Microbial processes are controlled by many different factors, of which several are extremely difficult to mimic in the laboratory. Physical parameters such as the high pressure, the composition of gases and the carbonate system, environmental conditions such as anaerobic and reduced systems, and finally, complex ecosystems with multi-species consortia are all very difficult to reproduce in the laboratory. There is a need for in situ experimental conditions and those can be achieved in underground laboratories. The MICROBE laboratory at the 450 m level in the Äspö hard rock laboratory, Sweden fulfils most of the requirements for in situ investigations (*Pedersen*, 2000). Several research projects about microbial processes under in situ conditions are under way at MICROBE.

Table 9. The importance of microbial processes in the safety analysis can be ranked according to its assumed effect, and the current knowledge about the process. This will give rough estimate of what processes are more important than other. However, it must be clear that new data from ongoing and future research may change the ranking in the table.

Microbial processes that may influence radionuclide migration	**Relative level of current knowledge**			**Ranking** **1 = high** **2 = medium** **3 = low**
	high	**medium**	**low**	
Immobilisation processes				
Bio-sorption			x	2
Bio-accumulation			x	2
Bio-transformation		x		3
Bio-mineralisation		x		2
Metabolic red-ox reactions		x		1
Mobilisation processes				
Bio-sorption	x			3
Bio-accumulation	x			3
Production of complexing agents			x	1

3.4 GAS MEDIATED TRANSPORT

Gas mediated transport and two phase flow could have an impact on the performance of a deep repository for radioactive waste in several ways. The following four possible problems have been identified in existing PAs:

- Overpressurisation in the engineered barrier or in the near field
- Release of radioactive and flammable gases at the ground surface
- Gas generation affecting contaminated groundwater flow pathways
- Transport through attachment at gas-water interfaces (colloids)

For all the identified possible problems the amount of generated gas is critical for if a free gas phase can be transported (continuous phase or bubbles) or if the generated gas is dissolved in the groundwater. This question will be discussed in more detail in Section 3.4.1.

3.4.1 Generation of gas and gas bubbles

The main mechanism by which gas could be generated in deep repositories are:

- Corrosion of metals in wastes and packaging
- Radiolysis of water and organic materials in the packages
- Microbial degradation of organic wastes

The amount of generated gas in a deep repository for used nuclear fuel can be expected to be 1 Mol H_2 per container and year [37]. Rodwell et. al (1999b) express their estimates as 1 Nm^3 per year and container (1 Mol = $24.3 \cdot 10^{-3}$ Nm^3). For L/ILW Rodwell et. al (1999b) suggest 260-350 Nm^3 per year per 10,000 m^3 L/ILW. Wikramaratna et al. (1993) use a maximum initial gas generation rate of 0.8 Nm^3 when trying to estimate the proportion of maximum total advection rate of dissolved gas. They arrive at the conclusion that a maximum of about 25 % of the generated gas can be dissolved in the groundwater.

Work describing the mechanisms controlling if the gas is generated as bubbles or as a continuous phase has not been found. Clearly this is an important issue.

3.4.2 Conceptualisations of gas flow

The first and most important task when trying to conceptualise gas flow in the geosphere should be to decide if it is possible for all the generated gas to dissolve in the groundwater or not. If this is possible the gas can be transported away from the repository near field in solution, either by diffusion, advection or a combination of these.

The capacity of a given repository concept to transport gas in solution is controlled by the effective diffusion coefficient for the dissolved gas in the host rock, the groundwater flux through the region of the repository, and the solubility of the generated gas in the groundwater.

The dominant conceptual model for gas migration through water saturated fractured crystalline rock is that gas will advance while displacing water through a network of fractures that provide the main part of the rock permeability. This displacing process will continue until a continuous flow path of gas is created to the ground surface. The pore sizes in the matrix blocks (the unfractured part of the rock) is assumed to be so small that the capillary pressure will prevent gas from entering the pores (water wetting rock). Dissolved gas can diffuse into the pore water of the matrix blocks but the porosity is assumed to be so small that this amount can be neglected (for the gas flow process).

Experiments show that flow in networks of fractures often is concentrated into flow channels (Pyrak et al., 1985; Moreno and Neretnieks, 1988; Neretnieks, 1987; Abelin et al., 1987; Bourke, 1987; Braney et al., 1991; Keller et al., 2000; Chen and Kinzelbach, 2002). However, it is unclear how these flow channels are formed. Some workers advocate the view that the predominant flow channels are along fracture intersections and other claim that channels form within fracture planes.

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[37] Sellin, P., SKB, Personal communication, 2002.

The front stability of a displacement process in a porous medium is controlled by the mobility ratio of the displacing and the displaced phase. If the displacing phase mobility (relative permeability for the phase divided by dynamic viscosity for the phase) is greater than the displaced phase mobility, an unstable front forming tongues and/or fingering could evolve. The fingering and heterogeneities may accelerate the advancement of the gas through the geosphere. This acceleration of the formation of gas pathways may help to minimise the potential for pressure build up as it will shorten the time required to create gas pathways to the surface.

Also the initial conditions could be important when conceptual models for two phase gas flow are considered. Two extreme scenarios affecting the pressure build up can be distinguished:

- The repository is fully water saturated and in equilibrium with the local hydrostatic pressure.
- The repository is only partially saturated with the gas present at atmospheric pressure.

In the latter case water is flowing into the repository and the local groundwater pressure is reduced below the normal hydrostatic pressure. The lowered pressure could lead to release of gas in solution. The potential for overpressurisation is predicted to be less in the latter case.

3.4.3 Sorption and transport of colloids on gas bubbles

Available information suggests that in a partially-saturated medium, colloids can be sorbed at the gas-water interface (Wan and Wilson, 1994a, 1994b; Wan et al., 1994). The concentration of colloids sorbed at the gas-water interface is a function of:

- The surface area available for colloid uptake and, therefore, total gas saturation.
- The affinity of colloids for the gas-water interface. Hydrophilic colloids, such as mineral fragments, have a low affinity. Hydrophobic colloids, such as organic colloids and microbes, exhibit higher affinities.
- The electrostatic charge on the colloid. More positively (less negatively) charged colloids exhibit a stronger affinity for the gas-water interface than negatively charged colloids.
- The salinity of the aqueous phase. Colloids are more likely to be sorbed at the gas-water interface under saline conditions.

Quantitative models of colloid sorption at the gas-water interface have been discussed by Neretnieks and Ernstsson (1997), Johnson and Elimelech (1995), and Choi and Corapcioglu (1997). Neretnieks and Ernstsson (1997) considered a system close to water saturation in which colloids were carried by mobile gas bubbles. They assumed (conservatively) that the gas-water interface became fully coated with a monolayer of colloids. In contrast, Johnson and Elimelech (1995) and Choi and Corapcioglu (1997) assumed that only a fraction of the gas-water interface may be available for sorption.

Few data exist to quantify the sorption of colloids at the gas-water interface and further work in this area may be required.

The possible significance of gas bubbles transport for radioactive waste disposal has also been reviewed by Hermansson et al. (1991), Sjöblom et al. (1995) and Goodfield and Rodwell (1998).

3.4.4 Entrainment of groundwater in bubble stream

Bubble flow itself could induce groundwater flow by entrainment of water in the bubble stream (Rodwell and Nash, 1992a, 1992b, Nash et al., 1997, Wikramaratna et al., 1997 and Godfield and Rodwell, 1998). Both the capacity for all the generated gas to migrate to the surface and the possible amount of entrained contaminated groundwater are unclear. Nevertheless it only requires a portion of the gas to migrate as bubbles for bubble flow mechanisms to have potential effect on contaminated transport.

3.4.5 Stability of gas pathways

Gas may be trapped in the rock at local constrictions of the transporting fracture. This may break up the continuous gas pathways. In addition, instabilities may lead to groundwater re-entering the previously gas-occupied pathways once pathways are formed to the surface. Intermediate between the formation of continuous gas streams and bubble flow (see Section 3.4.4) is the possibility of gas moving in the form of larger slugs driven by buoyancy forces.

The described phenomenon is suggested by the results of numerical calculations of gas migration in networks of linear channels. When the gas front is moving upwards in the fracture channels and reaches the surface there will be a change in the pressure distribution within the channels that allows water to re-enter and close off segments of the channel network (Thunvik and Braester,1990; Nash et al., 1999). As the gas generation continues the gas will re-flush the channels of water, creating a mechanism for a cyclic process of water transport to the surface. The phenomenon is also observed in laboratory tests of two phase flow in single fractures (Persoff and Pruess, 1995).

3.4.6 Field tests

Gas release at the ground surface may contain radioactive components. Even if the concentrations in the bulk gas stream are low these may pose a radiological hazard. The principal gases likely to be produced in the repository are hydrogen and methane. These gases are also flammable and could therefore also pose a risk for fire or explosion at the surface (probably only relevant for L/ILW). The choice of conceptual model to evaluate these risks is very important since the mechanisms of migration could effect whether the gas release is focused or widely distributed.

The analysis of field experiments (Lineham et al., 1996) has raised the question of what mechanisms might exist to cause lateral gas migration. According to Rodwell et al. (1999b) the relationship between patterns of soil gas anomalies, gas migration mechanisms and geological structures are not well established.

3.4.7 Models for two phase flow and bubble flow

3.4.7.1 General-continuum models

In addition to the data needed in single phase flow simulations (see Section 2.1) the two phase flow simulation needs a relationship between saturation and relative permeability and the corresponding relationship for capillary pressure (K-S-P function). This is one of the main difficulties of modelling fractured media in continuum models since it is difficult to obtain representative data describing the K-S-P function.

3.4.7.2 Discrete fracture models – network

The simplest form of discrete fracture modelling is to represent displacement of water through sets of parallel fractures or fracture channels. Thunvik and Braester (1990) extension to a simple set of intersecting fractures in two dimensions produced results in which instability of gas-filled channels was observed (see Section 3.4.5).

3.4.7.3 Discrete fracture models – single fracture

Murphy and Thomson (1993) have developed a model for two phase flow in rough discrete fractures. When the interface between gas and water moves in the model its position is tracked in computational cells of a finite difference grid through the use of predefined, parameterised, interface shape functions. A variety of modified versions of this model has been used to develop an understanding of gas migration from radioactive waste repositories (McCarthy and Rodwell, 1998).

Keller et al. (2000) have developed a numerical model which can be used to produce K-S-P functions given a fracture width distribution. Zhou (2001) has developed a similar model and studies effects of fracture width distribution, mobility ratio and fracture orientation on displacement processes.

Analytical studies on single fractures have been carried out by Jarsjö and Destouni (1998). The aim was to investigate the effects of groundwater degassing on the reduction in water permeability due to the presence of trapped gas. A model for bubble trapping probability was derived as a function of the properties of the fracture aperture distribution and the hydraulic pressure gradient.

3.4.7.4 Transport of gas-phase tracer

When modelling transport time for radioactive gas-phase tracers the simplest approach is to assume that these arrive at the surface the same moment the free gas-phase is developed in the repository. This assumption may be sufficient if the concentrations do not exceed the limit for a radiological hazard. The next step is to assume that they behave exactly as the bulk gases which transport them, i.e. moving at the same speed and dissolving in the groundwater at the same extent.

For more accurate calculations where radon is involved (short half life) a simple model has been developed (Baker et al., 1997; Rodwell et al., 1999a). In this the gas migration pathways are modelled as parallel fractures or uniform capillaries depending on whether the permeability of the formation is provided predominantly by a network of fractures or by intergranular pore space. The model assumes that a steady-state gas stream in witch radon can be transported is established. The radon is lost from the gas phase by decay and solution into groundwater in contact with the gas stream. Radon that occurs naturally in the rock can also be added to the gas stream. Partitioning of the radon between the gas stream and the groundwater is controlled by the solubility of radon, and by its decay and diffusion in the matrix pore water adjacent to the flow channels.

3.4.7.5 Gas bubble flow

A simple model for numerical analysis of gas bubble flow has been developed by Kostakis and Harrison (1999). A procedure for estimating the bubble size is derived. This procedure is used as input for a two dimensional finite difference model where the flow equations are solved. The numerical calculations have been checked against a simple analytical solution for gas flow between smooth parallel plates. The model shows god agreement with the analytical calculations but the authors stress the need for further verification against experimental results.

3.5 ‘OFF-DIAGONAL’ PROCESSES

3.5.1 Definition and description of processes

In the framework of the theory of irreversible thermodynamics, a given flux J_i (e.g. flux of heat, fluid, solutes, electrical current) can be expressed as

$$J_i = \sum_j L_{ij} X_j \tag{114}$$

where the X_j terms are driving forces (e.g. temperature, hydraulic, concentration, or electrical potential gradients), and the L_{ij} terms are the so-called phenomenological coefficients. The term direct or diagonal phenomena is used for the $L_{ii} X_i$ contribution to a flux J_i, and the term coupled or off-diagonal phenomena is used for a $L_{ij} X_j$ contribution ($j \neq i$).

The table below is a matrix of direct (main diagonal) and coupled (off-diagonal) transport phenomena.

Table 10. Onsager matrix – Matrix of direct (diagonal) and coupled (off-diagonal) transport phenomena (Soler, 2001; de Marsily, 1986; Horseman et al., 1996). Shaded boxes correspond to the phenomena considered to have a potential relevance.

	POTENTIAL GRADIENT X			
FLUX J	**Temperature**	**Hydraulic**	**Chemical**	**Electrical**
Heat	Thermal conduction	Thermal filtration	Dufour effect	Peltier effect
Fluid	Thermal osmosis	Advection	Chemical osmosis	Electrical osmosis
Solute	Thermal diffus. or Soret effect	Hyperfiltration	Diffusion	Electro-phoresis
Current	Seebeck or Thompson eff.	Rouss effect	Diffusion & Membr. Pot.	Electrical conduction

The off-diagonal phenomena that may have certain relevance in the far field of a repository are those concerning the fluxes of fluid and solute due to hydraulic and chemical gradients. The conceptual formulation of these processes is described below.

Temperature gradients in the far field of a repository for HLW/SF (vitrified high-level waste and/or spent nuclear fuel), especially at times equal or greater than the expected lifetimes of the waste canisters ($t \geq 1000$ years), are never expected to be significantly above natural background gradients. Heat generation by low-level waste is not significant. Also, for a fully saturated rock, any possible thermal-osmotic flux of water would be cancelled by an opposing advective flux (Soler, 1999, 2001), unless there were a source of water towards the repository area. Solute fluxes by thermal diffusion seem to be always negligible, given the small magnitude of the Soret coefficients (Soler, 1999, 2001).

Estimates regarding the possible role of thermal filtration and the Dufour effect on heat transport in Opalinus Clay suggest that the effects of these coupled heat transport mechanisms are negligible compared to heat transport by thermal conduction (Soler, 1999).

Regarding electrical potential gradients, there is no evidence regarding long-range potential gradients in rock formations. Although it is true that spontaneous potentials are measured in rocks, it is not clear what the connection is between a potential at a microscopic scale (e.g. surface charge on clays, formation of diffuse double layers), which may be the cause of such spontaneous potentials, and one at a macroscopic (metric) scale. Also, only very scarce information is available regarding the coupling coefficients for coupled transport phenomena driven by electric potential gradients.

3.5.1.1 Chemical osmosis

Chemical osmosis is the flow of fluid (solution) caused by chemical potential gradients. Chemical-osmotic flow across a semipermeable membrane is up the salinity gradient, or equivalently, down the activity-of-water gradient.

Rocks containing large proportions of compacted clays (or other minerals characterized by significant surface electrical charge, e.g. metal oxides) may act as semipermeable membranes due to the existence of ionic double layers on the clay surfaces. Since the structural charge on clay surfaces is negative due to isomorphic substitutions in the mineral lattice, a diffuse double layer of counter-ions (cations) in solution develops next to the mineral surface. If the rock is sufficiently compacted so the diffuse double layers of adjacent clay platelets overlap, the distribution of electrical charge in solution allows water and non-charged solutes to pass through the pores, but prevents anions from doing so. Due to electrostatic coupling, the migration of cations will also be prevented. Under such conditions, a clay-rich rock can potentially act as a semipermeable membrane, with chemical osmosis and hyperfiltration playing important roles in fluid and solute transport.

The chemical-osmotic flux of fluid can be expressed in terms of a flow law similar to Darcy’s law (Kemper and Evans, 1963; Kemper and Rollins, 1966; Barbour and

Fredlund, 1989). This flow law, in one dimension, and with units of m^3/m^{2}rock/s, has the form

$$v_{CO} = K_\pi \frac{\partial \Pi_h}{\partial x} = \sigma K \frac{\partial \Pi_h}{\partial x} \tag{115}$$

where K_π is the coefficient of osmotic permeability, σ is the coefficient of osmotic efficiency ($0 \le \sigma \le 1$), K is the hydraulic conductivity, and Π_h is the osmotic pressure head.

The coefficient of osmotic efficiency (σ) is a measure of how close to ideal a semipermeable membrane is. For an ideal membrane (no solute flux through the membrane is allowed) σ is equal to one. On the other hand, if there is no restriction on the flux of solute through the membrane, σ is equal to zero. Harrington and Horseman (1999) measured osmotic efficiencies in samples of Opalinus Clay (a compacted clay formation); they reported values of σ about 0.1.

The osmotic pressure head, Π_h, is defined as

$$\Pi_h = \frac{\Pi}{\rho g} \tag{116}$$

and the osmotic pressure, Π, is given by (Soltanieh and Gill, 1981; Merten, 1966)

$$\Pi = -\frac{RT}{V_w} \ln a_w \tag{117}$$

where V_w and a_w are the molar volume and activity of water, respectively. The activity of water can be calculated according to (Garrels and Christ, 1965)

$$a_w = 1 - V_w \sum_i \frac{c_i}{W_i} \tag{118}$$

where c_i and W_i are the concentration of species i in solution (kg/m^3) and its molar weight (kg/mol).

The maximum value of the solute flux associated with chemical osmosis (kg/m^2/s), in one dimension, can be expressed as

$$J_{CO} = c_i \, \sigma \, K \frac{\partial \Pi_h}{\partial x} \tag{119}$$

3.5.1.2 Hyperfiltration

The hyperfiltration flux (kg/m^2/s) is a flux of solutes against the hydraulic gradient (Groenevelt et al., 1980).

$$J_{HYP} = c_i \, \sigma \, K \frac{\partial h}{\partial x} \tag{120}$$

However, hyperfiltration can be thought of as a correction to the advective flux, due to the fact that an ideal semipermeable membrane will allow water to flow by advection through the pores but will prevent solutes from doing so. That means that the hyperfiltration flux, as expressed above, would be substracted from the advective flux.

Notice that this filtration or salt sieving effect should also apply to diffusion, i.e., there should be a correction to the diffusion flux in the same way that hyperfiltration corrects the advective flux. However, this is not necessary when the appropriate effective diffusion coefficient for a specific tracer is used (e.g., in an ideal semipermeable membrane, the effective diffusion coefficient for an ionic species should be zero).

3.5.2 Experimental and modelling support

Chemical osmosis and hyperfiltration are well understood from the point of view of the mechanisms behind the transport phenomena. They are due to the existence of diffuse ionic double layers in solution next to mineral surfaces in narrow pores, as is the case in compacted clays. Experimental and modelling support is also well established (Harrington and Horseman, 1999; Neuzil, 2000; Soler, 1999, 2001; Keijzer, 2000; and references within).

3.5.3 Future development and research on off-diagonal processes

There is evidence that the coefficients of osmotic efficiency cannot be derived directly from theory (Keijzer, 2000). Therefore, if chemical osmosis and hyperfiltration were to be included in performance assessments (e.g., if very large salinity gradients were expected in the geosphere) there would be the need for site-specific experimental work.

4 IMPLEMENTATION OF PROCESSES IN PA'S

4.1 INFLUENCE OF FLOW FIELD ON TRANSPORT AND RETENTION

The Finnish and Swedish PAs have used somewhat different model concepts. The Finnish PA used a porous medium description of the site and regional scale and a network model for the local (canister) scale block (40 m)^3. In the local model the flowrates of streams are tracked through different flowpaths to obtain the distribution of Flow Wetted Surface to flowrate, A_q/q, in the local scale block.

The Swedish PA (SR 97) uses a porous medium model directly from the canister scale where stream tubes are identified from the flow model. In both PAs the A_q/q is obtained for different flowpaths from canister locations to the biosphere. In the Finnish report the entity $A_q/q/2$ is denoted by WL/Q and called transport resistance, whereas in the Swedish report it is denoted by F and corresponds to A_q/q. The *WL/Q's* or *F*'s in both PAs play a central role for determining the residence times of the nuclides. There are no differences in principle between the PAs but there are differences in the details and how variations, uncertainties and conservatisms are handled. Below some more details in the two PAs are described.

Notation is found in APPENDIX 2.

4.1.1 Posiva

In TILA-99 (Vieno and Nordman 1999) four different sites were used in the PA. The water flow modelling was made over three different scales, the regional, the site scale and the canister scale. The regional and the site scales were over 10 and 2-3 km square regions and supplied gradient and head data for the canister scale model. Three- dimensional porous media models were used for the larger scales and a Discrete Fracture Network, DFN, model was used for the canister scale, which encompassed a cube with 40 m sides. The fracture statistics and the conductive fracture frequencies were obtained from measurements on cores, from 2 m packer tests in deep boreholes and from observations on outcrops.

In essence, streamtube modelling was used to follow paths from specific canister locations to a major fracture zone. In the modelling, of the transport the paths leading vertically upward from the repository were selected to be of most importance and were studied specifically. The basic ideas for transport that are described in Section 2.1 were applied to streamtubes and the network to obtain the matrix interaction entity LW/Q along the flowpaths.

Some details of the TILA-99 PA are worth describing in more detail because they emphasise the wish to describe those transport pathways that could have a dominating effect on the release and transport. The PA also shows how different alternative ways of modelling the flow and transport can be used to assess the impact of uncertainties in model concepts and data on the release of the nuclides to the environment. The PA also emphasises the possible role of the "fastest" pathways and those that could carry most of the nuclides.

In the DFN model there were attempts to directly estimate *WL/Q,* where *Q* was based on direct flow measurements as well as on combined DFN/continuum groundwater flow modelling. Estimation of *WL/Q* was based on the assumption of channelling of the flow in fractures both due to the limited extent of the fracture intersections and in-plane heterogeneity of the fractures.

Release paths of the radionuclides from the repository at 500 to 600 m depth to the 300 m level were calculated using deterministic site scale groundwater model. Release paths were terminated at the 300 level because it appeared that above that level release paths were in the fracture zones in all four sites and consequently the contribution to the total *WL/Q*, whether terminated at 300 level or at the surface was small. This also made comparison of different sites much easier.

The site scale model contains a few kilometres region around the repository and it is based on the continuum (porous medium) approach. However, the fracture zones (and the repository) are represented explicitly as two-dimensional discontinuities of the permeability. Also, depth dependence of the hydraulic conductivity is included in the model. Calculation of the release paths was performed by using particle tracking starting from a representative set of locations inside the repository.

The distribution of the flowrate at different positions along the release paths was assumed to be governed by the characteristics of the local fracture network and surrounding hydrological conditions. In the modelling this was further simplified by i) identifying three different possible fracture populations along the release paths (background fracturing, fracture zones and excavation disturbed zone around the repository tunnels) and ii) representing the local (surrounding) hydrological conditions at different locations along the release path by average local hydraulic gradient. Potential and analysed release paths from the deposition canister to the fracture zone are presented in the diagram of the Figure 37.

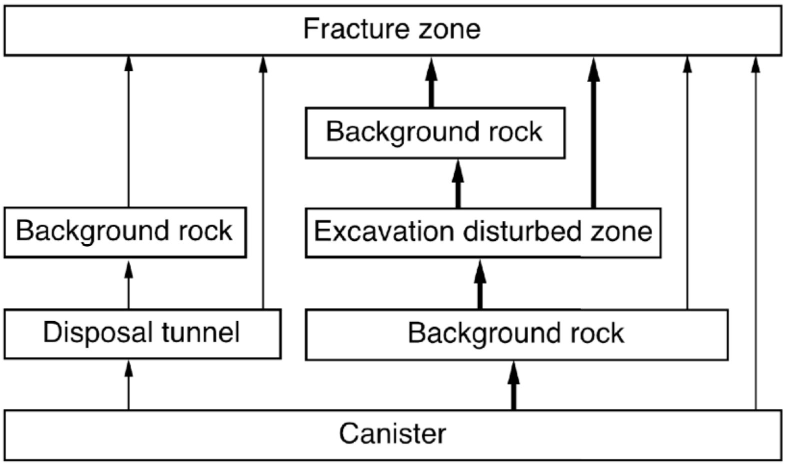

Figure 37. Potential release routes from the repository into the fracture zone. Analysed routes are drawn with thick lines (from Poteri and Laitinen, 1999).

This means that two different models were applied to estimate the *WL/Q*'s:

- Site scale continuum model gives release paths, composition of them (i.e. path divided into sequential legs through different fracture populations) and average local gradient of the hydraulic gradient.
- Local DFN models to integrate the *WL/Q* for different fracture populations.

Local DFN models are simulated in about 40-meter scale. It is assumed that the integrated *WL/Q* over the DFN model gives characteristic *WL/Q* for the analysed fracture population. This means that the *WL/Q*'s for the flow paths that are different in length or flowrate than the ones used in the simulations can be estimated by scaling the simulated *WL/Q*'s.

Each DFN model (i.e. fracture population) is simulated for about ten different realisations and each realisation is sampled for flow paths to be used in the integration of the *WL/Q* (total number of flow paths is 20 – 30). The flow paths are searched using two criteria: the least number of fractures or highest conductance. This means that the hydrodynamic control of the retention, *WL/Q*, is represented by a set of individual flow paths for each of the fracture populations (background fracturing, excavation disturbed zone and fracture zones).

The flow fields over the selected flow paths are solved numerically using DFN model. Note that only the fractures that are part of the studied flow path are included in the model. This means that at this point the transport path is a set of successive fractures that form a non-branching flow path. The small number of fractures makes it possible to use dense element mesh to simulate, for example, heterogeneous fractures.

The parameter *WL/Q* along a flow path is found by integrating (or summing) along the whole path

$$WL/Q = \sum_i \frac{L_i}{(Q/W)_i} \tag{121}$$

Where $(Q/W)_i$ is the flowrate per width in the fracture plane at the path segment i in the fracture plane and L_i is the length of the segment. The DFN flow path is divided into segments by using 1 m intervals along the mean flow direction. *Q/W* is estimated by average of the highest values of the *Q/W* at the end points of a segment. This means that *WL/Q* along a flow route is integrated for the flow channel of the highest flowrate. This will emphasise the most prominent pathways.

The "complete" DFN models including all water conducting fractures were used to estimate the flowrates through the sampled flow paths. This was performed by introducing test planes inside the DFN models and calculating the flowrates of the flow paths that go through the test planes. The calculated distribution of the flowrates was used to approximate the flowrates through the individual flow paths.

The transport of radionuclides through the streamtubes was calculated in TILA-99 using numerical model FTRANS**.** This stage of calculations combined the estimated *WL/Q*'s along the release paths and the corresponding material properties of the rock matrix. The calculations are based on the assumption of streamtubes that are represented by the analysed release paths. FTRANS is also able to handle decay chains.

A number of realisations were performed and a number of streams followed. The range of *WL/Q* that was obtained from canister to fracture zone ranged from about 10^4 to more than 10^6 years/m including all simulations and sites except Romuvaara where lower values were obtained. The larger of these values will allow practically none of the sorbing nuclides to reach the biosphere.

It may be noted, although this belongs to the near field and not the far field rock that TILA-99 models include the transport processes in the Excavation Damage Zone, EDZ, around the deposition tunnels. The same model is used for transport in the EDZ as for the local block.

4.1.2 SKB

In SKB SR 97 three different sites were modelled. The sites all contained fractured rock masses intersected by fracture zones. The flow fields were calculated (in three dimensions) using a stochastic continuum approach (see e.g. Gylling et al, 1999). The conductivities of the blocks varied stochastically and could also be dependent on depth and location in the rock mass. The rock was typically discretisized in cubic blocks 25 or 35 m. The flow could then be followed from different canister positions. Central cases and a number of variants were modelled to study the influence of boundary conditions, changes in hydraulic conductivity and impact of anisotropy.

Advective travel times to biosphere were calculated using particle tracking assuming a constant flow porosity (set to a typical value of 10^{-4}). Furthermore, it was assumed that the rock mass had a constant (although uncertain) flow wetted surface area a_R per volume of rock.

The surface area per volume of rock a_R (or rather the migration path width per unit rock cross section area) was obtained from estimates of the conductive fracture frequency (CFF) as explained by Andersson et al. (1998). The CFF, in turn, is estimated from the number of conductive bore hole test sections in relation to the total number of bore hole test sections. If flow is evenly distributed among all fractures there is a one-to-one relation between a_R and CFF, but in reality only few migration paths carry most of the flow, which means that the CFF might overestimate the a_R corresponding to the actual migration paths. This is also indicated by the discrete network analyses conducted by Geier (1996). However, estimating CFF from the number of flowing test sections generally underestimates CFF since it is then assumed that only one fracture per flow test section is responsible for the flow. This can be compensated to some extent by analysis of the fracture statistics. Andersson (1999), suggested that the approximation is a fair ”reasonable estimate” but suggest a ten times lower value for a pessimistic case. The “reasonable estimate was set to 1 m^2/m^3 rock in two of the sites and 0.1 m^2/m^3 in one of the sites.

With the assumptions of constant a_R and porosity, the transport resistance (or *F* as it was called in SR 97) could be directly obtained from the advective travel times of the particle tracks using:

$$F = (a_R L/q) = t_w\, a_w \qquad \text{(In TILA-99 notation } F_{TILA} = \frac{WL}{Q}\text{, i.e., } F_{TILA} = \frac{F}{2}\text{)} \qquad (122)$$

Where a_w is the flow-wetted surface per volume of water, and t_w the advective travel time calculated for this porosity. (The equation also shows that F is independent on porosity values, but t_w off course depends directly upon it).

Resulting values of F ranged between 10^4 years/m to about 10^7 years/m. Typical mean travel times of the water were from years to a few tens of years in two of the areas and 1000 years in one area with much lower conductivity. Typical spreads in travel times ranged over three orders of magnitude for about 95 % of the paths. Typical mean fluxes ranged from less than 0.001 to 0.01 m^3/m^2/year for two sites and $3 \cdot 10^{-5}$ m^3/m^2/year for one site. The spread in fluxes was similar to that in water travel times.

There were also direct estimates of F made in SR 97 using a DFN code (Dershowitz et al., 1998). In these analyses F was directly integrated along particle tracks in a DFN-model. The resulting F values were of the same range as the base case values. The DFN model assumed constant transmissivity in the plane of the fracture though.

The above results were subsequently used to simulate the residence time distribution of the different nuclides. The advection-dispersion model with matrix diffusion (see Section 2.1) including chain decay was used for these simulations. Matrix porosity, diffusivity and sorption data were obtained from laboratory measurements. Although dispersion was modelled with a Peclet number = 10, it was found that the differences in travel time for the nuclides along the different flowpaths had a much larger influence on the spread of the nuclide pulses than did the “hydrodynamic” dispersion. The subsequent analyses in SR 97 clearly demonstrate the very strong impact of the F value on the residence time. (TILA-99 used essentially the same expression for the same purpose).

4.2 IMPLEMENTATION OF WATER CHEMISTRY AND SORPTION IN PA

4.2.1 Application of transport equations

In all PA exercises described in the responses to the WP1 questionnaire there is no treatment of aqueous speciation and each solute is considered as a unique dissolved species. Similarly, sorption is treated by means of a linear distribution coefficient K_d, which may lump several retention processes together, including sorption (both surface and intracrystalline), precipitation and co-precipitation. This simplification allows sorption to be considered as a retardation coefficient in the transport equation, and no additional source-sink term is required.

The transport equation *in the fracture* is given by an expression such as

$$-v\,\frac{\partial c_i}{\partial x} + \frac{\partial}{\partial x}\left(D_L\,\frac{\partial c_i}{\partial x}\right) - R_i^f\;\lambda_i\,c_i + R_{i-1}^f\;\lambda_{i-1}\,c_{i-1} + \frac{F}{b}\,D_e^m\,\left.\frac{\partial c_i^m}{\partial y}\right|_{y=b} \quad = \quad R_i^f\,\frac{\partial c_i}{\partial t} \tag{123}$$

where v is the flow velocity in fractures [m s^{-1}]; c_i is the concentration of the i-th solute in fractures [mol m^{-3}]; D_L is the dispersion coefficient in fractures [m^2 s^{-1}]; λ_i is the decay constant [s^{-1}]; F is the proportion of fracture surface from which nuclides can diffuse into the matrix; b is the half of the fracture aperture [m]; D_e^m is the effective diffusion coefficient in the rock matrix[m^2 s^{-1}]; c_i^m is the solute concentration in the matrix [mol m^{-3}]; x is the transport distance along the fracture [m]; y is the distance into the matrix from the fracture surface [m], measured perpendicular to the fracture plane; and R_i^f is the retardation factor in the fracture.

The four terms on the left-hand-side of Equation (123) correspond to advection in the fracture, dispersion in the fracture, radioactive decay, radioactive production and matrix diffusion, respectively. In all PA exercises sorption is assumed to take place only in the matrix, i.e., the retardation factor in the fracture R_i^f is equal to one. Sorption on fracture surfaces and fracture infilling is not taken into account.

The transport equation *in the rock matrix* is expressed by an equation such as

$$\frac{\partial}{\partial y}\left(D_e^m \frac{\partial c_i^m}{\partial y}\right) + \phi\, R_{i-1}^m\, \lambda_{i-1}\, c_{i-1}^m - \phi\, R_i^m\, \lambda_i\, c_i^m \quad = \quad \phi\, R_i^m \frac{\partial c_i^m}{\partial t} \tag{124}$$

where R_i^m and ϕ are the retardation factor in the rock matrix and the matrix porosity, respectively. The retardation factor in the rock matrix is defined as

$$R_i^m \; = \; 1 + \frac{\rho K_d}{\phi} \tag{125}$$

1where K_d is the distribution coefficient for the matrix [m^3 kg^{-1}] and ρ is the bulk-dry density of the matrix [kg m^{-3}].

It is important to note that part of the amount of species that is considered to be sorbed (i.e., taken into account by the K_d) may actually be located in the diffuse double layer adjacent to the mineral surface, and could, therefore, be partially mobile (surface diffusion).

4.2.2 K$_d$ versus thermodynamic sorption models in PA

There is a general consensus on the use of linear sorption (constant K_d) modelling in PA exercises (see Equation (125)). This has been based on the simplicity of the mathematics and the linear convergence of the problem. This is highly relevant when a large number of calculations are required.

However, from the conceptual point of view, there are main problems related to the use of the constant K_d modelling in PA exercises:

- It does not take into account the chemistry of the pore solution and its variability.
- It does not account for the exhaustion of the sorbing capacity of the solids.
- Other relevant processes, such as precipitation/dissolution or coprecipitation/ codissolution (those called ‘irreversible sorption’) cannot be represented.

One may argue in favour of the constant K_d approach that neglecting precipitation keeps the PA exercise within the more conservative range. However, the effect of the first two points on the final result of the exercises is not easy to forecast a priori.

On the other hand, thermodynamic sorption models (TSM) can satisfactorily solve some of the main objections discussed above. They account for variations in the chemistry of the solution, including the effects of pH, ionic strength, aqueous complexation and other competitive ions (including major components). They also account for limitations in the number of sorbing sites, although they still do not account for possible precipitation and coprecipitation reactions. Moreover, TSM supply the theoretical basis for the estimation of unknown values of the equilibrium constants of surface complexation reactions.

TSM are, however, far from being used in PA exercises, mainly due to the following reasons:

- The large amount of parameters to determine: equilibrium constants, sorbing sites or exchange capacity, electrostatic corrections, etc.
- The difficulty of extrapolating from laboratory batch experiments to field conditions.
- The numerical problems of convergence for multicomponent non-linear problems.

Of these three objections, only the third one is intrinsic to the use of TSM in PA exercises (see Table 11). The first two points correspond to what the scientific community knows or ignores about sorption. These points can be relevant when selecting K_d values, as discussed below.

4.2.3 The use of TSM to select K_d values

An intermediate modelling strategy can be used when consensus among the PA modellers and the rest of scientific advisory community is reached. In 1995, the Performance Assessment Advisory Group proposed the creation on the NEA Sorption Forum with the aim of investigating how to develop sorption data and TSM to improve the confidence of PA modelling. The Forum organised two workshops (Oxford, 1997, and El Escorial, 2002).

Table 11. Comparison of cpu time to compute the Ni sorption in a 100 m long fracture containing 1 vol. % Na-smectite. Calculations performed with the code RETRASO (Saaltink et al., 1998). Option A: linear sorption; Option B: simultaneous modelling of cation exchange and three different surface complexation sites (Bradbury and Baeyens, 1997).

Adsorption model	**Computing time (s)**
No sorption	8
K_d (Option A)	12
B&B (3 sites) (Option B)	41

The main conclusion of the Oxford workshop was to use TSM and to introduce a chemical reasoning to constrain the range of K_d values used in PA (Altmann and Bruno, 2001). Radionuclide solubilities are used to constrain the concentrations expected from the source term in PA exercises. Solubilities are obtained from matrix leaching experiments, laboratory solubility measurements and thermodynamic modelling. Similarly, radionuclide sorption coefficients measured in the lab and TSM can be used to:

- Estimate the most appropriate K_d value for each region of the PA model (engineered barrier and the different lithologies of the geosphere).
- Estimate when the K_d value or the region limits should be modified.
- Reduce the uncertainty associated with K_d estimates by providing support by expert judgement.

As shown in Figure 38, the most frequent approach would be to base the K_d values on data obtained in the laboratory with crushed material. A correction would be needed to upscale the K_d value to field conditions. In doing so, the flow wetted surface and the mineral characterisation (fracture filling, coating, matrix fractures) would be required to use TSM. Reactive transport modelling can be a useful tool to combine TSM and transport processes (advection and dispersion/diffusion) helping to estimate the contact time between the solution and the sorbing solid, as well as the evolution of the system with time.

The first two objections to constant K_d models can be overcome by using TSM to optimise the range of K_d values used in the PA exercises. This methodology takes advantage of experimental data obtained in recent years and the theoretical interpretation of the results through TSM. By selecting good estimates for K_d, the first two objections to the constant K_d modelling referred to above (taking into account chemical variability and limited sorbing sites) can be overcome or at least minimised. One must be aware, however, that redox changes in the solution and precipitation and coprecipitation processes are still outside of the scope of the conclusions of the Oxford workshop. Moreover, the first two objections to the direct use of TSM models in PA exercises (the large amount of parameters to determine, and the difficulty of extrapolating from laboratory to field) are also included in the expert judgement step. Therefore, only the numerical problems involved in non-linear process (which is not simple!) are overcome with the Oxford workshop proposal.

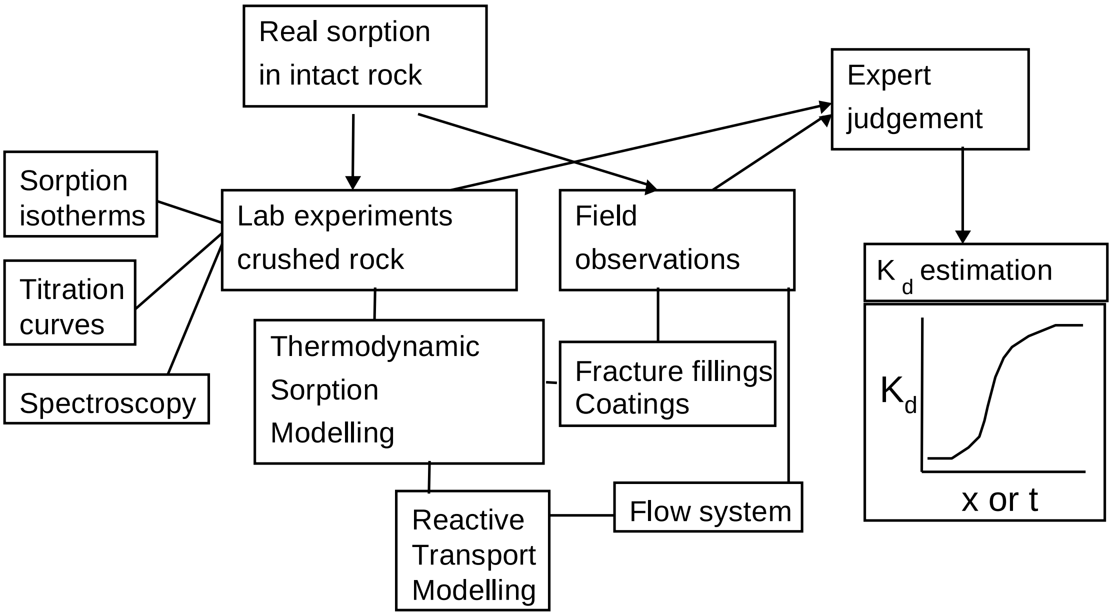

Figure 38. Schematic process of radionuclide K_d selection and estimation of associated uncertainties in PA exercise (modified from Altmann and Bruno, 2001).

4.2.4 Foreseen developments on sorption modelling

In discussing future work one must keep in mind two different sets of unknowns or uncertainties: those inherent to sorption conceptualisation and those related to upscaling from lab to field conditions.

1) Fortunately, conceptual models (surface complexation and/or ionic exchange) for the most relevant sorbing minerals present in fracture fillings, such as iron hydroxides and smectite, have already been formulated (Dzombak and Morel, 1990; Baeyens and Bradbury, 1997; Bradbury and Baeyens, 1997, 1999). However, to have a thermodynamic database for radionuclide sorption reactions should be an ultimate goal of a long-term research programme. This database would extend the work already done for aqueous speciation and water-mineral equilibria (Grenthe et al., 1992; Silva et al., 1995). A large effort has already been made to measure K_d values of different radionuclides on different materials (McKinley and Scholtis, 1992; Higgo, 1988; Stenhouse, 1995). Sorption of major components, susceptible to compete with radionuclides, should also be included. An interesting compilation has already been started by Vinzenz Brendler at Rosendorf, and presented in El Escorial NEA workshop (2002).

A TSM database has more inherent complexity than that of aqueous speciation, mainly resulting from the solid variability. Therefore, it would be interesting to reach some consensus within the scientific community to build a transportable database. Important points to decide are:

- To determine only one TSM for each mineral, whether non electrostatic or among the different electrostatic options.

- To fix the site density in order to obtain a normalised set of equilibrium constants for each mineral.
- To reach a standard experimental protocol: pre-treatment of the solid phase, surface titration, range of pH and ionic strength, possible precipitation at neutral and slightly alkaline conditions, etc.
- Surface complexes included in the models to fit the experimental sorption data should be in accordance with spectroscopic observations.

2) The problem of upscaling has been a major unresolved issue for the last decades and will probably still be so in the future. Thus, one of the largest uncertainties is the translation of K_d values measured on crushed material into undisturbed rock. The main uncertainties related to the application of TSM are based on:

- Identifying and quantifying the mineral and organic phases making up the solid-solution interface.
- Quantifying the surface area of the solid-solution interface or wetted surface, which is needed to know the total number of sorption sites or exchange capacity.

Moreover, these two main uncertainties are also variable with space and time. Uncertainties in this point may be large enough to invalidate part of the effort described in the previous item. Therefore, intensive work has to be done in parallel to the fundamental research described in item 1.

> 2.1) One possible way of progress could be the extension of sorption experiments from batch to flow systems with the crushed rock involved in PA (column) under controlled conditions. Once the TSM is selected, reactive transport modelling would allow the estimation of the effective sorption sites/exchange capacity as a fitting parameter, and it could be compared with the values measured in batch experiments. These values would include the wetted surface problem, and solid/liquid ratios more realistic than those obtained in batch reactors under continuous agitation. Correction factors ranging from 0.01 to 0.1 were necessary to extrapolate values from batch experiments to columns with crushed granite (ENRESA answer to the RETROCK questionnaire).
>
> More realistic experiments can be performed with column experiments with flow forced through fresh (non crushed) rock samples, or field experiments under controlled conditions, after an accurate mineralogical description of the fracture filling and rock matrix. Then, exercises of reactive transport modelling using TSM obtained in the laboratory (for example: Mont Terri project) can finally end up with a very constrained set of data for PA.
>
> These experiments assume the mineralogy is known in detail, and a TSM known for each mineral. Then, the bulk sample sorption properties are built up by component additivity (bottom-up approach). This approach has the problem of assigning a sorbing surface to each mineral. In practice, however, a sorbing phase (smectite, iron oxides) is often responsible for most of the sorption (see for example the iron oxides in Kongarra schists, Payne, 1999).
>
> 2.2) An alternative to this approach is performing batch experiments using a real rock instead of pure minerals (top-down approach). A TSM can be obtained from

the set of experiments. This approach takes advantage of the fact that PA exercises are not completely generic, but they always have a real rock to work with. It is convenient when no previous data is available and allows the justification and selection of ranges of K_d values. Satisfactory results have been obtained for uranium sorption on the Kongarra soil (Davis et al, 2002).

2.3) In a similar fashion, it is convenient to make sure that the estimations of sorption parameters based on TSM are consistent with the results of measurements based on the use of natural formation waters. The presence of potentially important organic agents, which may be present at trace concentrations and difficult to detect, could have an effect on sorption.

3) Finally, it is important to remember that, although the selection and estimation of uncertainties for K_d values in PA can be highly benefited from the application of thermodynamic sorption modelling, these models do not take into account processes such as precipitation and coprecipitation. Theses processes constitute a possible sink for radionuclides and their omission in PA exercises is currently assumed to be conservative. However, the validity of this assumption could, in the long term, be challenged by changing boundary conditions (see Section 4.6).

Current reactive transport models include fluid flow, solute transport and different models of surface complexation and cation exchange, together with precipitation/dissolution and coprecipitation/codissolution processes. Moreover, reactive transport models are also numerically affordable by current codes and machines, there is a continuous research on algorithm optimisation, and hardware development tends to reduce calculation times. Therefore, although the use of fully mechanistic models in PA within the next few years is not a realistic expectation, they are an alternative that should not be ruled out.

4.3 MATRIX DIFFUSION

4.3.1 Dealing with matrix diffusion in performance assessments

The key issues with regard to matrix diffusion for safety assessment purposes are, of course, dependent on the specific facts of a repository for radioactive waste under consideration. However, some aspects are independent of the specific layout of a repository and have to be evaluated previously and specified concerning their applicability and reliability. Such key aspects are the

- pore size distribution which may strongly affect the mobility of different radionuclides;
- spatial extent of the connected porosity;
- effects of possible surface charges which result in species-dependent diffusivities;
- effects of radionuclide-dependent sorption or other deposition processes on the (temporal) immobilisation of the solute in the rock matrix;
- applicability of values for porosity and diffusivity obtained from measurements using de-stressed rock samples under repository conditions – i.e., the influence of rock stress on the porosity and diffusivity of radionuclides;

- transferability of values for sorption derived from small scale laboratory experiments such as, e.g., batch sorption and diffusion experiments to performance assessment conditions;
- effects of a possible fracture coating and infill material which may reduce the efficiency of matrix diffusion due to covering of matrix pores by the coating or infill material;
- effects of time-dependent transport parameters on the geosphere efficiency especially if very long time-spans have to be considered;
- although the spatial variabilities and uncertainties in the values of the transport parameters in the rock matrix are less pronounced compared to those related to the flow field, their effect on radionuclide transport has to be ascertained.

In the SKB **KBS-3** (1983) performance assessment study radionuclide transport through the geosphere was carried out in the framework of a one-dimensional dual-porosity medium model. The distance for nuclide migration into the porous rock was limited to 100 m. For the reference case a single value for all dissolved radionuclides for the effective diffusion coefficient was specified and also the rock porosity was species-independent. Surface sorption was not considered since it was assumed that this process has only a limited effect on the results.

The description of the radionuclide transport through the geosphere in **Project Gewähr** (Nagra, 1985) was also based on the dual-porosity medium model. Diffusion into a limited domain of porous rock occurred from either open parallel fractures or – alternatively – from tube-like veins. Fracture aperture and vein radius were both constant and, hence, idealised quantities. The thickness of the altered zone adjacent to the fractures or veins was limited to 1 mm for fracture flow in the aplite/pegmatite dykes and 50 cm in the case of vein flow in kakirites. Further diffusion of radionuclides into the intact crystalline rock was conservatively ignored. The sorption capacity in the matrix was considered to be nuclide concentration independent and constant. Due to the lack of site-specific data, generic data from regional investigations and literature studies were applied in the performance assessment. The values for the rock porosity and for the pore diffusion constant in the matrix D_p were constant and nuclide-independent. However, for a series of relevant nuclides individual K_d-values for bulk sorption were compiled. Channelling or diffusion into stagnant water was not taken into account due to the lack of suitable data.

In the Swedish **SKB 91** (1992) performance assessment, geosphere transport calculations were performed by mapping the dual-porosity medium model with a stream tube model for the water flow. One-dimensional (limited) [38] matrix diffusion was taken into account; channelling and a restricted contact area between fracture and rock matrix based on field observations were considered in order to limit the effects of matrix diffusion in a conservative way. Only one value for the matrix porosity and the effective matrix diffusion coefficient D_e was specified, but nuclide-dependent values for the (linear) bulk sorption were applied.

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[38] The fissure spacing was assumed to be 5 m (Elert et al. 1992, p. 24); hence, the zero-diffusive flux boundary in the matrix was at 2.5 m.

The Finnish performance assessment **TVO-92** (Vieno et al., 1992) was related to the disposal of spent fuel in crystalline bedrock at a depth of 500 m. Five different possible sites for a repository for high-level waste were investigated. Again, radionuclide transport was dealt with by applying a 1D dual-porosity medium with constant transport parameters. The model neglected dispersion according to the general principles of the safety analysis, where one only was interested in the fastest flow paths from the repository to the biosphere. Hence, matrix diffusion was considered as the only dispersing and, together with linear sorption, retarding mechanism for migrating solutes. The geometry of the flow channels was represented by a planar fracture and diffusion happened into a limited porous rock zone adjacent to the fracture. Although the authors' conclusion was that diffusion of radionuclides into pools of stagnant water may have a more significant role than matrix diffusion of weakly-sorbing nuclides, the effects of this process were neglected in the performance assessment due to conservatisms reasons. For the same reasons, the effects of fracture surface sorption and sorption of radionuclides on possible fracture infill material were omitted in the study, whereas bulk sorption of solutes was taken into account by individual K_d-values. The extent of the diffusion-accessible zone – the altered zone – was limited to 1 cm. However, for weakly sorbing radionuclides the virgin rock behind the altered zone was considered to be the main sink. Hence, a heterogeneous rock geometry was considered. Anion exclusion was taken into account by individual values for the porosity and diffusivity for negatively charged particles and non-anions for both zones. But no element-specific diffusivities were applied. Both, the migration behaviour of single nuclides as well as that of decay chains were computed. Further transport mechanisms, such as surface diffusion and channelling, were not accounted for in the study.

Comparing the Swiss **Kristallin-I** (Nagra, 1994) performance assessment with the former Gewähr study, not much had changed regarding geometries of the water-conducting features in the geosphere and the most important transport mechanisms. The geosphere transport calculations in Kristallin-I were again performed within the framework of the dual-porosity medium model. However, much more reliable data for the transport parameters had become available in the meantime and, hence, the study was less burdened by conservatism assumptions. For example, for the dose-relevant nuclide ^{135}Cs, new sorption data were available and in the transport calculations sorption in the rock matrix was described by a non-linear Freundlich sorption isotherm formalism. This resulted in an increased transit time due to increased retardation and the release rates to the biosphere were significantly reduced by dispersion and radioactive decay. For all the nuclides, one single value for the diffusivity was specified. The transport properties of the porous rock accessible for diffusing radionuclides were assumed to be uniform; hence, matrix heterogeneities were neglected. The extent of the altered wall rock was limited to ≈ 5 cm with a relatively high value of 5 % for its porosity. Channelling was taken into account by pessimistic values for the specific surface area for matrix diffusion. Further processes affecting matrix diffusion such as surface diffusion or diffusion into stagnant fracture water were conservatively omitted.

In preparation for the upcoming reviews of licence applications, the Swedish Nuclear Power Inspectorate, SKI, developed an independent performance assessment called **SKI Site-94** (1996). Geosphere transport was formulated within the framework of the one-dimensional dual-porosity medium model accounting for water flow in a planar fracture and limiting matrix diffusion to maximum depths of 5 and 10 cm, respectively including chain decay. One single value for the diffusivity for all radionuclides was

applied. Sorption processes both onto the fracture surfaces and onto inner surfaces of the bedrock matrix were described by linear sorption isotherms. Generally, only spatially invariant and time-independent parameters were considered. However, the water velocity and the flow-wetted surface of the fracture were subject to spatial variability and to uncertainty. For the calculations both quantities were varied by two orders of magnitude. Channelling was implicitly taken into account by a conservative value for the flow-wetted surface. But further mechanisms, such as mineral precipitation and dissolution, were – for conservatism reasons – neglected based on the very low radionuclide concentration in solution.
Regarding the performance of the geosphere as a barrier for mobile radionuclides in the groundwater it is mentioned in the study that "*… the efficiency of the geosphere as a barrier …* ***is critically sensitive to various uncertainties*** *that have been evaluated in the hydrogeological model … .*" However, such an alarming conclusion was based on an accumulation of very pessimistic assumptions for the geosphere transport calculations due to "*… the variability and uncertainty in the distribution of flow paths, …, and the lack of data on the detailed fracture characteristics, which affect the relation between Darcy velocity and flow wetted surface along these flow paths.*" (SITE-94, 1996, p. 630).

The Swedish **SR 97** (1999) performance assessment was based on the KBS-3 repository type and restricted to high-level radioactive waste only. The assessment was done for three potential sites called "Aberg", "Beberg" and "Ceberg". The geosphere transport calculations were performed in the frame of the one-dimensional dual-porosity medium model. The maximum penetration depth was limited to half the distance between two active migration pathways, which was assumed to be 2 m for sites Aberg and Beberg and 20 m for site Ceberg. Pessimistic values were an order of magnitude lower for all three sites. However, it was recognised that such distances are still much larger than the actual penetration depth of sorbing nuclides. Channelling was accounted for by conservative values for the flow-wetted surface. Anion exclusion was taken into account by considering two different porosity values for anions and cations. Based on laboratory studies investigating diffusion and sorption, individual values for the diffusivity and for the K_ds for a series of performance assessment relevant radionuclides were applied accounting implicitly also for surface diffusion effects. Uncertainties in the transport parameters were considered by sensitivity studies and pessimistic assumptions.

The Finnish performance assessment **TILA-99** (Vieno and Nordman, 1999), based on earlier safety assessments such as TVO-92 and TILA-96 considered matrix diffusion again in terms of the dual-porosity medium model. Solute diffusion into stagnant water in the fracture was recognised as potentially important but was nevertheless neglected. Conservatively surface diffusion also was omitted which would – when included – enhance the effects of matrix diffusion. For a series of selected radionuclides individual and pessimistic K_d-values for linear sorption in the bedrock matrix were specified for five different scenarios (Vieno and Nordman, 1999; p. 116ff). The maximum penetration depth for matrix diffusion was based on laboratory investigations and natural analogue studies concerning connected porosity and was conservatively limited to 10 cm. Anion exclusion, which reduces the effect of matrix diffusion and thus enhances the transport of anions through the transport domain, was taken into account by individual values for the matrix porosity and diffusivity for non-anions and anions. Channelling was implicitly included by choosing suitable values for a lumped parameter that is also dependent on the flow-wetted surface. According to the chosen parameter values, it turned out that the geosphere is a very efficient barrier for sorbing radionuclides, but a poor one for non-sorbing solutes such as Cl and I, since matrix diffusion provides only limited retardation for them. In a sensitivity and “a what-if”-study the effects of different key assumptions on radionuclide breakthrough were tested. With regard to matrix diffusion a two-layer system with different diffusion properties was considered. The first layer represented altered rock with a thickness of 1 cm; the second layer virgin rock (thickness 9 cm) with a value for the diffusivity lower by a factor of ten when compared with the altered rock zone.

* * *

From these short extractions from eight different performance assessments the following summary can be drawn:

- Regarding the modelling matrix diffusion, there is a very consistent picture when comparing the methodology of different waste organisations. All organisations accept the idea of matrix diffusion and conclude that matrix diffusion, together with bulk sorption, is the main retarding mechanisms in the far field, i.e., the geosphere. Based on that, the geosphere can, for some radionuclides, add significantly to the safety provided by the multi barrier system of a deep-lying repository.

  A high degree of consistency can also be noted when following the model evolution over the last two decades. No new process which would affect sustainably the barrier efficiency of the geosphere, could be recognised. Such a comfortable result is based on a wealth of laboratory and field investigations on various host rocks and on natural analogue studies performed in many countries. It lays – inter alia – the foundations for a general acceptance of, and confidence in, the long-term predictions of geosphere transport modelling.
- All organisations describe the geosphere transport of radionuclides in terms of the one-dimensional dual-porosity medium model applying time-invariant parameters. The diffusion-accessible rock matrix is treated as homogeneous and matrix diffusion is spatially limited to pessimistic values regarding the extent of the connected porosity [39]. In the last two decades a significant reduction in the values for the maximum penetration depth can be recognised in performance assessments. Such a reduction is due to the increased understanding of the extent of the connected pore space, of the fracture mineralogy and on geochemistry based on extensive studies in the laboratory and in the field. Hence, a more realistic description regarding rock geometries and processes found its way into contemporary performance assessments [40].

  Since values for the diffusivity for the safety relevant nuclides do not differ many orders of magnitude, one single value only was often specified for all the species in the base case. However, individual values for linear sorption K_d’s for

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[39] When compared to non- or weakly sorbing solutes the matrix diffusion distances for strongly sorbing radionuclides are sometimes in the order of millimetres only considering similar time spans for radionuclide transport and neglecting radioactive decay for simplicity reasons. Hence, the representation of such a porous rock matrix as a homogeneous porous medium with averaged values for the transport properties may be questioned for such small distances (see also Byegård et al., 2002).

[40] Other trends for more realistic values with reduced uncertainty ranges can be observed for example for solubility limits (Berner, 1995; and Berner, 2002). However, regarding the nuclide dependent sorption capacity in MX-80 bentonite a trend towards higher sorption values can be observed (see Stenhouse, 1995 and Bradbury and Baeyens, 2003b).

bulk sorption were compiled. Some organisations accounted for anion exclusion by species-dependent values for the porosity and diffusivity; channelling was considered by choosing pessimistic values for the flow-wetted surface.

- However, for conservatism reasons, and due to the lack of reliable data, diffusion into stagnant fracture water and surface diffusion both were mostly neglected in the performance assessments.
- Slow temporal evolutions of the repository domain resulting in time-dependencies of the transport properties and spatial variabilities were taken into account by quantitative studies of alternative, often very pessimistic, scenarios. However, in addition a few probabilistic studies were carried out in order to address temporal and spatial transport properties.
- Uncertainties associated with the values for the transport parameters were generally handled by making conservative assumptions and performing sensitivity analyses.

4.3.2 Conclusions and outlook

Matrix diffusion in fractured hard rocks has been recognised as an important phenomenon and is being investigated by researchers worldwide. The transport process as such is well understood and can be represented in terms of Fick's first and second law in contemporary transport models. Due to the natural variability of the transport parameter values, such as (connected) porosity, diffusivity, extent of the diffusion-accessible rock etc., site-specific data are needed for reliable predictions in performance assessments.

In general, matrix diffusion seems to be limited, due to chemical and physical interactions and to the limited half-life of the radionuclides, to depths of the order of a few centimetres only. However, there is evidence, especially from natural analogue studies, for greater depths for strongly altered rocks. But even for rather small values for the penetration depth, the porous rock zones adjacent to water-bearing fractures act as an efficient sink for mobile radionuclides causing a marked dilution and retardation of the solutes. Detailed studies have demonstrated that the diffusion-accessible rock is very often identical to zones adjacent to fractures with flowing groundwater being physico-chemically altered.

In performance assessments, matrix diffusion is considered within the framework of the dual-porosity medium model and, hence, in terms of a classical continuum theory based on mass balance considerations with averaged parameter values constant in time and space. The extent of the connected porosity is assumed to be limited according to values from site-specific investigations or due to pessimistic assumptions. Chemical reactions of the solutes and the immobile phase are reduced to linear or non-linear sorption processes which are formulated in terms of a simple isotherm formalism; accounting for radioactive decay and ingrowth in case of nuclide chains is common.

The so-called flow-wetted surface is a crucial quantity of the process and it is very difficult to determine reliable values that can be applied in performance assessments especially if the geometry of the water-conducting features is very complex. Although extensive experimental and modelling work has been done so far in order to shed light onto this problem, the flow-wetted surface will continue to be a key-issue in forthcoming investigations.

Closely linked to the problem of flow-wetted surface is channelling, where flow and solute transport are unevenly distributed in the fracture plane. There is a general acceptance in the existence of channelling and it is taken for granted that it can significantly reduce the available interface area fracture/rock for matrix diffusion. However, due to the lack of data this phenomenon is mostly considered in a conservative way in performance assessments.

Anion exclusion is a further mechanism which affects matrix diffusion because it results in species-dependent porosities and effective diffusivities. Compared to sedimentary rocks, such as clay, anion exclusion certainly plays a minor role because the widths of the void space are much larger than those in clayish materials. Nevertheless, this mechanism deserves further research in order to reduce conservatisms in performance assessments and to demonstrate to the authorities, as well as to the public, that an adequate system understanding can, in principle, be obtained.

Surface diffusion that could promote solute diffusion into the host rock is mostly neglected in performance assessments due to the scarcity of data available. However, future work on this issue is needed in order to solve open questions concerning the relevance of this process and, if necessary, to provide the data for forthcoming safety analyses.

Solute diffusion into zones with stagnant water in the fracture is also omitted in performance assessments due to the lack of utilisable data and for conservatism reasons.

In the last couple of years reactive transport modelling has developed strongly and significant progress has been made at the research level. Parallel to such a development more and more thermodynamic as well as kinetics data have become available. This is due to new experimental methods such as, e.g., EXAFS (Extended X-ray Absorption Fine Structure spectroscopy) and LIBD (Laser Induced Break Down spectroscopy), etc. which provide the basis for a deeper insight into these processes. On the modelling side there are many models and codes capable of handling coupled reactive transport processes. However, the implementation of these models and their results in performance assessments are presently not at a mature stage. There are several good reasons for this:

1) The link between coupled models and experimental work is rather weak because very little experimental data can be applied to predict the temporal evolution of a repository and its environment. In order to overcome such a discrepancy, thermodynamic data and kinetics rates at the spatial, temporal and relevant temperature scale of a repository have to be provided in the future.

2) On the model side, critical benchmarking exercises for these different models and codes are necessary. Also sophisticated and advanced experiments on the laboratory and field scale will be needed for indispensable model refinements and in order to increase their robustness and reliability for long-term predictions.

3) Reactive transport modelling consists of two different aspects: hydrodynamic processes resulting in the migration and spreading of solutes within the flowing groundwater, and geochemical reactions with other dissolved species, as well as with

the solid phases of the host rock. Both issues have to be considered continuously and simultaneously and are dependent on each other. Such combined transport and geochemical models lead to extremely complex numerical procedures that very often fail to converge. Hence, in these cases the online interaction of the modeller is required to prevent an extensive use of such models with thousands of individual runs in performance assessments.

Due to its complexity and the strong potential for more realistic, i.e. less conservative predictions, coupled transport reaction modelling may become a key activity to evaluate the performance of a geological repository for radioactive waste in the future. Regarding matrix diffusion, the coupling of transport and dissolution and precipitation of mineral phases is a major topic. Precipitation in the fracture can seal preferential flow paths for mobile radionuclides; mineral precipitation in the connected pores of the matrix, however, can have a detrimental effect on matrix diffusion.

There are no concerns about the fundamental time-dependencies of all the processes affecting geosphere transport. The current state of a potential site and its properties is just a snapshot in its evolution. Major driving forces for the time-dependencies are climate changes (future glaciations) and larger geological events such as, e.g., fault movements, erosion etc. However, reliable data are very difficult to deduce and are therefore very scarce and – moreover – burdened with large uncertainties. Matrix diffusion as a small-scale process, too, may be affected by temporal changes on various scales. Due to chemical gradients causing mineralogical changes at the surfaces, the amount of flow-wetted surface and the connected porosity in the matrix are affected. In addition, aperture and pore opening and closing may be caused by stress or erosion processes. In the performance assessment models – which are in fact steady-state models[41] – only averaged and time-independent values for the transport parameters are applied; the temporal evolution of the parameters and their uncertainties are taken into account by a series of alternative scenarios, pessimistic assumptions for the transport parameters and sensitivity studies. Exploring natural analogues for particular processes may give further information of the long-term evolution of a repository site.

In summary: No new mechanisms have been found so far which have the potential to considerably jeopardise, from a performance assessment point of view, the beneficial potential of matrix diffusion to efficiently dilute and retard mobile radionuclides in the geosphere. Such a conclusion is – nota bene – based on a wealth of experimental and theoretical investigations performed worldwide on various systems over the last twenty years.

4.4 RADIOACTIVE DECAY

Radionuclide decay is computationally straightforward to account for in performance assessment. For nuclides that are practical to consider as single nuclides without decay

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[41] The term "steady-state models" is related to possible changes of the properties of the geosphere, especially the flow field, through which the migration of radionuclides may occur and which are – as a rule – not taken into account explicitly in performance assessments. However, the time-dependent distribution of the nuclides in the flowing fracture water or within the stagnant water of the adjacent porous rock is always considered in the models.

products, decay is represented by a sink term in the material balance equations describing transport and radionuclide retardation. For nuclides participating in decay chains, calculations are more complex since the nuclides (with reasonably long half life) in the chain need to be considered simultaneously by a series of equations coupled through sink and source terms.

From statistical and physical arguments one may show that the rate by which a certain isotope is transformed is linearly proportional to its concentration

$$\frac{dc_i}{dt} = -\lambda_i c_i \tag{126}$$

in which c is the concentration of element i with unit [mole/m^3], t is time [s] and λ_i is the radioactive decay constant for element i [s^{-1}]. For the first element in a decay chain, the mother isotope, this means that the concentration as well as the activity decays with time according to $\frac{c}{C_0} = e^{-\lambda t}$. The time corresponding to half of the initial concentration (c/C_0 = 0.5), is termed the half-life. All conceivable information that one might need in assessing radioactive decay has been compiled in table form (e.g. Lederer and Shirley, 1978). For nuclides commonly associated with radioactive waste disposal, half-lives varies between decades (e.g. H-3, Sr-90) to billions of years (e.g. U-238).

Even though, the basic formulation, Equation (126), may look simple, some applications of radioactive decay in transport analyses for radionuclides become rather complicated. For a series of isotopes in a decay chain, we may obtain the concentration of an individual member of the chain by solving a system of equations defined by (126); i = 1,2,…N, and a zero initial, concentration $c_i(t{=}0) = 0$ except for the mother isotope that has an initial concentration $c_1(t{=}0){=}C_0$. The solution can be given by the Bateman equation (Bateman, 1910):

$$c_i = C_{i,0}\, e^{-\lambda_i t} + \sum_{k=1}^{i-1} \left[C_{k,0} \left(\prod_{j=1}^{i-1} \lambda_j \right) \left(\sum_{j=1}^{i} \frac{e^{-\lambda_j t}}{\prod_{\substack{n=1 \\ n \neq j}}^{i} (\lambda_n - \lambda_j)} \right) \right] \tag{127}$$

This solution has been recognised in transport analyses included in nuclear waste management programmes (e.g. Hedin, 2001). The activities and their evolution with time are converted from the molar concentrations. It is necessary to sum the contributions from the mother as well as the daughter isotopes, i.e. summing over all i.

In a situation in which transport is important, the solution procedure generally makes use of Laplace transforms. The first example of an analytical solution that described radionuclide transport in a rock fracture with account taken to advection and matrix diffusion as well as radioactive decay of the first element in the decay chain, is given by Neretnieks (1980). If the transport formulation includes both dispersion and matrix diffusion simultaneously, close-form solutions have not been derived even to the first member of a chain. If dispersion is neglected, however, it is possible to obtain an analytical solution for transport of an arbitrary member in a decay chain in fractured bedrock with account taken to advection and matrix diffusion (Gureghian, 1994). If matrix diffusion is disregarded, Burkholder and Rosinger (1980) derived closed-form solutions to the case with account taken to advection and dispersion.

4.5 COLLOIDS

Since the early 1990s, there has been a growing awareness of the potential importance of colloids to radionuclide migration and, as greater computing resources and more data have become available, PA models have increasingly included colloids in quantitative analyses of repository safety. A key question relates to whether radionuclide sorption onto colloids is reversible or irreversible. Rapid reversible sorption will result in lesser impacts than irreversible sorption. Irreversible or slow sorption leads to the transport behaviour being defined by the properties and transport of the colloids, rather than the solute. The degree to which mechanistic models of chemical transport may be included in PAs is limited by our understanding of chemical processes, data constraints, and ability to represent the heterogeneity of natural systems.

The treatment of colloids in recent PAs was reviewed by Wickham et al (2000). The review considered twelve PA programmes in nine countries. The main findings are summarised below, and in Table 12:

- All programmes include colloid formation and colloid transport in their Features, Events and Processes (FEP) list.
- PAs of repositories for spent nuclear fuel and HLW that contain a bentonite buffer do not consider the effect of colloids on the source term. These PAs assume that all colloids are filtered by the bentonite buffer and cannot escape from the near-field (e.g., AECL's Concept Assessment, SKB's SR-95 and SR 97, NAGRA's Kristallin-I). There is considerable uncertainty over the scale of colloid generation from waste, glass and bentonite degradation. However, the PAs all assume that quality control measures will ensure adequate emplacement of the buffer, and that the buffer will perform as expected. Failure of the bentonite buffer to filter colloids is not considered as an alternative scenario.
- PAs of waste repositories with no bentonite/clay buffer have to account for mobilisation of radionuclides from the waste by colloids (e.g. HMIP's Sellafield Assessment, US DOE's WIPP CCA and Yucca Mountain TSPA-VA). Experimental observations have been used to document higher effective solubilities associated with radionuclide binding to mineral fragments, microbes, and organic matter. The concentration of colloids that may form in the repository is a key uncertainty.
- Some programmes have deferred consideration of naturally-occurring colloid transport in PA until further research has been performed (e.g., SKI's SITE-94, POSIVA's TILA-96 and TILA-99, PROSA).
- Some programmes have not modelled colloid transport in the geosphere, and have relied instead on arguments that such transport processes will be of low consequence to the performance of the disposal system. Estimates of consequence were made on the basis of theoretical considerations (AECL's Concept Assessment) or on the basis of experimental observations (US DOE's WIPP CCA).
- No PA has included a comprehensive treatment of colloid transport using mechanistic modelling. However, the modelling approach used in NAGRA's Kristallin-I, in the US DOE's TSPA-VA, and the approach for the Culebra at the WIPP site (US DOE's WIPP CCA) could be used to simulate different colloid velocities and colloid host-rock interactions. Also, the colloid transport calcula-

tions made in support of HMIP's Sellafield Assessment, Nirex's Nirex 97 and Japan's H-12 were based on mechanistic models. All programmes that have modelled the transport of radionuclides attached to colloids have used similar one-dimensional transport equations.

- A key uncertainty in assessing the effects of colloid transport is the degree to which the adsorption of radionuclides on colloids is reversible. Most PAs that have considered transport of radionuclides sorbed to colloids assume reversible attachment (e.g. Japan's H-12; Nirex's Nirex 97). The Yucca Mountain TSPA-VA is the only PA in which both irreversible and reversible sorption of radionuclides to colloids was included in PA calculations, and dose comparisons made.
- Five PAs have shown the effects of colloid transport through the geosphere to be potentially significant (NAGRA's Kristallin-I, Japan's H-12, HMIP's Sellafield Assessment, Nirex's Nirex 97, and the US DOE's TSPA-VA for Yucca Mountain). However, in the case of NAGRA's Kristallin-I, the significance was only a percentage increase of an already very small dose and did not influence site safety. In the case of HMIP's Sellafield Assessment, the calculations depended critically on assumptions concerning colloid concentrations and the reversibility of radionuclide sorption on colloids, and indicated that colloids could cause a large increase in dose in a small number of simulations. In the US DOE's TSPA-VA, in a small number of simulations there is a one order of magnitude increase in dose in the 50,000 to 250,000 year period.

Table 12. Treatment of colloids in some recent PAs, after Wickham et al. (2000) and Bennett et al. (1999).

Country, Organisation, PA	Key features (host rock, waste type, hydrological regime)	Colloids included in the FEP list	PAs assuming colloid filtration by bentonite	PAs accounting for colloids in the radionuclide source term	PAs deferring consideration of colloid transport	PAs eliminating geosphere colloid transport	PAs indicating colloid transport is potentially significant
Belgium, ONDRAF/ NIRAS	Clay, HLW, Saturated	Yes	No information	No	Yes	-	-
Canada, AECL, EIS	Crystalline, Spent Fuel, Saturated	Yes	Yes	No	No	Yes	-
Finland, Posiva, TILA-96, TILA-99	Crystalline, Spent Fuel, Saturated	Yes	Yes	No	Yes	-	-
Japan, JNC, H-12	Crystalline, HLW, Saturated	Yes	Yes	Yes	No	No	Yes
Netherlands, OPLA, PROSA	Salt dome, HLW, Variable	Yes	No	No	Yes	-	-
Sweden, SKI, SITE-94	Crystalline, Spent Fuel, Saturated	Yes	Yes	No	Yes	-	-
Sweden, SKB, SR-95, SR 97 SFL 3-5	Crystalline, Spent Fuel, Saturated	Yes	Yes	No	No	Yes	-
Switzerland, NAGRA, Kristallin-I	Crystalline, HLW, Saturated	Yes	Yes	Yes	No	No	Yes
UK, HMIP, Sellafield Assessment	Crystalline, LLW / ILW, Saturated	Yes	No	Yes	No	No	Yes
UK, Nirex, Nirex 97	Crystalline, LLW / ILW, Saturated	Yes	No	Yes	No	No	Yes
USA, DOE, WIPP	Bedded Salt, TRU, Variable	Yes	No	Yes	No	Yes	-
USA, DOE, Yucca Mountain TSPA-VA	Unsaturated ash-flow tuffs	Yes	No	Yes	No	No	Yes

In responses to the RETROCK questionnaire by PA programmes, there is uncertainty regarding the significance of colloids in assessing repository safety. Some consider that colloids may have either beneficial or detrimental effects. In particular, effects would be beneficial if radionuclides become irreversibly bound to colloids that are later immobilised, e.g. by filtration. The effects would be detrimental if radionuclide-bearing colloids remain mobile, and are excluded from matrix pores.

Specific issues of fundamental understanding related to colloids identified by one or more respondents were:

- Colloid production, including the possible generation of colloids from biofilms present on the crushed rock that may be used as tunnel backfill,
- Colloid stability and filtration during transport through fractured rocks,
- The effects of channelling on colloid-facilitated radionuclide transport,
- The nature of sorption processes of radionuclides on colloids.
- The presence of gas bubbles with respect to colloid-facilitated radionuclide transport.

Future research is likely to focus on these and other areas of uncertainty. Site-specific measurement of the concentration of colloids in groundwater samples will continue to be made in order to underpin the trends observed in the data of Figure 30. It is not easy to sample deep groundwaters without disturbing the natural colloid concentrations, for example, by generation of additional colloids during pumping. Therefore sampling and measurement have to be made with great care. Data from natural or anthropogenic analogues may be useful in demonstrating the extent to which radionuclides may be transported by colloids. Field migration experiments in URLs, and column experiments using granite with natural fractures, are ongoing or planned.

4.6 PRECIPITATION AND DISSOLUTION

Precipitation and coprecipitation phenomena are not currently taken into account in performance assessment exercises. The application of precipitation in PA requires a precise knowledge of the geochemistry of the system under consideration and the identification of the possible secondary phases that may precipitate. Notice that the identification of these potential secondary phases is not in many cases an easy task. For instance, the CSH and CASH phases that would precipitate in the context of a hyper-alkaline plume are themselves complex solid solutions and also, especially at low temperatures, poorly crystalline. Besides, a large amount of experimental work under a range of appropriate chemical conditions would be necessary to obtain, at least, phenomenological partition coefficients for the relevant radionuclides.

Although precipitation and coprecipitation are not considered explicitly in PA, the use of solubility limits for many radionuclides is common practice. These solubility limits are the maximum expected concentrations under a given set of conditions (e.g. near-field or far-field, or type of repository and host rock) and are based on the equilibrium between the solution and selected solid phases containing the radionuclide as a major component. Critical factors affecting these solubility limits are parameters such as pCO_2, pH, Eh and temperature. Another critical issue in the applicability of these solubility limits is the quality and availability of thermodynamic data for the relevant chemical species.

Precipitation and coprecipitation are considered as a sink for radionuclides and the omission of these processes in PA exercises is currently assumed to be conservative. However, precipitates could become a source of radionuclides in the future if hydrological or geochemical conditions were to change. For instance, the dissolution of uranophane formed in earlier times in the unsaturated zone may be a source of uranium in Palmottu (Blomqvist et al., 2001). Precipitation/dissolution should be included in long-term simulations when changing conditions are expected at the boundaries of the system.

Coprecipitation phenomena will be especially important in systems with a high degree of reactivity, i.e., when a significant amount of formation of secondary phases takes place. Therefore, besides the studies mentioned above, it would be very useful to study coprecipitation processes in the context of hyperalkaline plumes caused by the degradation of cement, since large amounts of secondary minerals (calcite, CSH and CASH phases, zeolites, phyllosilicates) are expected to precipitate, under those conditions, at or close to the interface between near field and far field. Additionally, the precipitation of secondary phases may lead to important changes in permeabilities and flow fields (Read et al., 2001; Soler and Mäder, 2002; Soler, 2003).

4.7 MICROBIOLOGICALLY MEDIATED PROCESSES

Microbial processes are generally not included in PA in a quantitative sense, in comparison with how, for example, colloids, sorption and geochemistry are treated. Microbial processes do in general add “new” concepts. Life processes obey the rules of chemistry, thermodynamics, and movement just as any process. The difference is that microbial processes add a metabolic, and therefore, catalytic dimension that is complicated to predict and sometimes difficult to understand. Modelling life processes is consequently more difficult than modelling most non-life processes due to the multi-component nature of the former.

Microbial processes should not be ignored in PAs. Two processes are judged particularly important (Table 9):

- Microbial production of chelating compounds in the repository environment; and
- the scavenging of intruding oxygen. This was for a long time expected to be solely an inorganic process. New results, reviewed in Section 3.3, have indicated the opposite to be true. Microbial processes will thus be an additional important oxygen scavenging process in repository environments.

Those two examples demonstrate that overlooking microbial processes may result in models and safety assessments that do not reflect the true situation in future radioactive waste repositories. Conservative assumptions are commonly used to overcome such problems. Therefore, our understanding of geosphere retention phenomena in the context of long-term safety of radioactive waste disposal will benefit from making optimal use of available knowledge on microbial processes in order to reduce such conservatism in future safety assessments.

4.8 GAS MEDIATED TRANSPORT

In addition to some of the original, published performance assessment studies, the present section is based on the work presented in the EC/NEA status report “Gas migration and two-phase flow through engineered and geological barriers for a deep repository for radioactive waste", Rodwell et al. (1999b).

A summary of gas migration in performance assessment of repositories in fractured crystalline rocks is presented in a list of five items:

- Gas escape through the far field at the gas generation rates predicted has not generally been considered a problem, even for low- and intermediate-level wastes, for which the gas generation rates are highest. No significant overpressurisations resulting from gas generation have been predicted in the reviewed assessments.
- A caveat that needs to be made about the above assertion is that there is presently considerable uncertainty about the saturation functions that should be used in calculations of gas migration through water-saturated fracture networks.
- The gas entry pressures have been estimated (when this has been considered) as generally too low to cause significant gas cushion development and expulsion of contaminated water from the vaults.
- With the exception of the above gas-cushion effect, the possible effect of gas migration on water-borne contaminant transport has not been considered in any published assessment.
- No performance assessment has been able to draw upon either site specific or generic large-scale experimental data as justification of the gas migration predictions made.

This means that contaminant transport by colloids attaching to gas bubbles has not been addressed in any of the reviewed assessments.

When steel canisters are used it is conceivable that hydrogen generated by corrosion could carry colloids very quickly straight up. Natural gases in the water taken up at depth could do the same as gas bubbles when pressure decreases in up-moving water.

4.9 OFF-DIAGONAL PROCESSES

Off-diagonal phenomena are not explicitly taken into account in performance assessment. However, it seems that the effects of chemical osmosis and hyperfiltration are fairly minor. Soler (1999, 2001) estimated the effects of these off-diagonal transport phenomena in the Opalinus Clay at the Mont Terri underground rock laboratory. The Opalinus Clay is a compacted clay formation, and as such, should show some of the characteristics of a semipermeable membrane. Although the osmotic efficiency of the formation is measurable (Harrington and Horseman, 1999), its value is small (about 0.1). And even if the osmotic efficiency were larger, the small hydraulic conductivity would mean that the overall osmotic permeability would still be small and very steep salinity gradients would be required to cause any major chemical osmotic fluxes. Even under the significant chemical gradients at Mont Terri (salinity gradients of the order of 200 mg/l/m), the effects of chemical osmosis and hyperfiltration on the transport of solutes are only minor, if not negligible.

On the other hand, chemical osmosis could play a role in the distribution of water pressures in a formation, e.g., as a cause of hydraulic overpressures (Neuzil, 2000). Therefore, chemical osmosis could be relevant when studying hydraulic regimes in site characterization in those cases where marked salinity gradients between formations exist.

5 SUMMARY

This report considers the present-day understanding and approaches to take into account retention and transport processes in the performance assessment (PA) models used in the evaluation of the long-term safety of deep geological repositories for radioactive waste. It is a product of Work Package 2 in the RETROCK Concerted Action, a part of EURATOM's research and training programme.

The environment in question is saturated sparsely fractured rock in the repository far-field, where the fracture network provides flowpaths for groundwater transporting radionuclides away from a repository. Fractures exist from microscopic to kilometre scales in complex configurations. They only make up a very small fraction of the total volume, whereas the pore system in the rock matrix between the fractures includes the majority of the groundwater and offers a large solid-liquid interface area. The radionuclides in various chemical forms interact physically and chemically with other matter in water, fracture surfaces, fracture infills and the rock matrix adjacent to the fractures. These interactions typically result in a significant retardation, and decay, of radionuclides compared to the velocity of the groundwater.

The PA models usually take into account retention phenomena using simplified concepts. They are complemented by a large variety of more detailed and realistic process-specific models that can be used to support the choice of data for PA models, as well as a number of specific arguments made in safety cases. While the fundamental understanding, the conceptualisations of the phenomena, the models and the computing resources develop, the extensive data requirements often become a most restrictive factor to the use of a model. The difficulties in obtaining data tend to hinder the utilisation of the most realistic mechanistic models, but major challenges are also encountered in obtaining relevant and defensible data for the principal simplified PA models.

All processes discussed in this report were mentioned in the responses to a questionnaire that was used in Work Package 1 to map the views and the ways to handle the topic in several published safety cases (Nagra, 2002b).

In the following, the current understanding and modelling practices of each retention and transport process are summarized in two categories: 1) the processes commonly modelled in PAs, and 2) the processes not represented explicitly in PAs.

5.1 PROCESSES COMMONLY MODELLED IN PA’S

The phenomena in the focus of the report are related to the flow field, sorption, and matrix diffusion. They together with radioactive decay provide the key terms to the transport equations of the PA models.

5.1.1 Influence of flow field on transport and retention

There is general consensus on the main processes controlling the flow field. It also is agreed that flow and bedrock structures affect retention together with the material properties. However, there are considerable differences in the conceptualisation and modelling approaches between some PAs. In addition, the possibilities to investigate geometrically complex flow paths in detail are highly limited. This all can lead to significant variation in the final results.

The transport resistance, the water residence time distribution and the water flow rate distribution are important flow related entities for radionuclide transport. However, in PA applications the matrix interaction on the residence time distribution of a tracer is commonly so strong that it totally dominates over the water residence time. The transport resistance is a central parameter that represents the hydrodynamic control on retention and has been in the focus of the project. The transport resistance is also called "flow wetted surface area per flow rate", denoted by *FWS/q* (an undividable quantity), *F* or beta (β). Its local distributions can be determined in field investigations using tracer tests, but the upscaling of the results to larger scales is not trivial.

Most of the participating organisations have evaluated flow and transport in their PAs using separate models, with flow models providing input parameters for transport models, but also integrated 3-D flow and transport modelling has been applied.

The report discusses the following transport modelling concepts for the flow paths: 1) continuous models with one-dimensional pathways encompassing both fractures and rock matrix, and 2) discrete fracture models where the fractures are explicitly or stochastically described and pathlines for the radionuclide transport are generated along the network of fractures or channels. The continuous models can assume homogeneous rock properties, with the possibility to vary properties between large-scale zones as in the Equivalent Porous Media model, or include variations in a stochastic way as in the Stochastic Continuum model. In the discrete fracture network models the individual flow paths are described physically in a as correct manner as possible. The individual fractures were earlier described as homogeneous planes, but in more realistic models heterogeneity is included. The trajectory approach, an application of random walks, is not described in the report, although it has been dealt with in RETROCK. In all approaches advection is the main transport process, combined with retention to include interaction with the rock matrix. In modelling the transport some form of the advection-dispersion equation is applied.

The possible existence of fast flow channels with small interaction area with the rock is often speculated. Such channels may exist on a local scale, but it is unlikely that they extend over such long distances that they constitute important transport pathways on the scale of interest for a PA. Solute diffusion into stagnant water in the fracture has been recognised to be potentially important for weakly sorbing radionuclides but has nevertheless been conservatively neglected so far.

5.1.2 Water chemistry and sorption

The water chemistry in the geosphere has a direct influence on many factors for retention, such as radionuclide speciation, redox conditions, sorption, precipitation and dissolution, conditions for microbial growth, formation and stability of colloids, and generation of gases. Furthermore, it indirectly affects transport and retention by its influence on the formation of fracture coatings and infills which in turn affects the flow, and the clogging of pores that may affect the matrix diffusion. Understanding the water chemistry of a site is important also for the evaluation of hydrogeology, its history and future evolution. The report discusses some aspects of aqueous complexation and redox reactions.

Sorption is basically considered as a reversible process of attachment of dissolved species to surfaces. In the basic empirical models the partitioning of solute between solution and adsorbed solute is described by coefficients derived from experiments. These models use linear equilibrium (constant K_d model), Freundlich isotherm or Langmuir isotherm. In another group of models, Thermodynamic Sorption Models (TSM), sorption reactions are represented by thermodynamic formulations, including surface complexation and ion-exchange.

Some minerals commonly filling fractures exhibit electrically charged surfaces with ionisable functional groups that are responsible for chemical reactions between the aqueous species and specific surface sites. Surface complexation models take into account such surface reactions applying experimentally derived parameters describing the solid phase, the reactions with ions and complexes in the solution and a number of parameters describing the electrical double layer. Competition between the different aqueous species for the finite number of surface sites is taken into account. The extensive need of parameters hinders the use of complexation models as parts of PA models, but they can be utilised as supporting tools.

Cation exchange describes a process where an exchangeable cation located in an intracrystalline site or surface site of a mineral is exchanged with a cation from the solution. Because the capture of a cation from the solution is always coupled with the release of a cation from the surface, an ‘equilibrium constant’ can be defined and used in the ion-exchange modelling. The ability of a mineral to sorb through an ion-exchange mechanism is commonly expressed as the cation exchange capacity.

Typically, sorption is only modelled in the rock matrix, where the available surface area is overwhelming compared to the fracture surfaces or fracture infills. In all the examined PA exercises the sorption of radionuclides is described with linear equilibrium sorption (K_d model) or with the Freundlich sorption isotherm formalism, which means considerable simplification and neglecting of chemical interactions. It does not take into account the chemistry of pore solutions and their variability, the competition between the sorption sites or between the species, or the non-ideal behaviour of the solutes in solutions and sorbed species. The sorption coefficients or K_d values are empirically derived for conditions as similar as possible to the conditions prevailing at the site. TSMs can be used to add confidence to the selection of K_d's.

Despite its limitations the K_d approach can be regarded as a valuable PA tool. A step towards more realism is the use of intermediary approaches to account for changes in groundwater chemistry or for regions of different host rock types. This can be done by using different K_d values for different sections of migration routes and different periods of time.

5.1.3 Matrix diffusion

Matrix diffusion is a physical process by which solutes – being transported in the flowing groundwater within fractures of a porous medium – are transferred to the stagnant water in the pores of the rock matrix adjacent to these fractures. Dissolved radionuclides have access to pore water by molecular diffusion. In the case of sorbing radionuclides the accessible surface area may be increased by orders of magnitudes when compared to the accessible surface in fractures. Matrix diffusion is considered as a very important retention process.

The fundamental understanding of the process is deemed to be relatively good and convincing evidence of its existence has been found through tracer experiments in laboratories and in-situ and through natural analogues. The conceptual and mathematical treatment of matrix diffusion as a Fickian process is highly consistent in the organisations contributing to RETROCK. Perhaps the uncertainties mostly pertain to the empirical data.

Matrix diffusion depends in a complex way on various properties, and the interpretation of field experiments in particular is difficult, including the distinction between different phenomena. The principal material properties needed for the modelling are the rock porosity, the diffusion coefficient of the solute in water and the formation factor for describing the effect of the geometry of the pore system. The efficiency of matrix diffusion also is largely controlled by the above mentioned entity "flow wetted surface area (the surface through which diffusion can take place) per flow rate".

The views on the extent of the connected pore space vary. For strongly sorbing radionuclides, an additional amount of rock available has a small effect on their release rates from the geosphere, since only a few millimetres of matrix is needed for significant retention to occur. For weakly or non-sorbing radionuclides greater penetration depths are more meaningful, although for the latter the modelling of matrix diffusion suggests only marginal retardation. A related question is the long-term stability of the matrix pores, since their volume and connectivity might be reduced by pore clogging caused by precipitating materials.

Matrix diffusion is incorporated in all the examined PAs in the dual-porosity medium transport models. For the non-sorbing radionuclides it even is the only retarding mechanism regarded. Since the diffusivities for the safety relevant nuclides do not necessarily differ very much, only a common single parameter value is often specified for all the species in the base case of an analysis. Sometimes species-specific values for the porosity and diffusivity are used in order to take anion exclusion into account. In regard to the hydrodynamic control, the determination of the *FWS/q* is a key difficulty.

The theoretical basis of matrix diffusion, special cases and data acquisition are presented extensively in the report.

5.1.4 Radioactive decay

A prominent feature of radioactive waste is the radioactive decay, which gradually decreases the radiotoxicity of the waste with time. The phenomenon is well understood for the PA purposes and the data uncertainties are minor. For radionuclides that are practical to consider as single nuclides without decay products, decay is represented by a simple sink term in the transport equations. For the nuclides in decay chains, transport calculations become more complex since the nuclides (with reasonably long half life) in the chain need to be considered simultaneously by a series of equations coupled through sink and source terms. For simultaneous modelling of matrix diffusion and dispersion, close-form solutions have not been derived.

5.2 PROCESSES NOT REPRESENTED EXPLICITLY IN PA’S

The following processes are usually not represented explicitly in the PA models: colloids, precipitation/coprecipitation, microbial activity, gas-mediated transport, and off-diagonal Onsager processes. Their influence may be considered indirectly through parameter variation, their omission may be justified by simplified scoping calculations, or they are simply relevant for certain repository concepts only.

5.2.1 Precipitation and coprecipitation

Precipitation can be considered as a further step of surface sorption. The aqueous complexes are incorporated to the surface of a solid substrate by losing the hydration water dipoles and establishing chemical bonds with atoms of the crystalline structure of the solid. This mechanism leads to the accretion of the solid structure.

Coprecipitation is the removal of a trace element from a solution and its incorporation, as a minor component, into a secondary phase formed from the major components of the system. The result is that the remaining concentration of the trace element in solution is lower than the one calculated assuming equilibrium with respect to phases containing the same trace element as a major component, i.e. lower than the concentration calculated using solubility limits.

Dissolution can be regarded as reverse precipitation and coprecipitation. Dissolution starts when a solution in contact with a mineral becomes undersaturated with respect to that mineral.

Precipitation and coprecipitation can act as sinks for radionuclides. They are currently not taken into account in PAs, which is assumed to be conservative. However, precipitates could become sources of radionuclides along with changes in hydrological or geochemical conditions favourable for dissolution, or they could cause pore clogging as mentioned in the context of matrix diffusion.

The modelling of precipitation in a PA would require precise knowledge of the geochemistry of the system under consideration and the identification of the possible secondary phases that may precipitate. Thermodynamic chemical equilibria can be readily calculated if the data are available, but an equilibrium only gives the minimum energy of the system. Kinetics would offer a way to analyse the chemical evolution and allow the incorporation of reaction rates, i.e. the rate at which reactions proceed. However, there are very few data on precipitation kinetics for relevant systems. For example many parameters are required to model the highly non-linear nucleation that is thought as the first stage of precipitation. Before the inclusion of detailed precipitation kinetics in the modelling becomes achievable, one can use experimental rate laws.

The treatment of coprecipitation in equilibrium is based on the thermodynamics of solid solutions and the law of mass action. However, in most cases the lack of knowledge of the detailed chemistry of the system has led to the use of phenomenological partition coefficients. These describe the ratio of the molar fractions of the solid end-members to the total concentrations of solute, but their applicability is restricted to the range of conditions under which the experimental work has been performed. An alternative way to model coprecipitation is by means of conditional solubility constants. This concept is based on the assumption that the activity of the minor component in a binary solid solution is equal to its molar fraction in the bulk solid. Coprecipitation will likely play an important role, when significant amounts of secondary phases will be formed. The modelling approaches are mostly empirical, and work concerning the thermodynamics of solid solution formation and the influence of nucleation and reaction rates on coprecipitation phenomena would be needed for a better understanding and description of the processes.

5.2.2 Colloids

Colloids are particles in the size range from 1 nm to 1 µm that can remain suspended in water. In disposal systems, natural colloids and waste- or repository-derived colloids may enhance the migration of radionuclides so that nuclides become fixed to a mobile solid phase, which is transported close to the velocity of the groundwater.

Colloids can be of both organic and inorganic origin and be formed in numerous processes like condensation of hydrolysed ions of radionuclides, alteration or physical erosion of minerals, direct precipitation of minerals in the groundwater, degradation of organic material, generation of organic macromolecules, or forming of hydrophilic coatings on the surfaces of microbes. Microbes may behave as relatively large colloids, too.

In natural groundwater the colloid concentrations have been found to be very low, typically ranging from 0.1 ng/ml to 100 µg/ml, which has been used as an argument to neglect the colloid-facilitated transport in PAs in the case of naturally occurring colloids. Depending on the repository concepts and the construction methods, colloids can be formed in the repository near-field and migrate to the far-field, where they would add to the natural colloid population. On the other hand, the colloid concentrations are decreased by the decomposition of colloids.

The attachment of radionuclides to colloids is diverse. In process models it is usual to handle sorption of nuclides on colloid particles and to assume chemical equilibrium, which does not well represent in this kind of dynamic systems. Only few data are available with which to quantify kinetically controlled sorption processes. Thus it is often only possible to assume that the net rate of sorption of radionuclides on colloids will lie in between the two extreme cases: reversible (equilibrium) sorption and instantaneous irreversible sorption. For saturated systems, it is conservative to assume that radionuclides are irreversibly bound to colloids.

Models for colloidal transport need to deal with questions such as colloid formation, aggregation and decomposition, colloid-radionuclide interaction, colloid interaction with fractures and hydrodynamic effects on colloid transport. Colloids themselves are exposed to retention in the geosphere e.g. owing to mechanical filtration and electrostatic effects.

Mechanistic models aiming at realism can include diffusion-limited aggregation, and exchange of radionuclides between dissolved, mobile sorbed and immobile sorbed phases, governed by reaction rate constants. They are not used directly in PA transport modelling, due mainly to their high data requirements, and the fact that, in their current form, they are suitable only for simple systems. Studies to enhance mechanistic models, and to improve the realism of PA models with respect to colloid-related processes, are currently underway.

5.2.3 Microbiologically mediated processes

Microbes are characterised by their almost infinite ability to bio-degrade and bio-synthesize naturally occurring compounds in the environment. Microbial reactions control the chemical composition of many environments, including groundwater.

Microbes occur either as unattached, planktonic cells passively floating or actively swimming in the free water phase, or are attached to solid surfaces. Any solid surface adjacent the water phase with living microbes is predestined to develop biofilms. If growth conditions are appropriate, microbes start to grow and divide.

The processes can have a direct or indirect effect on radionuclide transport. A direct effect involves a contact between a microbe and a nuclide, resulting in a change in speciation. Indirect effect is caused by environmental changes, generated by microbial metabolism. Finally, all microbial processes except bio-sorption require an active, energy driven metabolism. Therefore, their modelling must include microbial energy turnover rates.

Microbial processes can significantly alter the mobility of radionuclides in the environment. At a general level, microbes in biofilms act immobilising, except those who produce complexing agents. On the other side, radionuclides can be mobilised by planktonic cells that bio-sorb or bio-accumulate radionuclides.

As for the immobilisation mechanisms, in bio-sorption radionuclides attach to the surfaces of microbe cells and in bio-accumulation nuclides become actively uptaken by microbes. Microbial energy metabolism has a significant ability to lower the redox potential in the environment and thus plays a substantial role in O_2 reduction in granitic media. Further, some of the reduced electron acceptors may result in bio-mineralisation processes that act as radionuclide traps. Microbes can catalyse the direct transformation of radionuclides to less soluble forms via metabolic processes.

The potential for mobilisation of radionuclides due to the chelating effect of bacterially produced ligands is unknown and thus a possible concern in PAs. The effect has been observed in preliminary experiments and is being further studied.

The database from laboratory research on the microbial processes described in the report is extensive, but sparse from in-situ experiments under repository conditions.

Microbial processes are generally not included in PAs in a quantitative sense. They obey the rules of chemistry, thermodynamics, and hydrodynamics just as any process. The difference is that microbial processes add a metabolic, catalytic dimension that is complicated to predict. Two particularly important processes to be considered in the research are the above mentioned microbial production of chelating compounds and the scavenging of oxygen intruding into repository environments.

5.2.4 Gas mediated transport

Gas in the far-field could affect groundwater flow paths and flow rates, cause rapid transport through attachment of colloids at gas-water interfaces or through the release of radioactive gases. Gas-mediated migration can be an important issue only, when the gas release and the radionuclide release overlap.

The main mechanisms by which gas could be generated in repositories are corrosion, radiolysis and microbial degradation. The effect of gas strongly depends on its amount. Small volumes can be dissolved in the groundwater but once the solubility limit is exceeded a free gas-phase is formed, either as a continuous phase or as gas bubbles. The amounts will vary substantially between different repository concepts, depending on the type of waste, the type of packages and the repository design. Disregarding dissolved oxygen carried by glacial melt waters, the generation of gases will constitute no problem, if they can be transported dissolved in the groundwater, either by diffusion or by advection.

The dominant conceptual model for the migration of a free gas phase through water saturated fractured crystalline rock is that gas will advance by displacing water in the fracture network. The displacement in combination with a pressure build-up will continue until the capillary pressure in the network is overcome and a continuous flow path of gas reaches the ground surface. During this phase, the displacement of water may have forced contaminated water through the geosphere. Next the groundwater can re-enter the gas-occupied pathways. The mechanism can be repeated as a cyclic process.

A flow of gas bubbles could induce groundwater flow by entrainment of water in the bubble stream. The effectiveness of the process is yet unclear. Few data exist to quantify the sorption of colloids at the gas-water interface and thus the possibility for transport of radionuclides attached to colloids.

Two-phase flow of gas and water in a fractured medium can be treated by extending the hydrological models for one-phase (water) flow. However, the capillary characteristics of the flow paths are very sensitive to the dimensions and shape of the actual fractures, and thus site-specific and very difficult to measure. A two-phase flow continuum model needs a relationship between saturation and relative permeability and a corresponding relationship for capillary pressure. Obtaining of this data is difficult. In discrete fracture models, based on either single or networked fractures, the capillary characteristics can be derived from assumed fracture properties. The required tracking of the gas-water interface makes the network applications computationally demanding.

As for radionuclides in the gas-phase, advanced transport modelling has been developed especially for estimating the behaviour of radon.

In PAs the effects of gas have been evaluated usually by a combination of bounding estimates and simple calculations.

5.2.5 ‘Off-diagonal’ processes

In the so-called off-diagonal Onsager processes chemical, thermal, hydraulic or electrical potential gradients provide the driving forces for the fluxes of solute, thermal energy, fluid or electrical current. The effects of osmosis and hyperfiltration (caused by ion exclusion) have been studied in some safety cases, and the results suggest that these processes are not relevant in the repository far-field.

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APPENDIX 1

SOLUTION OF THE EQUATIONS FOR FLOW IN A FRACTURE WITH MATRIX INTERACTION AND WITH VARIABLE PROPERTIES ALONG THE FLOW PATH

This note addresses the question of how to account for variable diffusion and sorption properties along a flow path with arbitrarily varying flow dimensions when a solute can diffuse in and out of the rock matrix over the Flow Wetted Surface, FWS, the water contacts underway. It will be shown that if one follows a water package in streamtube, i.e. a constant flow rate *q*, a very simple solution is obtained in which the matrix interaction is simply the integral along the flow path of a group of parameters. This implies that the RTD of a solute at the outlet of the flow path can be obtained by integrating, or summing two parameter groups along the flow path. One group gives the volume of the pathway, which in turn determines the water residence for the known flowrate. The other group determines the matrix interaction parameter, which accounts for how strongly the matrix diffusion influences the concentration of the solute.

This implies that in a fracture network it is sufficient to know the flowrate, size, aperture and matrix interaction parameter of each fracture the fluid package passes to determine the necessary parameters.

Definition of problem and solution

Notation is found in APPENDIX 2.

The equation describing transport of a solute with advective flow in a stream and matrix diffusion of the solute can be written

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} = a_w D_e \frac{\partial c_p}{\partial z}(z=0) \qquad \text{for x>0 and t>0} \qquad (128)$$

$$\frac{\partial c_p}{\partial t} = D_a \frac{\partial^2 c_p}{\partial z^2} \qquad \text{for all x>0 and z>= 0} \qquad (129)$$

It is assumed that a_w, D_a, D_e and u depend on x but not on t. There is total mixing perpendicular to the flow direction but no mixing in the flow direction.

Introduce a new variable into (129)

$$Z = z\frac{1}{\sqrt{D_a}} \qquad (130)$$

(129) becomes

$$\frac{\partial c_p}{\partial t} = \frac{\partial^2 c_p}{\partial Z^2} \qquad (131)$$

and (128) becomes

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} = \frac{a_w D_e}{\sqrt{D_a}}\frac{\partial c_p}{\partial Z}\ (Z=0) \qquad (132)$$

Introduce new variables θ to follow the stream with its velocity *u(x)* and a length variable *X*. Noting that we can chose to follow a stream with constant flowrate *q* in a streamtube and that $a_w/u=2W/q$, *X* can be written as the RHS of (133)

$$X = \int_0^x \frac{a_w D_e \, dx'}{\sqrt{D_a} \; u} \;=\; \frac{2}{q} \int_0^x w(x') \, \frac{D_e}{\sqrt{D_a}} \, dx' \tag{133}$$

$$dX = \frac{2wD_e dx}{\sqrt{D_a} q} \tag{134}$$

Introduce the water residence time to travel from 0 to x

$$t_w = \int_0^x \frac{dx'}{u} \tag{135}$$

and a new time variable

$$\theta = t - t_w \tag{136}$$

With these transformed variables (132) and (131) become

$$\frac{\partial c}{\partial X} = \frac{\partial c_p}{\partial Z}(z = 0) \tag{137}$$

$$\frac{\partial c_p}{\partial \theta} = \frac{\partial^2 c_p}{\partial Z^2} \tag{138}$$

The Laplace transforms of (137) and (138) are

$$\frac{\partial \tilde{c}}{\partial X} = \frac{\partial \tilde{c}_p}{\partial Z}(z = 0) \tag{139}$$

$$\frac{\partial^2 \tilde{c}_p}{\partial Z^2} = p\tilde{c}_p \tag{140}$$

(140) is solved with boundary conditions $\tilde{c}_p(z = 0) = \tilde{c}$ and $\tilde{c}_p(Z -> 0) = 0$ from which

$$\frac{\partial \tilde{c}_p}{\partial Z}(z = 0) = -\tilde{c}\sqrt{p} \tag{141}$$

and

$$\frac{\partial \tilde{c}}{\partial X} = -\tilde{c}\sqrt{p} \tag{142}$$

The solution to (142) with the BC that $c = c_o$ at x = 0. This gives the integration constant = c_o /p, and the solution is

$$\frac{\tilde{c}}{c_o} = \frac{e^{-\sqrt{p}X}}{p} \tag{143}$$

The inverse Laplace transform of (143) gives

$$\frac{c}{c_o} \;=\; \operatorname{erfc}\left(\frac{X}{2(\theta)^{1/2}}\right) = \operatorname{erfc}\left(\frac{X}{2(t - t_w)^{1/2}}\right) \tag{144}$$

For a Dirac pulse the solution is

$$c\,q \;=\; \dot{m} \;=\; \frac{M \cdot X}{2\sqrt{\pi}}\frac{e^{\frac{X^2}{4(\theta\;)}}}{(\theta)^{3/2}} \;=\; \frac{M \cdot X}{2\sqrt{\pi}}\frac{e^{\frac{X^2}{4(t-t_w)}}}{(t-t_w)^{3/2}} \tag{145}$$

where M is the injected mass. For later reference introduce

$$G \;=\; X \cdot q \;=\; 2\int_0^x MPG(x')\,w(x')\,dx' = 2\int_0^x w(x')\frac{D_e}{\sqrt{D_a}}dx' \tag{146}$$

$MPG = \dfrac{D_e}{\sqrt{D_a}} \cong \sqrt{D_e K}$ is called the Materials Property Group. K is the volumetric sorption coefficient $K = K_d\,\rho$

Thus only t_w and X are needed to use Equations (144) and (145). In a fracture network where one can follow a path by e.g. particle tracking the contribution to the residence time t_w in each fracture the particle passes will be the volume of that fracture divided by the flowrate in that fracture. In the same way the contribution to the matrix interaction parameter X will be total FWS (size) of that fracture times its MPG, divided by the flowrate in the fracture.

APPENDIX 2

NOMENCLATURE OF CHAPTERS ON THE INFLUENCE OF FLOW FIELDS AND MATRIX DIFFUSION

Nomenclature on the influence of flow fields

Symbol	Meaning
a_R	Specific FWS surface area per volume of rock
a_w	Specific FWS surface area per volume of water
A_q	Total FWS along a streamtube carrying a flowrate q
$A(s)$	Cross section of streamtube in porous medium at point s
$2b(s)$	Fracture aperture in fracture at point s
c	Concentration of solute
c_o	Concentration at a surface
c_p	Concentration in matrix pore water
CFF	Conductive Fracture Frequency
D_L	Dispersion coefficient
D_p	Diffusion coefficient in pore water
D_w	Diffusion coefficient in free water
$f(Q)$	Distribution of flowrates
$f(T)$	Distribution of transmissivities
i	Hydraulic gradient
K	Volume based sorption coefficient
K_h	Hydraulic conductivity
L	Length of flowpath
M	Mass of solute instantaneously injected in a stream
Pe	Peclet number, uL/D_L
q	Flowrate in streamtube
Q	Flowrate
R	Retardation factor in matrix
R_a	Retardation factor due to surface intersection
s	Distance along flowpath
S	Average distance between flowing fractures
t	Time
t_w	Water residence time
u	Water velocity
V	Volume
V_q	Volume of streamtube
$W(s)$	Local width of a streamtube in a fracture
x	Distance along flow direction
z	Distance into matrix
Greek symbols	
ε_f	Flow porosity of rock mass
ε_p	Porosity of rock matrix
σ_{cLog10}	Standard deviation in log normal distribution of transmissivities of fractures
λ	Decay constant
Λ	Dimensionless decay constant

Nomenclature on matrix diffusion

Symbol	Unit	Meaning
a_L	[m]	Longitudinal dispersion length
a_T	[m]	Transverse dispersion length
b	[m]	Half of the fracture aperture
C	[mol m^{-3}]	Solute concentration
C_f	[mol m^{-3}]	Solute concentration in the liquid phase in the fracture
C_p	[mol m^{-3}]	Solute concentration in the stagnant water in the porous rock matrix
$C_{background}$	[mol m^{-3}]	Natural solute (element) concentration in the transport domain
C_0	[mol m^{-3}]	Tracer concentration at the up-stream boundary
D	[m^2 s^{-1}]	Diffusion coefficient in a viscous liquid
$\boldsymbol{D}$	[m^2 s^{-1}]	Hydrodynamic dispersion tensor
$\boldsymbol{D}_a$	[m^2 s^{-1}]	Apparent diffusion tensor
$\boldsymbol{D}_e$	[m^2 s^{-1}]	Effective diffusion tensor
$\boldsymbol{D}_p$	[m^2 s^{-1}]	Pore diffusion tensor
$\boldsymbol{D}_s$	[m^2 s^{-1}]	Surface diffusion tensor
$\boldsymbol{D}_w$	[m^2 s^{-1}]	Diffusion tensor in free water
d		Derivative
d	[m]	Thickness of the porous rock zone accessible for matrix diffusion
dF/dV_f	[m^{-1}]	Interface fracture/rock area for matrix diffusion per unit volume of fracture
F	[m^2]	Cross-sectional area
F	[-]	Formation factor
f		A given (time-dependent) function, e.g. the radionuclide release function
G	[-]	Geometry factor
J_f	[mol s^{-1}]	Mass flow in the fracture
J_p	[mol s^{-1}]	Mass flow in the matrix
j	[mol m^{-2} s^{-1}]	Diffusive flux; Rate of diffusive mass transfer per unit area and unit time
j_D	[mol m^{-2} s^{-1}]	Diffusive solute flux
$j_{\mathrm{disp.}}$	[mol m^{-2} s^{-1}]	Dispersive solute flux
$j_{\mathrm{adv.}}$	[mol m^{-2} s^{-1}]	Advective solute flux
j_0	[mol m^{-2} s^{-1}]	Asymptotic (steady-state) diffusive solute flux
K_a	[m]	Surface-based sorption equilibrium coefficient for sorption in the fracture
K_d	[m^3 kg^{-1}]	Linear sorption equilibrium distribution coefficient for sorption in the rock
K_f	[mol$^{1-N_f}$ m$^{3N_f-2}$]	Coefficient of the Freundlich isotherm for sorption in the fracture
K_p	[mol$^{1-N_p}$ m^{3N_p} kg^{-1}]	Coefficient of the Freundlich isotherm for sorption in the rock matrix
k	[J K^{-1}]	Boltzmann's constant ($k \approx 1.381 \cdot 10^{-23}$ Joule/K)
L	[m]	Migration distance along the fracture
l	[m]	Length of a segment of the pathway along the fracture
N_f	[-]	Exponent of the Freundlich isotherm in the fracture
N_p	[-]	Exponent of the Freundlich isotherm in the rock matrix
Q	[m^3 s^{-1}]	Water flow rate
Q_f	[mol m^{-3} s^{-1}]	Sink/source term for the solute in the fracture
Q_p	[mol m^{-3} s^{-1}]	Sink/source term for the solute in the matrix
R_f	[-]	Retardation factor or function in the fracture
R_p	[-]	Retardation factor or function in the rock matrix
$\tilde{R}_f$	[-]	Rescaled distribution ratio for sorption in the fracture
$\tilde{R}_p$	[-]	Rescaled distribution ratio for sorption in the rock matrix
r	[m]	Radius of spherical particles

Symbol	Unit	Meaning
r	[m]	Length of the position vector
S	[mol kg^{-1}]	Amount of solute absorbed onto the rock per unit mass of porous medium
S_f	[mol m^{-2}]	Amount of solute absorbed per unit area of fracture surface
S_p	[mol kg^{-1}]	Amount of solute absorbed per unit mass of porous rock matrix
T	[K]	Temperature
T_L	[s]	Solute release time to the geosphere
t	[s]	Time
t_{adv}	[s]	Solute advection time
V	[m^3]	Volume
V_f	[m^3]	Volume of flowing water
v	[m s^{-1}]	Averaged particle velocity
v_f	[m s^{-1}]	Water velocity in the fracture
W	[m]	Fracture width (in y-direction)
w	[-]	Any variable of the Heaviside step function
x	[m]	Cartesian co-ordinate in matrix diffusion direction
y	[m]	Cartesian co-ordinate in fracture width direction
z	[m]	Cartesian co-ordinate in direction of the advective solute flow

Greek symbols

α	[-]	Rock capacity factor
Θ	[-]	Heaviside step function
∂		Partial derivative
δ	[‰ V-SMOW]	Difference in ‰ relative to Vienna Standard Mean Ocean Water
δ	[-]	Constrictivity
δ_f	[m^{-1}]	Sorbing surface per total rock volume
δ_p	[m^{-1}]	Flow-wetted surface per unit volume of flowing water in the fractures
ε_f	[-]	Flow porosity (ratio of water-conducting fracture volume and total volume)
ε_p	[-]	Connected or diffusion-accessible porosity
ε_r	[-]	Residual (isolated) porosity
$\varepsilon_{\mathrm{tot}}$	[-]	Total porosity (Ratio of total void space and total rock volume)
η	[kg m^{-1} s^{-1}]	Viscosity
λ	[s^{-1}]	Decay constant
ρ	[kg m^{-3}]	Solid-phase density
τ	[-]	Tortuosity
τ_0	[s]	Matrix diffusion time
∇	[m^{-1}]	Nabla operator