R-03-20

Strategy for the use of laboratory methods in the site investigations programme for the transport properties of the rock

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June 2003

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ISSN 1402-3091
SKB Rapport R-03-20

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Abstract

This report comprises a strategy for the handling of laboratory investigations of diffusivity and sorption characteristics within the discipline-specific programme "Transport Properties of the Rock" in the SKB site investigations. The aim of the transport programme is to investigate the solute transport properties at a site in order to acquire data that are required for an assessment of the long-term performance and radiological safety of the deep repository. The result of the transport programme is the Transport Properties Site Descriptive Model /Berglund and Selroos, 2003/, i.e. a description of the site-specific properties for the transport of solutes in the groundwater at a site.

A strategy for the methodology, control of sampling and characterisation programme and interpretation of the results, is proposed. The basis for the laboratory investigations is a conceptual geological model based on the geological model produced in the geology programme. Major and minor types of rock and fractures are defined and characterised according to the quality of the general database and site-specific needs. The selection of samples and analyses is determined in close co-operation with the geology, hydrogeology, hydrogeochemistry and rock mechanics programmes. The result of the laboratory investigations is a retardation model, which is used as an input in the Transport Properties Site Descriptive Model. The interpretation and production of a retardation model is described and exemplified.

Lastly, method-specific strategies and recommendations are given, including strategies for the selection of tracers in the experiments and for the treatment of the sampled geologic materials.

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1 Background

A site investigation is an important part in the process of localising a deep repository for spent nuclear fuel. In 2002, the Swedish Nuclear Fuel and Waste Management Company, SKB, commenced site investigations in several municipalities in Sweden /SKB, 2001a/. The overlying objective of these investigations is to produce detailed proposals on how to construct and operate a deep repository.

1.1 Goals of the site investigations programme

A general geoscientific programme for investigation and evaluation of sites has been presented earlier /SKB, 2000/. The general programme has then been expanded and described in more detail in so-called discipline-specific programmes /SKB, 2001b/. Both the general and discipline-specific programmes are generic and constitute a basis for site-specific execution programmes. The main goals of the investigations are to /SKB, 2001a/:

- "Present the necessary data on the site for a site-adapted layout of the deep repository and the assessment of the deep repository's long-term radiological safety,
- achieve fundamental geoscientific understanding, i.e. analyse the reliability and assess the reasonableness of the assumptions made with respect to the current states of the site and naturally ongoing processes, and
- identify objects that may require special environmental considerations during construction and operation of the deep repository".

The main product of the investigations is a *site description,* which is an integrated description of the site (geosphere and biosphere). The collected data that are used for design and safety assessment are interpreted and presented in a *site-descriptive model.* The site-descriptive model consists of a description of the geometry and different properties of the site and comprises, together with databases, the backbone of the site description.

1.2 Goals of the programme "Transport properties of the rock"

This report is related to the discipline-specific programme "Transport properties of the rock" which is described in /SKB, 2001b/. The programme for the transport properties of the rock describes which of the rock's transport properties that will be determined and the characterisation and interpretation methods that will be used in the site investigations. An important base for the discipline-specific programme is SR 97 /SKB, 1999/ and the TRUE-project at Äspö Hard Rock Laboratory (Tracer Retention and Understanding Experiment) /Winberg et al, 2000, 2002/. The most important properties, or suitability indicators, for the discipline were identified in /Andersson et al, 2000/:

- “Groundwater flow on the deposition hole scale,
- transport resistance,
- diffusivity and matrix porosity of the rock mass, and
- sorption properties (sorption coefficients) for the different substances that may be transported with the groundwater”.

With reference to the main goals of the investigations and the suitability indicators given above, the focus of the transport programme is to furnish the data on the transport properties of the rock that are required for an assessment of the long term performance and radiological safety of the deep repository. More specifically, this means to /SKB, 2001b/:

- “determine site-specific parameters (matrix diffusivity, matrix porosity, sorption coefficients, transport resistance) for reactive (sorbing) substances of importance for safety assessment of a deep repository, and
- determine site-specific parameters for non-reactive (non-sorbing) substances (dispersivity, flow porosity, travel time, fracture aperture) to be used for calculations with and calibration of flow and transport models, which are supposed to contribute to a geoscientific understanding of the site.”

The programme for the transport properties of the rock is divided into three parts: field measurements to obtain site-specific transport parameters, laboratory experiments on site-specific rock material and modelling of transport properties. By means of an integrated analysis of these parts, a *transport properties site descriptive model* will be prepared. The transport properties site descriptive model, which is a site-specific description of the transport properties of the rock, is the main product of the transport programme and it constitutes a part of the site-descriptive model. The methodology and strategy for preparation of the transport model is described by /Berglund and Selroos, 2003/.

1.3 Goals of this work

The aim of this report is to present a strategy and a more detailed structure of the execution programme for the sampling and use of laboratory methods for characterisation of retardation properties (mainly porosity, diffusion and sorption properties). The strategy as presented in this report should guide the practical performance of the laboratory measurement program, although this is a general strategy and the investigations always should be adapted to the site-specific conditions. The final product of the laboratory investigations is the measured retardation data (including geometrical references of the samples) and an interpreted retardation model, which is further described below. The retardation data and the retardation model are delivered as an input to the task of preparing the transport properties site descriptive model as mentioned above.

Our ambition in writing this report has been to establish a characterisation level for the retardation properties of the rock that will meet the general goals of the site investigation and the detailed goals described in the transport programme. With regards to the different goals mentioned above, the main goals of the laboratory measurement programme are to:

- determine site-specific retardation parameters for solutes (sorbing and non-sorbing) and rock materials of importance for safety assessment of a deep repository, and
- obtain a geoscientific understanding of the retardation (porosity, diffusivity and sorption) properties of a site; i.e. to understand how the different geologic processes and materials of a site affect the retardation properties.

The laboratory measurement programme shall supply the safety assessment with required data. In order to fulfil the safety assessment goals, parameters and materials that are identified to have a high sensitivity or high uncertainty in the safety analysis should be given priority over parameters or materials of lower impact for the safety analysis. The laboratory measurement programme should also build a geoscientific understanding of the relation between geological and mineralogical conditions and the retardation processes of a site. This means that the focus of the laboratory measurements should be directed towards both parameters with impact on long-term processes that are of more importance for the long-term safety assessment, but also towards parameters that may focus more on short-term processes but that are important for the geoscientific understanding of a site. As an example, the retardation properties of the rock materials along and close to the water flow paths are important in a short to long-term perspective and especially for the geoscientific understanding, while the rock mass further away from the fractures is at the present stage considered to be very important in a long-term safety assessment perspective. However, diffusing radionuclides must pass through the altered materials near fractures or fracture zones before the intact rock is reached. Consequently, a confirmation of the assumed existence of a connected pore system through the altered zone is important not only for the understanding of short-term processes, but also as a basis for safety assessment. In order to meet the goals of the investigation, both the fracture materials and the rock mass should be given sufficient characterisation resources.

It is important to emphasise that the proposals and recommendations in this report are general, aiming at being used as a basis for site-specific programmes. Depending on the sites characteristics and the needs of the receivers/users of data, sampling and laboratory method needs may vary from site to site. Furthermore, the necessary degree of detail in data and acceptable limits for uncertainty in data will be decided during the investigation process. This will be done by a stepwise crosschecking against the intentions of the programme, reliability assessments of the integrated model descriptions and the needs of the users. Hence, the required degree of site-specific knowledge and detail is not yet specified for the laboratory programme. The programme should also be open for implementation of new knowledge that is gained during the course of the investigations and for new methods that are currently being developed.

1.4 Outline of this report

The structure of this report is as follows. Chapter 2 outlines the conceptual model and the sampling and characterisation needs for different structures and rock units are described. The general characterisation plan is presented in Chapter 3. A working methodology for the laboratory investigations is presented in Chapter 4. In Chapter 5 a control scheme for the sampling and selection of laboratory methods is proposed. Chapter 6 presents the interpretation step of laboratory data and results and exemplifies how the retardation model can be visualised for a tentative site. Method-specific strategies and recommendations are given in Chapter 7. Some final comments are given in Chapter 8.

A comparative study of methods for laboratory diffusion measurements is included in Appendix A. The study was done on 13 samples using liquid phase through-diffusion (tritiated water tracer), gas phase through-diffusion (helium tracer) and electrical conductivity measurements on all samples. The objective with this study was to investigate the compliance between the methods and to give recommendations for method selection for diffusion measurements. Lastly, there is a need for the planning of the site investigations to estimate the sampling requirements for laboratory measurements at a site. In Appendix B, a quantification of the laboratory programme using a tentative example as input in the proposed control scheme is performed.

1.5 Transport processes

Figure 1-1 shows schematically the processes that influence the transport of radionuclides through the rock. Radionuclides can be transported by advection with the flowing groundwater. Diffusion (the naturally occurring spreading of a substance caused by random molecular movements) along the flow paths can also be important, especially under stagnant flow conditions. An important aspect of this is matrix diffusion, by which radionuclides diffuse into the stagnant water in micro-pores or micro-fractures of the rock. Thereby the radionuclides are transported more slowly than the flowing water in the fractures. The timescale for advection relative to the timescale for matrix diffusion determines the relative importance of the latter process.

Another factor of crucial importance for radionuclide transport is sorption, by which radionuclides adhere to the surfaces of the fracture system and the rock matrix. The chemical environment in the water determines the speciation (chemical form) of the radionuclides, which is fundamental for the sorption processes. Matrix diffusion and sorption are generally considered as the two most important retention processes for radionuclides in the geosphere.

Furthermore, immobilisation may occur, which are other important processes by which solutes become irreversibly incorporated within immobile solid phases within the geosphere. Another factor that may be of importance for retention is sorption on colloidal particles and transport with them, see e.g. /Laaksoharju et al, 1995; Wold and Eriksen, 2000/. Some radionuclides can also be transported in the gas phase. Finally, radioactive decay affects the radionuclide content of the groundwater and must therefore be included in the description of the transport processes. A more detailed description of the transport processes is provided in SR 97 /SKB, 1999/.

This report deals with material properties that are related to sorption and diffusion processes. Consequently, processes as advection, dispersion, channeling effects, immobilisation and colloidal properties are not within the scope of this report. It should also be noted that the transport properties of the canister and buffer materials are not within the scope of this work.

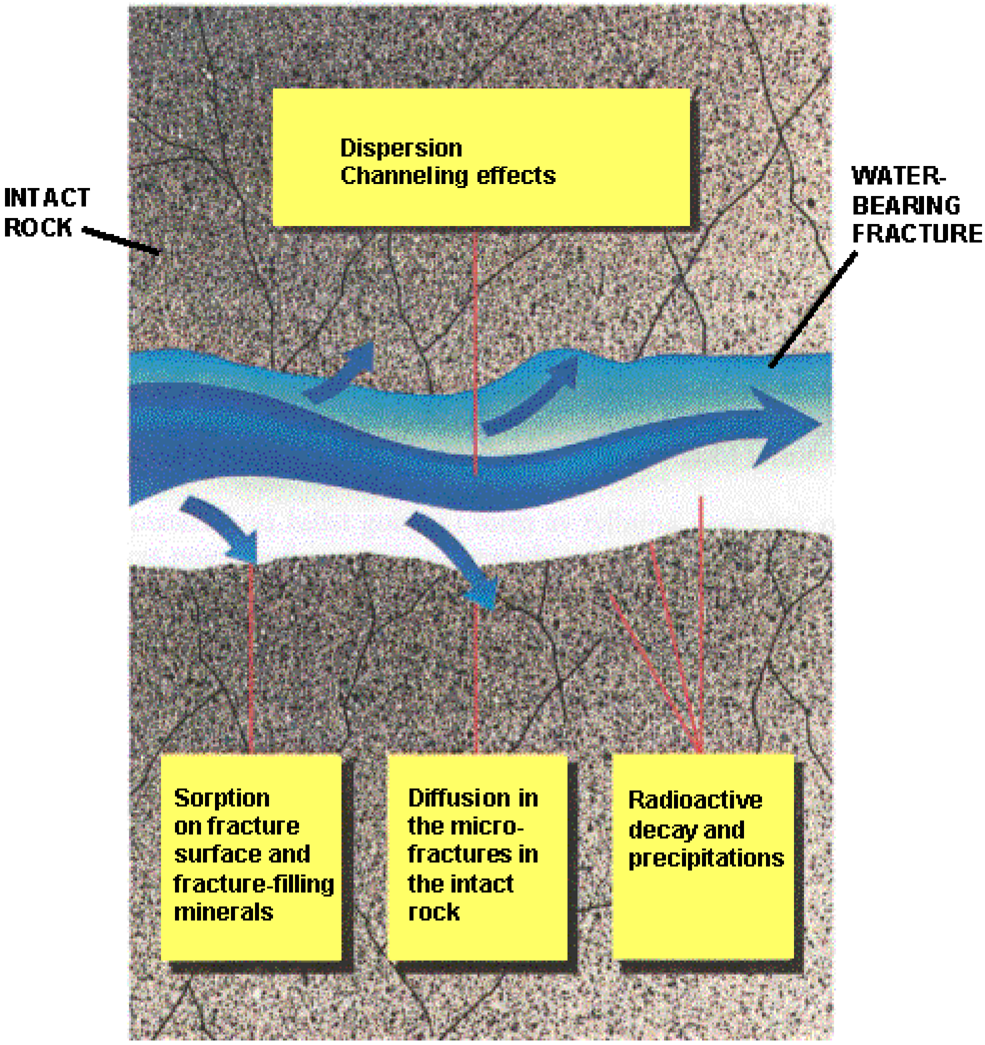


Figure 1-1. *An illustration of the mechanisms that influence transport of radionuclides from the geosphere to the biosphere /SKB, 2001b/.*

1.6 Characterisation methods

An overview of all characterisation methods – laboratory, field and modelling methods – that are planned to be used in the transport properties investigations is given in /SKB, 2001b/. The methods concerned in the laboratory investigations are summarised in Table 1-1.

Laboratory measurements on rock samples and drill cores provide direct information on the retardation properties of the rock matrix and the fracture materials. The parameters that are determined are the matrix porosity (defined as open porosity in SS-EN 12670), porosity distribution and diffusivity of the rock materials, and the sorption coefficients for a number of combinations of rock materials, radionuclides and groundwater compositions. These measurements are performed on rock cores or crushed rock from several different parts of the candidate rock volume under well-controlled conditions. The analysis must also take into account to what extent selected drill cores have been altered from the *in situ* conditions due to the change in rock stress conditions after extraction. A brief description of the primary laboratory methods is given in the following sections.

Table 1-1. Summary of main investigation methods (as proposed to be used in the laboratory investigations), evaluated parameters and references.

Investigation method	Primary investigation parameters (information)	Secondary investigation parameters (information)	Comment (reference)	SKB Method Description / alternative method description
Through-diffusion measurements	Matrix diffusivity, D_e	Sorption coefficients, K_d, (K_a) Matrix porosity, ε_p	/Byegård et al, 1998, 2001; Ohlsson and Neretnieks, 1995, 1997/	SKB MD 540 001
He-gas through-diffusion measurements	Verification of pore connectivity (tracer breakthrough)	Matrix diffusivity, D_e	/Hartikainen et al, 1996; Laajalahti et al, 2000; Maaranen et al, 2001/	/Maaranen et al, 2001/
Electrical conductivity measurements	Spatial variability in formation factor (matrix diffusivity), F (D_e)	–	/Ohlsson, 2001; Lövgren and Neretnieks, 2002a/	SKB MD 230 001
Batch sorption measurements	Sorption coefficient, K_d	Surface sorption coefficient, (K_a)	/Byegård et al, 1998, 2001; Ohlsson and Neretnieks, 1995, 1997/	SKB MD 540 002
Water saturation porosity measurements	Matrix porosity, ε_p	–	/Byegård et al, 1998, 2001; Ohlsson and Neretnieks, 1995, 1997/	SS-EN 1936 / ISRM 1979

PMMA porosity measurements	Porosity distribution Porosity gradient	–	/Siitari-Kauppi, 2002; Byegård et al, 1998, 2001/	SKB MD 540 003
Surface area	–	Specific surface area (*A*)	Used for sample screening and selection in the batch sorption experiments	ISO 9277:1995 (Nitrogen gas adsorption, BET-measurements)
Cation Exchange Capacity	–	Cation exchange capacity (CEC)	Used for sample screening and selection in the batch sorption experiments	ISO 13536
Methods under evaluation				
Electro-migration	Sorption on internal rock surfaces (K_d)	–	Method development in progress	–
In situ formation factor logging	Spatial variability in formation factor / matrix diffusivity, F / D_e	–	Method development in progress /Lövgren and Neretnieks, 2002a/	–
In situ single borehole sorption measurements	Sorption and diffusion properties under *in situ* pressure and rock stress conditions	–	Method study in progress	–

1.6.1 Batch sorption measurements

In batch sorption measurements, crushed rock or mineral grains are contacted with groundwater and the distribution of a dissolved species between the aqueous and the solid phase is measured /see e.g. Byegård et al, 1998/. Thereby, the mass related sorption coefficient, K_d, can be calculated from the ratio of the concentration of the species in the solid and aqueous phase. By using several different size fractions, the sorption coefficient for internal rock surfaces (K_d) and outer surfaces (the surface related sorption coefficient, K_a) can be assessed. The method is further described in section 7.3 and in the method description for batch sorbtion measurement /SKB, 2003b/.

1.6.2 Through-diffusion measurements

Matrix diffusivity measurements are carried out by measuring how quickly an added substance diffuses through a piece of a drill core, so-called through-diffusion measurements /Ohlsson and Neretnieks, 1995; Byegård et al, 1998/. The measurement is normally performed on a 1–5 cm thick sawn-out slice of a drill core placed in a measurement cell where one side of the core piece is in contact with a synthetic groundwater and the other with a synthetic groundwater tagged with the radionuclides to be studied. Samples are then taken on the untagged side, and the effective diffusion coefficient D_e for the rock matrix can be calculated based on the concentration increase on the untagged side. This measurement also provides indirect determinations of matrix porosity (by measurement and modelling of through-diffusion of tritiated water, HTO) and sorption coefficients (by measurement and modelling of through diffusion or concentration profiles of selected sorbing tracers).

Through-diffusion measurements are relatively time consuming when used for dense rock samples and therefore measurements are limited to rather short samples. However, it has the advantage of being the only one of the three methods (HTO-diffusion, He-gas diffusion and electrical conductivity measurements) that is measuring throughput of the actual molecule of interest (HTO) in the phase that is of interest in the bedrock, i.e. the water phase. It is thus the technique that best reflects the real situation in the bedrock and is therefore proposed as the calibration method.

1.6.3 Gas diffusion measurements

Gas diffusion measurements is a relatively new method for determination of matrix diffusivity and matrix porosity by through-diffusion of helium through pieces of rock /see e.g. Hartikainen et al, 1996; Laajalahti et al, 2000; Maaranen et al, 2001/. Diffusion in the gas phase is generally about four orders of magnitude faster than in the liquid phase. Hence, the main advantage of this method is that it is relatively fast. In the He-gas method, helium is used as tracer. The injection cell at one end of the sample is initially filled with helium, and the surface at the other end of the sample is continuously flushed with nitrogen. The helium concentration of this nitrogen is then measured as a function of time and the effective diffusivity can be evaluated based on the break-trough curves. Since the method is much faster than through-diffusion of HTO in the liquid phase, it enables measurements of thicker samples within a reasonable experimental time.

1.6.4 Electrical conductivity measurements

In electrical conductivity measurements, the electrical conductivity in the rock disc is measured in a sample saturated with a known electrolyte /see e.g. Ohlsson, 2001 or Lövgren and Neretnieks, 2002a or SKB, 2003d/. The formation factor, F, is obtained by relating the electrical conductivity of the sample to the electrical conductivity of the electrolyte that the sample was saturated with. The effective diffusivity can then be calculated since $F = D_e/D_w$, where D_w is the water diffusivity, which is known. Electrical conductivity measurements are easy to perform and it is probably the most practical and economical method when handling a large amount of samples. The disadvantage is that electrically conducting minerals may lead to an overestimation of the formation factor. However, the method is suitable for investigations of spatial variability, for which a relatively large amount of samples need to be measured. A fraction of these samples can then be calibrated by using through-diffusion of HTO.

1.6.5 Porosity measurements

The porosity of the rock matrix can be determined in several different ways by means of laboratory measurements on slices of rock cores. The most common method is the water saturation technique, which is determined according to standard methods /SS-EN 1936, ISRM 1979/.

A recently developed method, the ^{14}C-PMMA method /see e.g. Siitari-Kauppi, 2002/, provides information on the porosity distribution on a microscopic level. The method is used to measure matrix porosity, the two-dimensional distribution of porosity and can also be used to evaluate porosity gradients in altered fracture materials or excavation disturbed materials. The method entails drying slices of drill cores and impregnating them with a ^{14}C-tagged polymethylmethacrylate monomer, whereby both the matrix porosity and its spatial distribution in the rock matrix are determined. This provides information for estimation of penetration depth for radionuclides.

A third method is to calculate the matrix porosity by modelling of through-diffusion measurements with tritiated water (HTO) (see above). A comparative study of the three methods /Byegård et al, 1998/ shows a good agreement. The water saturation technique is used as a standard method, but certain selected samples are also measured with the other methods, which provide other important information (see above).

It should be mentioned that porosity measurements are also done within the geology program. However, since porosity is a governing factor for the retardation processes (diffusion into the pores of the rock matrix followed by sorption on the pore surfaces) the transport characteristics have to be studied in close relation to the porosity. Therefore, selection and investigation of the rock material is necessary to be done very much from a porosity perspective and including porosity is therefore necessary when deciding a strategy for the laboratory investigation of the retardation properties.

1.7 Terminology

A similar terminology as defined within the GEOTRAP workshops /GEOTRAP, 2001/ has been used for the definition of retention and retardation processes in this work:

- **Immobilisation:** processes by which solutes become irreversibly incorporated within immobile solid phases within the geosphere (over the time scales of relevance to performance assessment).
- **Matrix diffusion:** transfer of radionuclides by diffusion (a process resulting from random motion of molecules by which there is a net flow of matter from a region of high concentration to a region of low concentration) between flowing groundwater in fractures to stagnant water in rock matrix pores.
- **Retardation:** reversible processes (**sorption** and **matrix diffusion**) that delay the time taken for solutes to traverse the geosphere.
- **Retention:** the combined effect of **retardation** and **immobilisation** processes that in combination leads to a decreased net flow rate of solutes through the geosphere.
- **Sorption:** a collective name for a set of processes by which solutes become attached by physical or chemical reactions to solid surfaces within the geosphere. The term is taken to include processes that are reversible over the time scales of relevance to performance assessment.

For the purpose of this work, the following material terminology is defined:

- **Altered wall rock**: rock adjacent to fracture surface showing alteration of one or several mineral types. The alteration is usually accompanied by changes in porosity and texture compared to the intact rock.
- **Breccia fragments:** rock fragments >2 mm in size, caused by brittle tectonic activity.
- **Cataclasite:** Rock that has been formed by cataclasis (repeated shear fracturing, which acts to reduce the grain size of the rock), i.e. deformation that is less extreme than in the case of mylonite.
- **Clay minerals:** hydrous silicates with a crystal structure of two- or three-layer type in which silicon and aluminium ions have tetrahedral coordination with respect to oxygen while aluminium, ferrous and ferric iron, magnesium, and other ions have octahedral coordination with respect to oxygen or hydroxyl ions. Exchangeable cations may be found on the surfaces of the silicate layers, in an amount determined by the excess negative charge within the composite layer.
- **Fault gouge:** unlithified fragments of rock and minerals usually including clay minerals found in faults. For practical reasons a grain size limit of <2 mm have been used for fault gouge classification in the SKB core mapping routine. The grain size distribution may show large variations whereas some samples are dominated by clay minerals and others are not.
- **Fracture coating:** minerals grown on the fracture wall. These can be formed by alteration of the wall rock or by precipitates from fluids that have passed through the fracture.
- **Matrix porosity:** the open porosity according to the definition in EN-12670 ("Natural Stones – Terminology"), i.e. the ratio between the volume of the open pores and the apparent volume of the rock specimen.
- **Mylonite:** a fine-grained rock formed by extreme micro brecciation during tectonic movements.
- **Porosity**: the same meaning as matrix porosity.
- **Rock mass**: The rock units between the distinguished fractures and fracture zones. Note that the term rock mass is therefore related to scale. Looking in detail, minor fractures are distinguished from the rock mass whereas in larger scale approaches the same fractures may be included in the rock mass concept.
- **Sample:** a coherent piece of rock material from one location.

Additionally, the following terms are used:

- **Retardation model:** the retardation model, as proposed in this work, is an interpreted description (including interpreted data) of retardation properties for the typical rock types and structures (different types of rock, fracture and local minor and major fracture zones) at a site. It consists of a rock type description, description of the typical layers for fractures and fracture zones and a database with interpreted porosity, sorption and diffusion data for the different materials. The retardation model, which is the final product of the laboratory investigations of the retardation properties of the rock, is further described in Chapter 6. It is delivered as an input to the task of preparing the Transport Properties Site Descriptive Model.

- **Transport Properties Site Descriptive Model:** the Transport Properties Site Descriptive Model is the product of discipline-specific programme “transport properties of the rock” in the site investigations programme and it comprises a part of the Site Descriptive Model /SKB, 2001b/. The Transport Properties Site Descriptive Model is an integrated geological and hydrogeological site descriptive transport model that describes transport of solutes in the groundwater. The model includes retention data. The modelling within the discipline is aimed at obtaining a geoscientific understanding of the site and delivering transport parameters to the safety assessment. The development of the Transport Properties Site Descriptive Model is further described by /Berglund and Selroos, 2003/.

2 Basic conceptual model of bedrock transport properties

2.1 Geological-structural model

The structure geological model used by SKB /Andersson et al, 2000; SKB, 2001b/ consists of rock mass units and four different size classes of structures: regional fracture zones, local major fracture zones, local minor fracture zones and fractures within the rock mass, see Table 2-1 and Figure 2-1. This structural model will be used in this work as a basis for describing different types of structures, although classification of structure units into different characteristic types may be necessary in order to accurately describe the variation of transport properties within a given structure size class.

Table 2-1. Classification and naming of fracture zones and fractures and ambition level for geometric description during site investigation /from Andersson et al, 2000/.

Name	Length	Width	Ambition for description
Regional fracture zones	> 10 km	> 100 m	Deterministic
Local major fracture zones	1–10 km	5–100 m	Deterministic (with uncertainties)
Local minor fracture zone	10 m–1 km	0.1–5 m	Statistical (some deterministic)
Fractures	< 10 m	< 0.1 m	Statistical

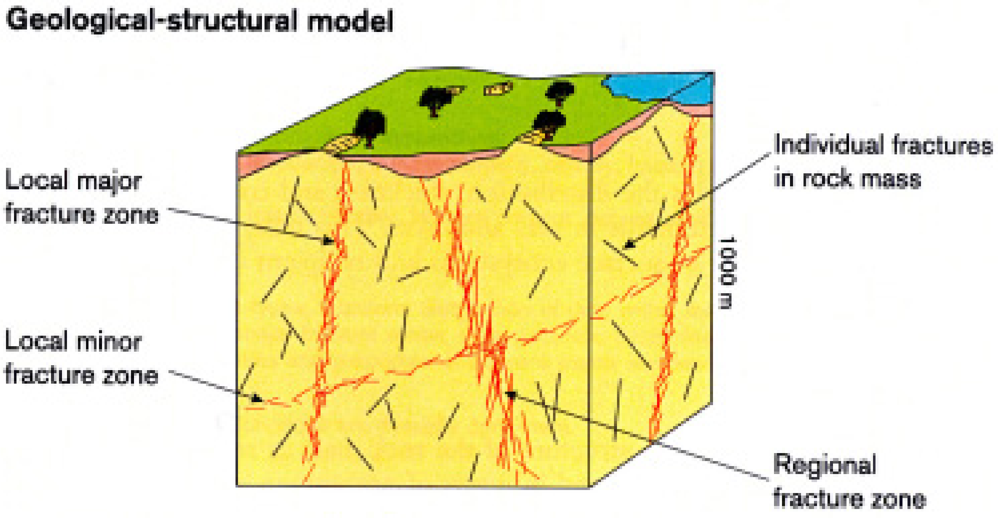


Figure 2-1. *SKB structural geological model /from SKB, 2001b/.*

In the repository for spent nuclear fuel, it is required that the deposition tunnels and deposition holes do not pass, and have a respect distance to, regional and local major fracture zones /Andersson et al, 2000/. It is also required that deposition holes are not intersected by identified local minor fracture zones and a low fracture density is preferred.

In case of a leakage of dissolved radionuclides from a defect canister through the bentonite buffer, escaping radionuclides can be transported through the surrounding rock by flow and/or diffusion through the more or less connected network of water-conducting fractures and fracture zones. Matrix diffusion from fractures or fracture zones into pores with stagnant water and sorption on minerals in contact with the groundwater may occur in all structures discussed here, as well as on the walls of the deposition hole.

2.2 Classification tools and terminology

2.2.1 Rock type classification criteria

The characterisation of different rock types is based on a number of different properties according to the rock type description as defined in the geology programme /SKB, 2001b/.

2.2.2 Structure type classification criteria

Rock structures are divided into size classes (individual fractures in the rock mass, local minor fracture zones, local major fracture zones and regional fracture zones) and are characterised within the geology and hydrogeology site investigation programmes based on a number of different properties /SKB, 2001b/. For the description of retardation properties, structure units may need to be classified into different types within a given size class. The purpose is to enable distinction of different types of a structure unit if *substantially* different retardation properties are documented or suspected (in the early phase of the investigations). The classification approach is similar to that used by /Mazurek et al, 1997/, but simplified in order to be adapted to the required detail of the site investigations. A possible classification of a structure unit into a specific type will be based on a qualified judgement of the integrated retardation properties of the structure. The classification grounds should be well documented and transparent in order to be re-interpreted during the evolution of the site investigation.

Structure type classification will evolve as the site investigation proceeds. Thus, the number of different structure types and their individual properties needed to characterise a given size class will not be known in the initial phase of the site investigation. Fracture samples taken early in the investigation phase may therefore be unclassified until later in the investigation phase.

2.3 Ambition level for characterisation of rock types and structures

In this section, the ambition level for the laboratory measurement programme is presented, with regards to the goals as described in section 1.3. First, the importance of the different properties to be investigated is discussed in relation to the goals of the laboratory program.

2.3.1 Discussion of the relative importance of retardation properties

Safety Assessment perspective

Several temporal scales are relevant for the transport modelling according to /Berglund and Selroos, 2003/. The same authors distinguish between a tracer test time scale (a few months to a few years, and a safety assessment time scale (typically a few thousand or tens of thousands of years).

In the safety assessment time scale, the effective rock matrix diffusivity, D_e (which is coupled to the formation factor), and the mass related sorption coefficient, K_d, of the *intact rock mass* are usually regarded as the most important retardation properties in present day models for simulation of radionuclide transport /e.g. Neretnieks, 2002b, 2003; Berglund and Selroos, 2003/. In addition to matrix diffusivity and sorption coefficient, matrix porosity was also identified as one of the suitability indicators for the transport /Andersson et al, 2000/. Furthermore, it is important to establish the connectivity of the pore system in order to support the model used for safety analysis. The flow wetted surface is an important and uncertain flow parameter, however, the investigation of this parameter is handled in the field experiment programme /Andersson, 2000/.

The other parameters that are included in the measurement programme (porosity distribution, porosity gradients and surface sorption coefficient, K_a) may not be of the same importance in a safety assessment perspective. However, these parameters should be measured according to the general programme /SKB, 2001b/ and the final judgements of their importance and possible use, or discrimination, in the safety assessment is a question for the safety assessment and not for the measurement program. This argumentation also applies for the retardation properties for fracture infills and thin fracture coatings, that for conservative reasons often are neglected in safety analysis.

In the tracer test time scale, a description of the fracture transport properties and sufficient data to provide support for evaluation of tracer tests and for the description of early stages of radionuclide transport scenarios is needed /Berglund and Selroos, 2003/.

Geoscientific understanding perspective

From the geoscientific understanding perspective, the requirement for quantitative data is weaker than for safety analysis use, but the needs for a qualitative description of the present and future retardation processes at a site is strong. The retardation processes that may occur in the most frequent, or from the transport perspective most important, fracture types and rock types should be well understood in order to establish a solid foundation for the safety analysis and in order to enable alternative analysis approaches.

A description of retardation properties, in primarily qualitative but also quantitative terms, on a detailed fracture (or fracture zone) scale is needed to provide support for modelling of tracer field experiments in the short term. Such experiments are in turn performed to support the models used in the long-term safety analysis. The detailed fracture properties description is also important for the general understanding of the long-term solute-rock interactions within the altered zones.

For rock types, the pore connectivity and scale effects (for sorption and diffusion measurements) is of high importance for the geoscientific understanding of the sorption and diffusion processes. The quantification as such of data for the other parameters is less important for the understanding.

Porosity distribution, pore connectivity and matrix porosity is of higher importance for the fractures and fracture zones in order to facilitate primarily qualitative, but secondly also quantitative, analysis of the impact of alteration profiles on the retardation properties of fractures. The description of retardation properties in different zones of alteration profiles need not to be as quantitative as for the rock type description. It is desirable to, at least, obtain information on whether the parameter values are higher or lower in the alteration zones than in the unaltered rock. The important point is to obtain an understanding of the transport processes in the altered zone near the fractures, since migrating radionuclides have to pass through the altered zone before the internal surfaces and pore system of the intact rock can be reached. A verification or demonstration of the existence of a continuous pore system from the fracture rim zone, through the altered fracture materials and into the intact rock is therefore of particular importance for the safety assessment.

2.3.2 Ambition level for rock type characterisation

It is desired from the safety analysis perspective /Berglund and Selroos, 2003/ to obtain statistical distributions of the diffusion and sorption parameters (primarily for D_e and K_d) for the more frequent rock types and rock types within the large rock units in the geological model. However, a geostatistical description with spatial correlation lengths etc is not needed. This means that a sufficient amount of data is needed to establish histograms and to perform a simple statistical analysis. It is also desired to obtain appropriate volume coverage of sampling points within the investigated site. At the very minimum level, 9 samples are needed for each rock type or parameter if sampling is done in the corners and middle of the rock volume (imagined as a cube).

For less frequent (or less important) rock types and rock types within smaller rock units, the data basis should at minimum allow identification of typical parameter values or possibly intervals. Because an adequate amount of measurements may not exist to perform a statistical analysis, the judgement of what is typical is done both when selecting samples to be measured and based on the actual measurement data. Restricted volume coverage of the sampling of the less frequent/important rock types will be accepted.

2.3.3 Ambition level for structure characterisation

The fracture studies should mainly relate to fractures that are water-conducting and, if possible, for which the groundwater chemistry is known. However, fractures can also be studied if the groundwater chemistry is unknown, thus introducing uncertainties in the selection of a representative groundwater. The uncertainties are further discussed in section 2.5. Sealed fractures may also be studied, although open fractures are in focus. Several reasons can be foreseen to study sealed fractures, e.g. simply due to lack of material from open fractures or in order to study fracture properties at different stages of the fracture evolution.

The fractures or fracture zones to be studied are mainly those exhibiting alteration in the host rock, since their estimated occurrence, e.g. at Äspö, is about 90% /Smellie, 2003/. However, unaltered fractures may be important from a transport perspective. Owing to a lack of fracture filling phases these fractures may be relatively conductive and should therefore be included in the investigations.

The characterisation level should give enough detail to enable specific mass transfer models for different major types of fractures or fracture zones within a site to be used for modelling purposes in the tracer test time scale. The characterisation and interpretation methods should build on the experiences from the TRUE-projects /Winberg et al, 2000, 2002/ and other international migration experiments, e.g. the experiences from the Grimsel Migration Experiments /Smith et al, 2001/.

The ambition for the different materials or layers within the altered zone near the fractures is that the data basis should at a minimum allow identification of typical parameter values or intervals. The data basis should be sufficient to enable judgement or calculations of the penetration (diffusion) depth into the fracture wall rock as a function of time. Because an adequate amount of measurements may not exist to perform a statistical analysis, the judgement of what are typical parameter values is done both at the selection of samples to be measured and based on the actual measurement data. Restricted volume coverage of the sampling of the fractures and fracture zones will be accepted due to the expected sample amounts.

In the interpretation of fracture tracer test retardation data, there is a possibility to compare the results of laboratory and field experiments. Another important potential area of comparison is natural analogue studies, in which measurements of *in situ* matrix diffusion profiles are done. The profiles are usually determined by measurements of U-decay series or other trace elements and gives information of the diffusion penetration during timescales within the last 1 Ma.

2.3.4 Ambition level for the sorption measurements

It is considered non-realistic to perform sorption experiments using all the elements in the spent nuclear fuel that have radionuclides of interest for the performance assessment for all site specific conditions. A selection of elements, rock materials and groundwater compositions that are appropriate to include in the present investigation therefore has to be done. The sorption measurements also need to be performed at different levels of complexity in order to reduce the number of measurements, that otherwise multiplies quickly to very large numbers. Furthermore, the use of a diagnostic method for a general scanning of a large number of rock materials in the process of selecting important material and decreasing the number of materials for further investigations is proposed.

The strategy for selection of radionuclides is to use a low number of radionuclides representing elements with different oxidation states. The rationale with doing this classification is that a relatively large number of rock materials could be investigated at a low intense level, i.e. using less laborious methods to obtain a general view of the sorption capacity. Consequently, investigations at more resource demanding levels should be reserved for a few numbers of combinations of groundwater compositions and rock materials.

All sorption measurement will contain a predictive phase, i.e. based on available experimental conditions and the available sorption database, a prediction of the sorption coefficient will be made parallel to the actual experiment. The comparison of these two values will make a base for the general validation of the available sorption databases and also be the basis for a potential simplification made in a safety assessment. The batch sorption programme is presented in detail in Chapter 7.3.

2.3.5 Ambition level for the diffusion measurements

The ambition of the diffusion programme is to use a combination of methods in order to investigate:

- the repository scale spatial variability in matrix diffusivity (or formation factor),
- pore connectivity up to ~10 cm sample size,
- determination of the matrix diffusivity in the water phase, and
- the sample scale variability.

The outline of the investigations is proposed as follows:

- The large-scale variability in matrix diffusivity/formation factor within the repository volume is determined (or scanned) for a relatively large number of samples using laboratory electrical conductivity (EC) measurements of a standard size.
- Comparative verification measurements using through-diffusion technique with HTO as tracer are done for a selected fraction of the EC measurements (using the standard sample size).
- The pore connectivity and heterogeneity in the sample scale is investigated for a few rock samples of the major rock types by determination of matrix diffusivity as a function of sample size. This gives information on the connectivity of the pore system that can be used for an assessment of the matrix diffusivity at different temporal and spatial scales. By using several replicates of the samples the sample scale variability can be judged.
- The homogeneity within the repository volume of the major rock types is investigated by selecting samples from different parts within the repository volume for the through-diffusion measurements described above.

- A few integrated samples from each fracture and fracture zone type are exposed for through-diffusion experiments. Assessment of diffusion properties of individual alteration layers within fractures is done based on porosity data.

- Experiments in order to verify the hypothesis of unlimited pore connectivity are proposed to be done by gas diffusion experiment using a 10 cm-sized rock samples for the major rock type.

2.3.6 Ambition level for the porosity measurements

Matrix porosity is a parameter that is handled within the geology program. However, quantitative and qualitative information of the porosity is produced in the laboratory measurements as supporting data in the diffusion experiments and in order to investigate the porosity distribution in the alteration zone near the fractures. The ambition is to:

- achieve a quantitative and qualitative understanding of the porosity distribution (porosity gradient from fracture surface and distribution of porosity) and pore connectivity in the fracture materials by using the PMMA-method /Siitari-Kauppi, 2002; SKB, 2003c/. The porosity distribution is also aimed for as supporting data for the geoscientific understanding of the major rock types.

- Enable co-variation analysis of diffusivity and porosity data by measurement of porosity as a supporting parameter for electrical diffusivity and through-diffusion samples.

2.4 Geological variables and samples

In order to perform an accurate site investigation of retardation properties of the rock, the sampling should concentrate on typical representatives for the different units and also on extremes. It is important to cover extreme retardation properties and variations in retardation properties since the transport pathways are not always necessarily in contact with the most frequently occurring materials. The geological variables and sample aspects are discussed below and are summarised in Figure 2-2.

2.4.1 Rock types and textures

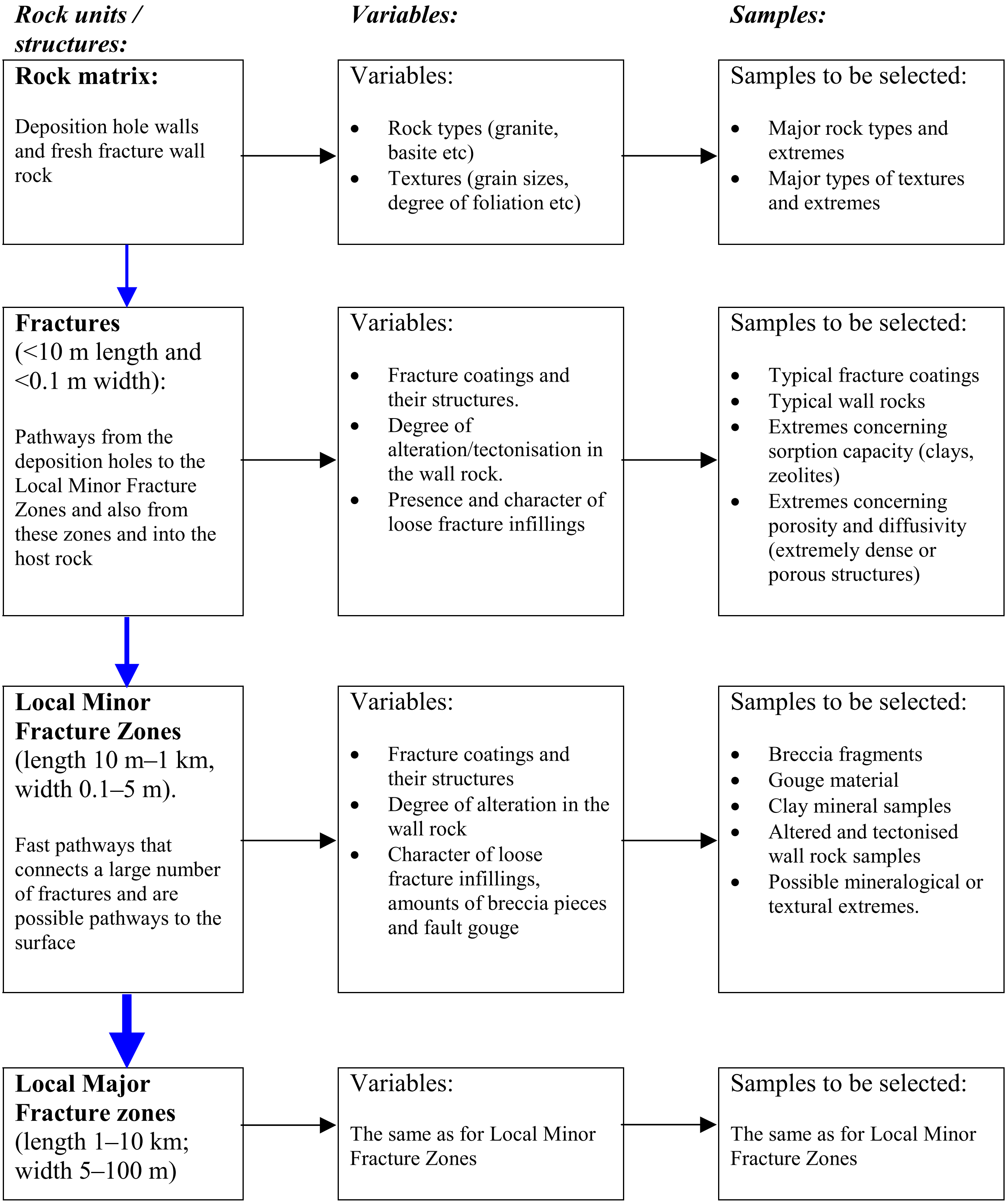
Dominating rock types of the area and textural varieties of these should be included in the sampling (for example different parts of a granite body may show differences in grain sizes and structures like degree of foliation etc). Less frequent rock types may be more fractured and thus constitute larger parts of the hydraulic pathways, which need to be considered when choosing the samples.

2.4.2 Fractures

The most frequently occurring fracture minerals will be shown by the core logging and these should be represented in the sorption studies. Loose material (fault gouge) has a very large active surface area and usually has significant components of clay minerals and should therefore be included in the sampling. For sorption, porosity and diffusion studies it is important to select fracture and wall rock samples so that different textures and degree of alteration/tectonisation of the host rock will be represented.

2.4.3 Local Minor and Major Fracture Zones

The different "components" of the fracture zones should be sampled (typical fracture coating minerals, fault gouge, breccia fragments, altered and tectonised wall rock). For example the wall rock may be relatively dense mylonite or porous and heavily altered host rock and it is important to cover different types of extremes. The amounts of gouge material, breccia fragments and the porosity in the structure is important for the radionuclide retardation in the structure.



Rock units / structures:	*Variables:*	*Samples:*
Rock matrix: Deposition hole walls and fresh fracture wall rock	Variables: • Rock types (granite, basite etc) • Textures (grain sizes, degree of foliation etc)	Samples to be selected: • Major rock types and extremes • Major types of textures and extremes
Fractures (<10 m length and <0.1 m width): Pathways from the deposition holes to the Local Minor Fracture Zones and also from these zones and into the host rock	Variables: • Fracture coatings and their structures. • Degree of alteration/tectonisation in the wall rock. • Presence and character of loose fracture infillings	Samples to be selected: • Typical fracture coatings • Typical wall rocks • Extremes concerning sorption capacity (clays, zeolites) • Extremes concerning porosity and diffusivity (extremely dense or porous structures)
Local Minor Fracture Zones (length 10 m–1 km, width 0.1–5 m). Fast pathways that connects a large number of fractures and are possible pathways to the surface	Variables: • Fracture coatings and their structures • Degree of alteration in the wall rock • Character of loose fracture infillings, amounts of breccia pieces and fault gouge	Samples to be selected: • Breccia fragments • Gouge material • Clay mineral samples • Altered and tectonised wall rock samples • Possible mineralogical or textural extremes.
Local Major Fracture zones (length 1–10 km; width 5–100 m)	Variables: The same as for Local Minor Fracture Zones	Samples to be selected: The same as for Local Minor Fracture Zones

Figure 2-2. *First geological conceptual model used for selection of samples for sorption and diffusion measurements: This model is assumed to be based on the surface mapping and the drill core mapping of the 2-3 core drilled boreholes from the initial site investigation (preliminary general geological model version 1.2 according to /SKB, 2001b/.*

2.5 Handling of uncertainties – general considerations

Uncertainties are introduced in all phases of the transport programme, from drilling, sampling, sample treatment and measurements to evaluation methods, modelling concepts etc. These uncertainties have to be accounted for and documented to provide confidence in the end result. Handling the uncertainties involved in constructing a site descriptive model has been documented in detail by /Andersson, 2003/. The issues that are considered to be of particular relevance for the laboratory measurement programme of retardation properties are listed and discussed in general terms below.

It should be noted that a low uncertainty not necessarily is required for all parameters, it is however essential that an uncertainty assessment is done for all parameters. Parameters that have a high importance or high sensitivity in the transport modelling or safety analysis should be prioritised in the laboratory investigations programme in order to minimise the uncertainty for these parameters. Inversely, parameters that have a low impact/sensitivity in transport modelling or safety analysis can be accepted with a larger uncertainty.

2.5.1 Conceptual uncertainty

Conceptual uncertainty concerns the uncertainty originating from a lack of understanding of processes and their interrelationships. Although conceptual uncertainty mainly is an issue for the safety assessment, the process understanding is discussed here since it is a question for the interpretation of retardation properties in form of a retardation model.

In the interpretation stage (described in Chapter 6), the characteristics of the different rock and fracture types is analysed and interpreted, including composition and parameter values with a description of the data uncertainty (see below). However, the conceptual uncertainty in the model needs to be addressed and questions asked, as e.g.: are the number of rock types, fracture types etc sufficient/too few/too many in the model, do we understand the processes involved for qualitative interpretation of laboratory and field experiments, are the model interpretations relevant etc. The conceptual uncertainty at this level cannot be measured or quantified directly; nevertheless, judgements of confidence can be made by e.g. internal and external reviews.

2.5.2 Spatial variability

Spatial variability concerns the variation in space of a parameter and is of importance for the matrix diffusivity and sorption properties, especially considering that the groundwater composition may vary strongly with the repository depth, which has a strong influence on the sorption properties. The influence of spatial variability is implemented in the laboratory programme by the following measures:

- measurement of sample scale variability (by using several size fractions, specimen thicknesses, sample replicates and directions in the measurements),
- measurement of large-scale variability by attempting to distribute sampling positions within the entire rock volume,

- use of resource efficient methods that enables multiple sampling positions (e.g. electrical conductivity measurements with frequent sampling along boreholes), and
- by addressing the variability in groundwater compositions in the sorption programme by using different groundwater compositions.

2.5.3 Temporal variability

Temporal variability concerns the variation of a parameter value in time. For sorption measurements, several time effects can play an important role, such as sorption reaction kinetics, mineral weathering (dissolution and alteration), diffusion kinetics etc. The impact and handling of these effects in the measurement programme is further discussed in section 7.3.5.

For diffusion measurements, time and space effects are coupled if the pore system of the rock is heterogeneous, which there are many indications of. In a heterogeneous pore system, the effective matrix diffusivity is dependent on the observation time and scale over which the observation is done. Therefore, the measurement programme involves observation over different sample sizes in order to investigate the possible impact of the heterogeneity of the pore system.

2.5.4 Scale

Scale concerns the spatial resolution of the description. For a spatially varying property, the scale is the size over which properties are averaged. Scaling effects should be considered for sorption and diffusion properties since there are indications of a coupled temporal-spatial dependency in the sample scale. Extrapolation of data from the measurement scale (parts of millimetres to centimetres) to larger scales requires attention to the combination of the time and scale effects.

2.5.5 Data uncertainty

Data uncertainty concerns uncertainty in the values of the parameters of a model. The uncertainties may be caused by e.g. measurement errors, interpretation errors or extrapolation of parameters that varies in time and/or space.

The measurement uncertainties for different methods are handled and reported according to the method descriptions. This means that, according to good laboratory practice, the combined uncertainty in data (from different sources of errors) should be reported, usually with a coverage factor of 2 (which corresponds to a 95% confidence interval). The uncertainty can either be assessed by a measurement uncertainty analysis, or be estimated based on repetitive measurements.

The measurement uncertainty for parameters of interest in the laboratory investigations is usually much smaller than the “natural” variability in the property that is measured. The parameter variation width or uncertainty can be given as max/min values or using statistical measures (e.g. standard deviation) depending on the amount of available data. It is important to recognise that the variability in the material properties is considered to be the main source of uncertainty in interpreted data. Consequently, the uncertainty estimation for interpreted model data should primarily focus on extrapolation errors and material variability.

The uncertainty in the retardation model is also dependent of the model concept; i.e. the interpreted amounts of fracture and fracture zone types and their compositions. This uncertainty can, to some extent, be tested by measurement of additional samples and evaluation of the impact on the re-interpreted model: if the model is changed it points towards a poor understanding/interpretation/data basis, if the model remains unchanged it points towards a robust model.

2.5.6 Sampling and material handling induced errors

Uncertainty is introduced due to sample disturbances caused by e.g. drilling (pressure release, porosity generation), sawing, crushing etc. These activities may lead to changes in porosity, which has an impact on the diffusion measurements, and mineral surfaces exposed to sorbing tracers. These issues are addressed in the strategy for the laboratory programme by using crushed and intact materials. However, laboratory experiments under natural pressures are not within the scope of the programme. Assessment of the effect of pressure release for intact rock samples will have to be done by comparison and extrapolation based on other experiments performed under natural pressure conditions. Examples of reference experiments are the laboratory diffusion measurements conducted under mechanical pressure by /Skagius and Neretnieks, 1986/, *in situ* diffusion/migration experiments in the Grimsel Test Site /Smith et al, 2001/ and *in situ* diffusion experiments such as the Long Term Diffusion Experiment currently being conducted at the Äspö Hard Rock Laboratory /Byegård et al, 1999/. The impact of sample disturbances is further discussed in section 7.2.

2.6 Database

Rock samples for laboratory analysis are usually taken from drill cores or as wall rock samples from surface or underground outcrops. Sampling of drill cores are registered in SICADA (SIte ChAracterisation DAtabase) according to SKB routines. All data in SICADA have a geographic reference, i.e. data are linked to a point on the surface, along a tunnel or a borehole /Munier and Hermansson, 2001/. Additional data on further subdivisions and preparations of the samples, geological description, *in situ* stress state, classification and information about performed analyses would be valuable add to the database and each field should be linked to the unique sample identification number. Such a sample data and analysis information sheet is exemplified in Table 2-2. The possible classification of the sample is an important part of the sample data sheet for the interpretation of analysis data in order to produce a retardation model for a site.

All measured retardation data should be included in SICADA, i.e. CEC, K_d for selected species, porosity values/gradients and diffusivities for fresh rock types, different fracture coating minerals, altered and tectonised wall rocks, fault gouge and breccia fragments of various compositions. The analysis data is inserted in fields in the database that are linked to the sample ID. Some examples of analysis data are given in the end of Table 2-2.

Table 2-2. Fictitious example of database sample data, analysis information and analysis data to be entered in SICADA for an open fracture drill core sample.

	Main sample:	**Subdivisions of main sample:**			
Sample ID #:	**KXTT3 15.50–15.60 m**	**KXTT3 15.50SC**	**KXTT3 15.50–15.51**	**KXTT3 15.51–15.53**	**KXTT3 15.53–15.60 F1**
Sample original location:	KXTT3 Äspö HRL 2980 m (378 m depth) TRUE-1 site	<<	<<	<<	<<
Sample type:	35 mm drill core, open fracture intersection (15.50 m)	Grains	Rock disc	Rock disc	Crushed material
Sample size:	35x100mm	0–1 mm	35x10 mm	35x20 mm	<63 µm
Sampling date:	1999-05-01	1999-05-15	1999-05-15	1999-05-15	1999-05-15
Sampling method:	Abrasive high speed cutting	Scraped off with spoon	Low speed diamond sawing	Low speed diamond sawing	Low speed diamond sawing
Sampled by:	NN (SKB)	NN	NN (Geoprep AB)	NN (Geoprep AB)	NN (Geoprep AB)
***In situ* stress state**	–	–	–	–	–
Sample preparation:	–	–	Low speed abrasive grinding	Low speed abrasive grinding	Crushing and dry sieving (DIN xxxxx) to fractions: F1: <63 µm F2: 63–500 µm F3: >500 µm
Prepared by:	–	–	NN (Geoprep AB)	NN (Geoprep AB)	NN (SGU)
Sample destroyed:	Yes	Yes	No	No	Yes
Rock type (geology programme):	Äspö-diorite	–	–	–	–
Sample description (transport programme):	–	Surface coating...0.5 g. thickness ~1mm	Mylonite, thickness ~10 mm	Altered Äspö-diorite, thickness ~20 mm	Äspö-diorite
Classification (transport programme):	Fracture/Major rock type	Fracture coating	Fracture mylonite	Fracture altered rock type	Major rock type
Type (transport programme):	Mylonite fracture/Äspö-diorite	Chlorite	Mylonite	Altered Äspö-diorite	Äspö-diorite
Classified by:	NN	NN	NN	NN	NN
Analyses:	–	Mineralogical composition (Method:xxx)	Through-diffusion measurement (SKB method)	Through-diffusion measurement (SKB method)	Batch sorption measurement (SKB method)
		BET-area (ISO XXX)	Porosity (ISO YYY)	Porosity (ISO YYY)	Porosity (ISO YYY)
		Batch	Electrical	Electrical	BET-area

	Main sample:	**Subdivisions of main sample:**			
Sample ID #:	**KXTT3 15.50–15.60 m**	**KXTT3 15.50SC**	**KXTT3 15.50–15.51**	**KXTT3 15.51–15.53**	**KXTT3 15.53–15.60 F1**
		sorption measurement (SKB method)	Conductivity Measurement (SKB method)	Conductivity Measurement (SKB method)	(ISO XXX)
Analysis data:					
Fracture transmissivity:	data	–	–	–	–
Porosity (ISO):	n.m.	n.m.	data	data	data
BET-area:	n.m.	data	n.m.	n.m.	data
CEC:	n.m.	data	n.m.	n.m.	data
$K_d(Sr^{2+})$ Water A	n.m.	data	n.m.	n.m.	data
$K_d(Cs^{+})$ Water A	n.m.	data	n.m.	n.m.	data
$K_d(Am^{3+})$ Water A	n.m.	data	n.m.	n.m.	data
Diffusivity (HTO):	n.m.	n.m.	data	data	n.m.
Formation factor (HTO)	n.m.	n.m.	data	data	n.m.
Formation-factor (EC):	n.m.	n.m.	data	data	n.m.
Etc...	**Etc...**	**Etc...**	**Etc...**	**Etc...**	**Etc...**

n.m. = not measured

A significant amount of retardation data (e.g. from Äspö HRL) already exists but is not compiled in SICADA. Existing data that can be used for comparisons with new data should be imported to SICADA in order to simplify such comparisons.

3 Characterisation plan for rock types and structures

The number of samples required to characterize a rock parameter depends on the homogeneity of mineralogy, structure and porosity of the rock material. Increasing heterogeneity and variability will increase the sampling need. An exact number of samples required to obtain a satisfactory statistic basis for the description of some property of a specific rock unit is therefore difficult to define beforehand.

Nevertheless, based on the geological variables and sample types discussed above and the parameters and methods for characterisation given in /SKB, 2001b/, a tentative rock characterisation plan is outlined in this chapter and presented in Table 3-1. The plan is based on measurements of samples from *three deep cored* boreholes per site. If more than three deep boreholes would be drilled, the total number of samples and measurements may not necessarily have to be increased; instead they can be spread out over several boreholes.

The plan should be regarded as a guide aimed to provide an estimation of a basic or minimum characterisation measurement programme at a site for the initial and complete site investigation, with regards to the goals described in Chapter 1 and the ambition levels described in section 2.3. However, in the real case all sampling and characterisation needs will have to be decided site-specifically after geological judgements with respect to the geological homogeneity and characteristics of the site.

The impact of sample disturbances caused by sampling and sample preparation is discussed in section 7.2.

3.1 Chemical composition of the groundwater

The chemical composition of the groundwater is site-specific and may also vary within a site. Sorption properties are dependent on the sorbing solute, mineral properties and the groundwater composition (pH, ionic strength, redox conditions, ionic composition etc). Measurements of sorption properties using different groundwater compositions may therefore be needed. This will multiply the number of sorption measurements rapidly. An alternative approach could be to perform a study of the influence of varying groundwater composition for the major rock type(s) and/or the most abundant fracture materials in order to limit the number of sorption experiments required. We recommend that a typical groundwater composition and variations of groundwater compositions that needs to be considered are based on site-specific data and are defined in collaboration with the hydrogeochemistry programme, see also sections 4.2.1 and 5.1.3.

The influence of water chemistry on diffusion properties is usually small enough to be neglected for low-salinity waters. Generally, ionic diffusion coefficients decrease with increasing salinity in a multi-component system. As an example, the decrease in diffusion coefficients between ionic species in freshwater and seawater is less than 10% /Li and Gregory, 1974/. It is therefore recommended that measurements of diffusion properties are performed using a water composition that is typical for the site.

However, if strongly saline waters exist at a site (ionic strength >0.5 M), additional measurements or scaling of data using theoretical relationships should be considered.

3.2 Sorption coefficient determinations

It is proposed that a minimum number of 15 samples for each major rock type is sampled and used for batch sorption experiment. This will enable a study of the statistical variation of the sorption characteristics of the major rock types. For the minor rock types identified within a site, it is foreseen that it will not be feasible to use such a large number of samples; the minimum number is therefore set to 3.

For the material which will be in closest contact with any “flowing water”, i.e. gouge material, fracture coating, breccia fragments, mylonite/cataclasites and altered wall rock, it is proposed that a classification of the fractures are performed. From each fracture type, 3–5 samples will be used for batch experiment. It is most likely that the actual available amount of rock material from the fracture intercept will be a practical limiting factor.

3.3 Diffusivity determinations

The determination of matrix diffusivity in the rock matrix is at minimum proposed to be performed according to:

- 50 rock samples per borehole (1 per 20 m) using electrical conductivity (EC) measurements are used to measure the large-scale variability of formation factor/diffusivity within the repository volume; i.e. a total number of 150 determinations using the electrical conductivity method (no extra sample replicates are used here).
- 15 of these samples (1 per 10 EC measurements) are selected for comparative verification measurement using through diffusion technique with tritiated water (HTO) as tracer (no extra sample replicates are used here).
- 2 rock samples from each major rock type are cut to 0.5, 1, 3 and 5 cm samples with triplicates for each sample thickness. These samples are used for study of
  - the diffusivity versus sample length (pore connectivity study),
  - the homogeneity of the major rock type in the sample scale (by using triplicates from the same rock sample), and
  - the homogeneity of the major rock type within the repository volume (by using 2 different rock samples per major rock type in combination with the other through-diffusion samples above).
- 3 integrated samples from each fracture type and 3 integrated samples from each local minor/major fracture zone type are exposed for diffusion experiments. It is estimated that 20% of these samples are large enough to isolate >1cm thick samples of pure mylonite/cataclasite and altered wall rock to be used for individual diffusivity determination of these materials.

- Evaluation of sorption coefficient for sorbing tracers in one intact rock sample per major rock type. This experiment can be included in the same diffusion cells as HTO, why no extra samples are needed in this case.

- Pore connectivity verification for one 10 cm sample for each major rock type using the He-gas method.

In situ electrical resistivity measurements, single hole tracer tests (in-situ sorption experiments) and electro-migration experiments are methods that are under development and can therefore not be planned at this stage.

3.4 Porosity determinations

The porosity determinations to be performed in the laboratory programme are proposed according to:

- porosity measurements using standardised water saturation technique for the intact rock samples for diffusion measurements mentioned above. A reduction can be made by e.g. not measuring porosity for each EC-measurement. However, porosity is an important factor that the diffusivity/formation factor can be correlated to, e.g. Archie’s law /Parkhomenko, 1967/. Hence, we recommend porosity measurements for all EC/HTO-diffusion samples. Porosity measurements are also relatively inexpensive.

- 15 measurements of porosity using the PMMA method (1 sample per rock type/fracture type/local major or minor fracture zone type). These measurements are analysed for porosity gradients and distributions.

Table 3-1. Tentative rock characterisation matrix. This is a plan for the laboratory programme to be conducted during the initial and complete site investigations of one site. The plan is based on sampling drill cores from three deep boreholes at one site. Numbers given in the table are recommended minimum number of samples to be measured for each sample type and for a given method if nothing else is stated as a footnote. Example: A minimum of 15 samples from different locations within a site are recommended for batch sorption measurements of K_d for each major rock type. Note that samples as defined here are individual rock samples from different locations on a site. A sample may be further divided into sub-samples or replicates in a specific method, which is not considered in this rock characterisation matrix. Sample replicates etc are discussed in section 6 and/or in the specific method descriptions.

Table 3-1			**Rock types** (min. # of samples for each rock type)		**Fracture / Local Minor/ Major FZ types** (min. # of samples for each fracture / LM/M FZ type)					
Property	Method	Parameters	Major rock types	Minor rock types	Breccia fragments 12)	Gouge 1)	Fracture coating 2)	Mylonite/ Cataclasite	Altered wall rock 5)	Extremes
Sorption Coefficients	Batch sorption	K_d ($K_a^{3)}$)	≥15	≥3	≥3	≥3	≥3	≥5/5	≥5	?
	Through-diffusion	K_d (Level 2) 6)	≥1	–	–	–	–	≥1/1	≥1	–
Matrix Diffusivity / Form. Factor	Through-diffusion	D_e vs. length (pore connectivity and foliation, HTO 8))	≥2 4)	–	n.a.	n.a.	n.a.	–	–	–
	Electrical conductivity (EC) – lab	D_e or F (spatial variability, fixed length)	**Screening, one sample taken per 20m in the drill core (total 150 samples)**		n.a.	n.a.	–	–	–	?
	Through-diffusion	D_e or F (quantitative data, fixed length, HTO 8))	**Calibration, 1 sample out of 10 EC samples is selected (total 15 samples). Selection directed to obtain volume coverage / homogeneity of the major rock types.**		n.a.	n.a.	≥3 9)	≥3/3 9)	≥3 9)	?
Pore Connectivity Verification	Gas diffusion	Minimum penetration depth	≥1 (~10 cm)	–	–	–	–	– 10)	– 10)	?

Table 3-1			**Rock types** (min. # of samples for each rock type)		**Fracture / Local Minor/ Major FZ types** (min. # of samples for each fracture / LM/M FZ type)					
Property	Method	Parameters	Major rock types	Minor rock types	Breccia fragments[12)]	Gouge[1)]	Fracture coating[2)]	Mylonite/ Cataclasite	Altered wall rock[5)]	Extremes
Matrix Porosity[8)]	DIN/ISO (water absorption)	ε_p	According to the Geology programme and method descriptions for batch sorption, through-diffusion and electrical conductivity methods.		All samples	–	–	All samples	All samples	?
	PMMA	ε_p and ε_p-distribution and ε_p-gradient from fracture[11)]	≥1	≥1	≥1	n.a.	n.a.	≥1	≥1	?
Surface Area	BET (ISO 9277:1995	*A*	Same as for batch sorption (screening and sample selection method)[7)]							
Cation Exchange Capacity	CEC (ISO 13536)	CEC	Same as for batch sorption (screening and sample selection method)[7)]							

[1)] Lack of material may demand separate methodology for gouge. [2)] Fracture coatings are scraped off from surfaces. [3)] K_a is measured only if a certain difference in BET-surfaces between the smallest and largest size fractions of the crushed material is obtained (according to the method description for batch sorption experiments, SKB TD-540 002). K_a-data will be obtained for the same amount of samples as used for the batch sorption K_d experiments if BET-areas differs enough between the size fractions (see section 6.3.4). [4)] Sub-samples of different thickness (e.g. 0.5, 1, 3, 5 cm) are cut from each rock sample in order to study the pore connectivity dependency of diffusion distance/penetration depth using HTO tracer. Rock samples should cover the main existing foliation types on the site (along/across foliation direction). [5)] The alteration types are linked to the major rock type and if the same type of alteration is found in e.g. fractures and fracture zones a total of the proposed number of samples for one structure unit is enough irrespective of the sample origin. [6)] Through-diffusion geometry using the same tracers as in Level B of the batch sorption method in order to verify the impact of sample disturbance (crushing vs. intact material). K_d is evaluated from the concentration profile within the sample, i.e. long samples are used and analysed before breakthrough has occurred. [7)] BET-surface and CEC (cation exchange capacity) are done (according to Level C in section 6.3.3) for the batch sorption samples as a first screening in order to select 25% of the samples for further sorption measurements. [8)] Matrix porosity is also obtained as a secondary parameter in the evaluation of all through-diffusion experiments using HTO tracer. [9)] If the thickness of the layers are >1cm, isolation of the different layers (mylonite/cataclasite/altered wall rock) is done. If the thickness of the layers are <1 cm, experiment is performed using an integrated sample of all the layers. [10)] Verification of pore connectivity in alteration material is possible if desired and if sample supply is not limiting. [11)] Porosity distributions and gradients (for fracture materials) are evaluated from the same impregnated sample. [12)] Breccia fragments only apply for local minor/major fracture zones.

4 Working methodology

The working methodology for the programme for the transport properties of the rock is described in /SKB, 2001b/. Generally, the programme is dependent on a relatively large quantity of site-specific data and of the work done in related disciplines before a meaningful evaluation and modelling of the transport properties can be done. The contributions from the other disciplines are shown in Figure 4-1. During the complete site investigation, the work with laboratory and field measurements and transport modelling will be performed in an iterative process, see Figure 4-1.

This work comprises analysis of existing laboratory data, supplementary data collections and interpretation of the retardation properties for the major rock types and structures, which is further described below. The overlap with the transport properties evaluation and modelling work, described in the report "Transport Properties Site Descriptive Model – Guidelines for Evaluation and Modelling" /Berglund and Selroos, 2003/ is indicated in Figure 4-1. The development of the Transport Properties Site Descriptive Model comprises the work of producing an integrated geological-hydrogeological transport model for a whole site, whereas this work focuses on collection, analysis and interpretation of retardation data, which will be delivered as an input to the transport modelling work in the form of a retardation model.

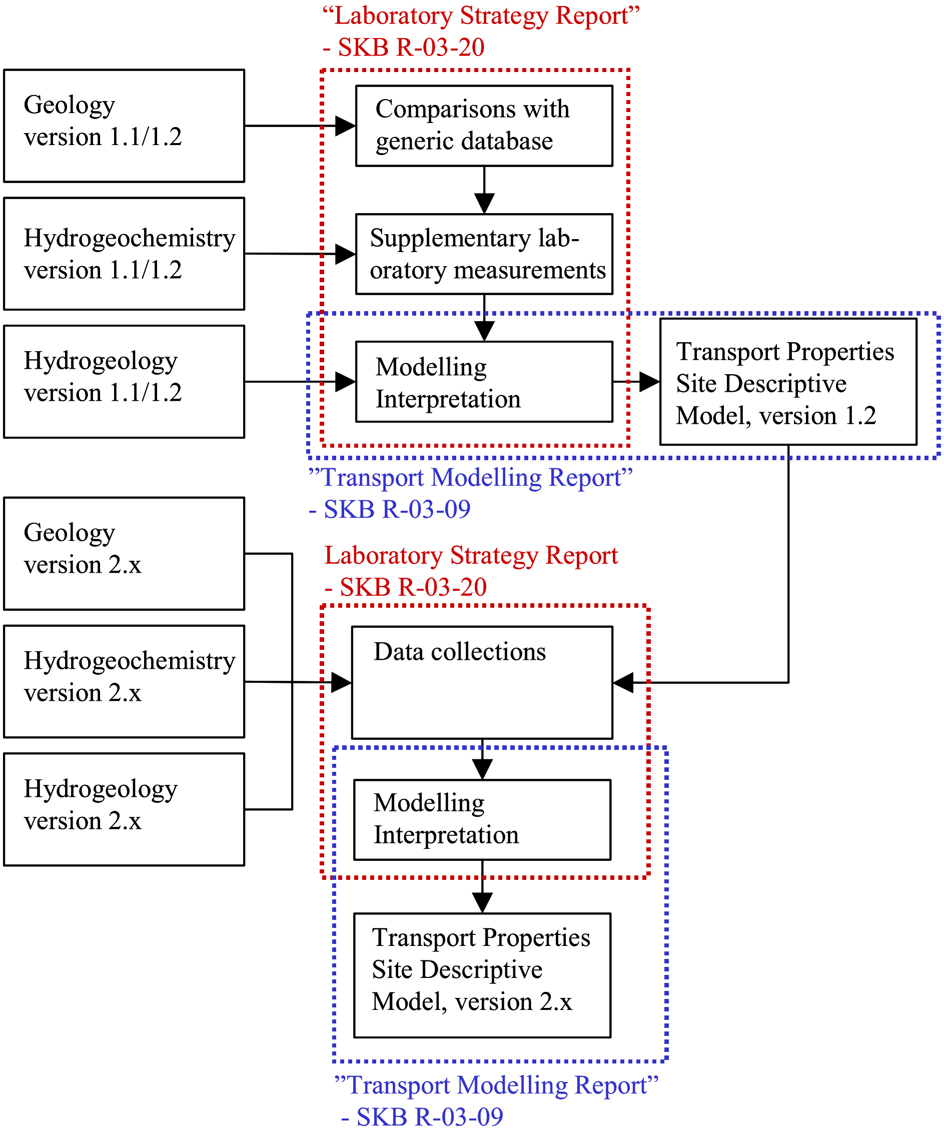


Figure 4-1. *Working methodology for development of Transport Properties Site Descriptive Models and links to related disciplines /from SKB, 2001b/. The scope of this work and the work included in the development of the Transport Properties Site descriptive Model /Berglund and Selroos, 2003/ is indicated within the dotted frames.*

4.1 Working methodology for the laboratory measurement programme

A more detailed general working methodology for the laboratory programme is presented in Figure 4.2. In the early phase of the site investigations focus will be on building a database of parameters that are important for the retardation properties. The starting point for sampling and laboratory measurements is mainly the Geological model versions 1.1 and/or 1.2 and the generic database compiled from existing data from various field and laboratory measurements.

In the first step during the initial investigations of a site, the database is compared with the information on rock types, fracture types etc from the Geological model version 1.1 and/or 1.2 and groundwater and hydrological data from the hydrogeochemistry and hydrology programs. It is thus a requirement that a generic database exists at this point. The generic database at that stage will be made up from a combination of data from the following sources:

- Site-specific data from investigations of material from Finnsjön and Äspö, review is in progress /Byegård, 2003/.
- The Äspö Task Force Task 6C report /Dershowitz et al, 2003/ which is a semi-synthetic model based on compilation of data from the TRUE Block Scale Experiment at the Äspö HRL.
- The SKB generic sorption database /Carbol and Engkvist, 1997/ and the corresponding diffusivity database /Ohlsson and Neretnieks, 1997/.

Based on the results of the comparison, and the proposed characterisation programme in this report, the need for sampling and analysis is defined and a sampling and measurement programme is started. Collected data are inserted in the database. The control of the sampling and analysis programme is further described in Chapter 5.

In the next step, primary retardation data are analysed and interpreted to a descriptive retardation model, which is further described below and in Chapter 6. The interpreted retardation model (including quantitative interpreted data) is delivered as an input to the development of the Transport Properties Site Descriptive Model. However, since laboratory and field measurements are time consuming, the Transport Properties Site Descriptive Model 1.2 will likely have to be developed without the results of the first laboratory measurements.

After the initial investigations of the site and when the first laboratory measurements are reported, the database could be used to compile a "parameterisation" of the retardation properties along potential flow paths using the updated conceptual geological model version 2.x from the complete site investigation. This interpretation and parameterisation is further developed in Chapter 6. Data collection, updating of the database and re-parameterisation of the retardation properties will be repeated in an iterative process.

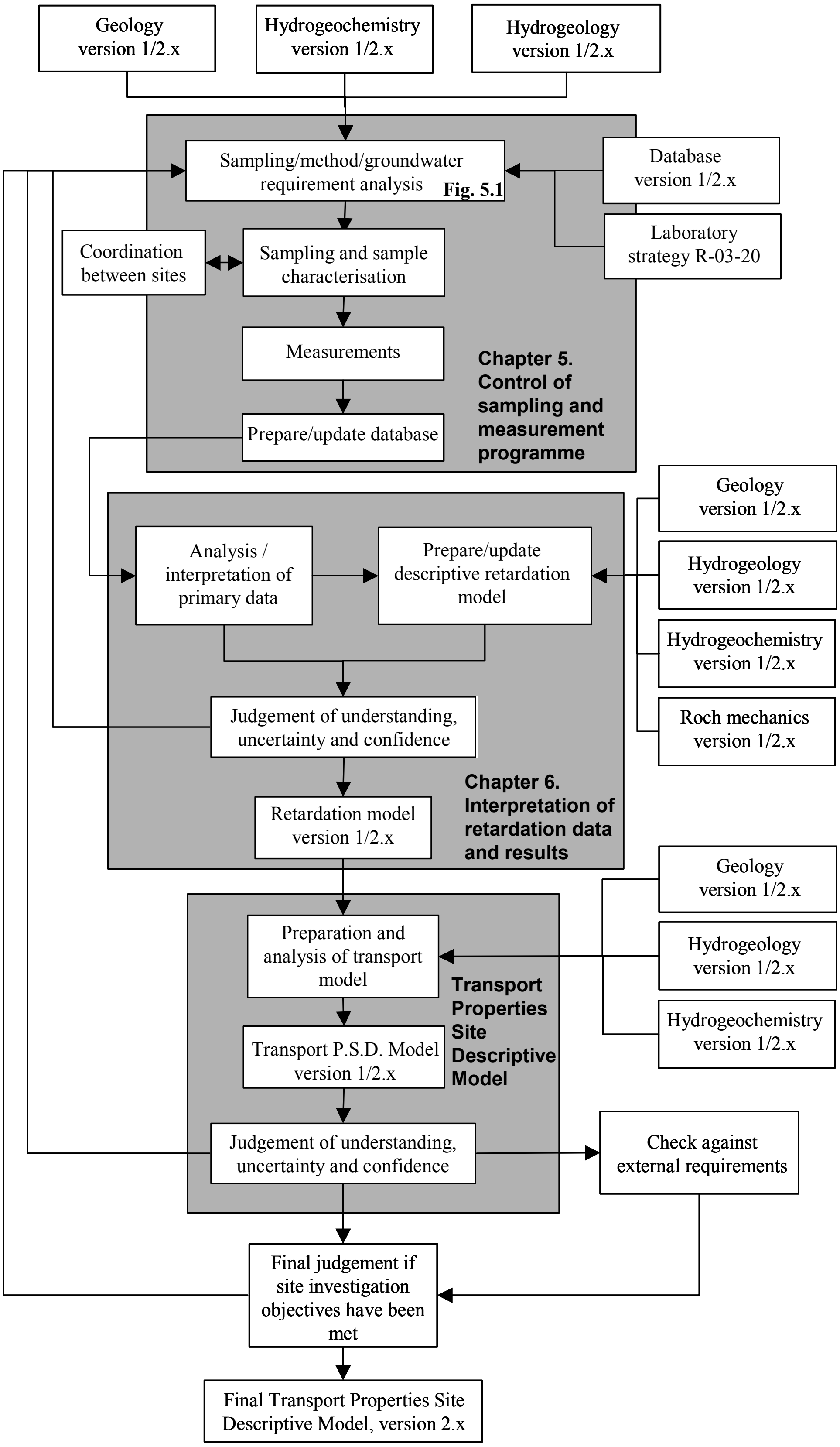


Figure 4-2. *Working methodology for the laboratory programme showing the control of sampling and measurements (Chapter 5), the interpretation of retardation data (Chapter 6) and the development of the Transport Properties Site Descriptive Model which is controlled by /Berglund and Selroos, 2003/.*

4.2 Interaction needs

4.2.1 Other subject areas

Geology programme

The geology programme will provide rock type and structure unit descriptions according to /SKB, 2001b/, which will constitute the basis for the sampling and laboratory measurement programme of transport parameters. A close collaboration with the geology programme is foreseen for the laboratory sampling and measurement programme.

Hydrogeology programme

The hydrogeology programme provides data on flow distribution in structures and borehole sections, which contributes to the selection of suitable borehole sections for tracer tests. The method description for transport modelling needs a link between different fracture types defined in this work and a hydrogeological property, preferably fracture transmissivity. This would simplify the treatment in the modelling of different types of structure units having different retardation properties, providing that a correlation exists between the fracture type and the hydrogeological properties. A proposed solution to this problem could be to use the transmissivity from flow logging as a link. The requirement is that sampling of fractures is done only for fractures that have an evaluated transmissivity.

Hydrogeochemistry programme

The hydrogeochemistry programme contributes hydrochemical and geochemical data of great importance for sorption and retardation properties. The composition of typical groundwaters for a site should be defined in collaboration with the hydrogeochemistry programme.

Rock mechanics programme

The rock mechanics programme provides data on the stress state (magnitude and direction) of the samples based on measurements or interpolations. This information is mainly used as supporting data for interpretation of laboratory measurements, but may also in some cases be used as sample selection criteria.

4.2.2 Safety analysis and transport calculations

The laboratory measurement programme should be performed in close co-operation with the transport modelling team (i.e. the developers of the Transport Properties Site Descriptive Model) which are the main receivers and users of data /Berglund and Selroos, 2003/. In order to ensure that the data requirements for safety assessment are fulfilled, it is important to have a dialogue with and receive feedback from this group already from the planning stage to the point of data delivery. The aim of the dialogue is also to support safety assessment with presentation of results and how the transport data is organised. Furthermore, safety analysis and transport calculations may have requirements on special data representation and extrapolation of site data that can be done in co-operation with the safety analysis. Important information on parameter sensitivity and uncertainty can also be transferred from the transport modelling and safety analysis to the laboratory investigation programme. This information can be used in order to give priority to reduce uncertainty for parameters that have a strong impact on the transport calculations or safety analysis.

5 Control of sampling and laboratory measurement programme

5.1 Sampling and method requirement analysis

The control of sampling and analysis needs to be flexible and adapted to local site conditions; therefore the proposals given here are aimed as a guideline for the real case. A critical first sampling should be initiated as soon as the core logging of the first three deep boreholes is finished. This sampling should include samples that are required for time-consuming laboratory measurements, so that those can be started in an early phase of the investigations. In order to maximize the experimental time, planning of the first sampling activities should start as soon as the preliminary evaluation of the core logging of the first three boreholes is finished.

The first round of sampling activities, exemplified in Figure 5-1, should be initiated in a planning meeting with representatives from the geology, hydrogeology, hydrogeochemistry and the laboratory investigation programmes. A first conceptual geological model according to Figure 2-2 is developed based on the general geological model and a groundwater typical for the site is defined based on the results of the hydrogeochemistry program. The decision for sampling and analysis should be based on qualified judgements with consideration to the general and programme specific goals of the site investigations (see Chapter 1).

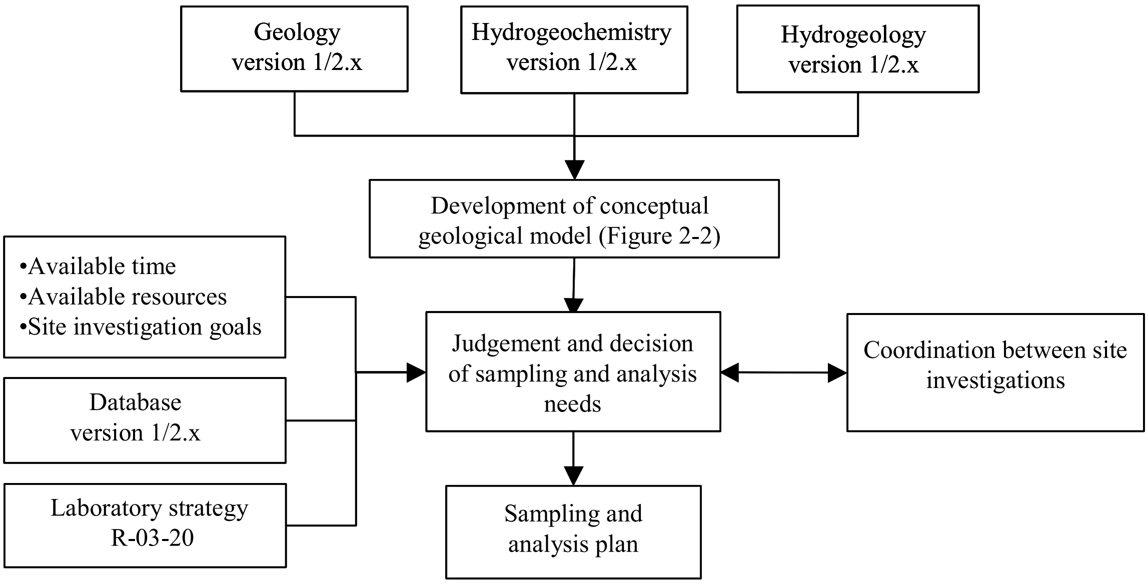


Figure 5-1. *Flow chart for the decision of sampling and analysis needs. The sampling and analysis plan will be based on judgements from the representatives of the different programmes involved.*

5.1.1 Sampling positions

Sampling for laboratory measurements will primarily be directed to selected parts of drill cores based on the desired sample type (rock type, fracture type etc) and the variation in geological property that is searched for. If possible, the different sampling locations for a certain sample type should firstly be well distributed throughout the bedrock volume at the repository level and secondly above and below the repository level in order to cover variations within the site volume. These sampling directives can probably be fulfilled concerning rock types and different fracture types whereas the sampling of fracture zones will be largely given by the drill core intercepts. It is important that the sampling is directed to cover the main geometrical units defined in the general geologic model. It is also generally desired that, if possible, samples for geological characterisation and measurement of retardation properties are positioned next to each other along the drill core. Thereby, supporting data from the geology programme may be coupled to the transport data and covariation analysis is enabled. The priority order for choice of sampling locations of a specified sample type can be summarised as:

1. Desired sample type at repository level depth.
2. Distribution of desired sample type in site volume at repository level depth.
3. Distribution above and below repository level depth.
4. Sample major geometrical/structural units.
5. Remove samples next to each other from the drill core (desired for samples for different analysis methods within the transport programme and samples removed for the geological characterisation).

If several tests should be applied on the same sample it is important that the subdivision of the sample yields comparable units. It is therefore suggested that the sub samples are tested concerning homogeneity in porosity, density and if possible chemical composition. For rock samples this can easily be done but for e.g. fracture samples where the amounts of material are much more limited it is a more complicated task.

The database will be based on the geographical position of the samples as the main description. It is therefore advantageous in the case where several different analyses will be performed that the different samples of geologic material are taken as close to each other as possible. Furthermore, in order to facilitate reference of the data to the transport modelling, it is advantageous if the data can be referred to hydraulic parameters determined close to the sampling position.

5.1.2 Classification and model test

The quality of the retardation model and of the ability to classify sample types can be tested by use of additional control samples. When the sampling is done, one or a few extra samples are removed for each sample type. Laboratory measurements, analysis and development of a retardation model are done as planned for the main samples. Then the control sample is measured and it can be tested if the properties of this sample fall within the prediction of the model for that sample type.

5.1.3 Groundwater selection

Based on the groundwater characterisation of the site, a groundwater composition that is typical for the repository depth is determined in collaboration with the hydrogeochemical programme. This water composition will be used in most laboratory experiments. Additionally, groundwater of different composition of importance at a site should be defined. Typically, groundwater of higher and lower ionic strength could be selected as additional groundwater types. These may be used in additional sorption measurements for selected elements.

5.2 Sample analysis

In order to decrease the number of samples to be removed from the drill core repository, the main sample can be divided into sub-samples to be used in the different methods. Some samples may also be used in sequence for non-destructive methods. Measurement of several transport parameters on the same main sample is desired from a statistical point of view, since this will enable a parameter covariation analysis /Berglund, 2002/.

For the major rock type samples, sufficient amounts of core material are expected to be available for measurements of several parameters on each sample. The supply of fracture samples may be limited, i.e. that fewer analyses can be done on each such sample. In case of limited access to samples, priority should be given to analysis of the property that is judged as least well known or most important for the safety analysis.

The logistics for sample “flow” and analysis will be controlled by the sampling and analysis plan. The majority of the samples will, after sampling and sample characterisation, first be analysed for porosity and then for sorption or diffusion properties. In the present stage, it is not meaningful to describe the sample and analysis logistics in more detail since it depends too much on the site characteristics.

6 Description of the retardation model

The interpretation of retardation data is a collective task for the representatives from the different disciplines involved in the measurement programmes. The interpretation and analysis gives an updated retardation model and a judgement of the quality of the retardation model and of the database. The judgement of quality results either in a continued and updated sampling and analysis plan or, eventually, in a final database and retardation model.

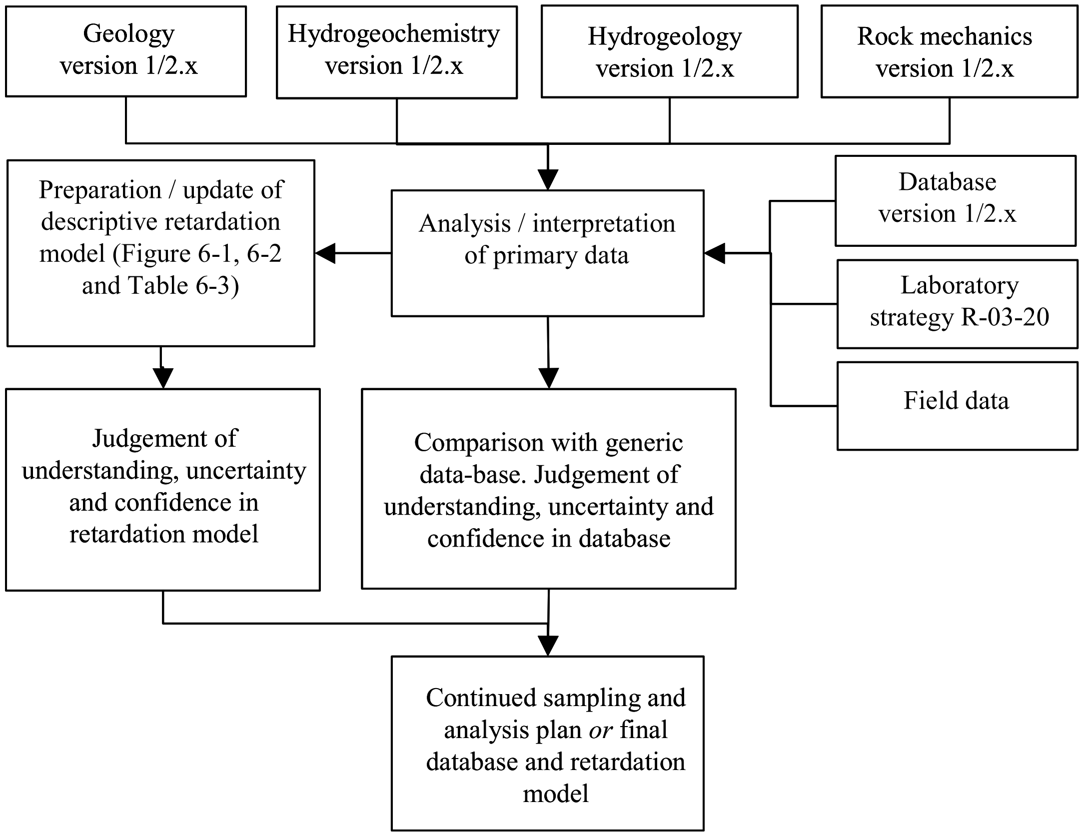


***Figure 6-1**. Flow chart for the interpretation of primary data and preparation of the retardation model.*

6.1 Interpretation of primary data

In the interpretation of primary data a compilation of data for different sample types defined in the first geological model is done. Data are compared and analysed regarding:

- observed differences in properties between different rock types etc,
- impact of structural/textural variations, alteration, site depth etc,
- homogeneity/heterogeneity in defined rock sample types,
- identification of extreme values or materials,
- uncertainty in data, and
- a general comparison of laboratory and field data (provided that field data are available).

It is important that uncertainty in data is analysed and described, both in terms of sample variations (the true variation in a property between different samples) and in measurement uncertainties (the uncertainty in the measurement of a sample property which is caused by a number of different sources of errors in the measurement method).

6.1.1 Comparison and judgement of database

The site-specific database is compared to the generic database in order to identify deviations and to establish the level of agreement in data. The result of the comparison is used for a decision of continued sampling and analysis needs. Furthermore, specific needs of data may come up based on the site-specific geological and hydrogeochemical conditions. For a final acceptance of the site-specific database, a general consensus in the understanding and confidence in the quality of the database is required. Specifically, the agreement and deviations from the generic database should have been confirmed and identified. It is also important that the remaining uncertainty in the retardation database is on an acceptable level in relation to other data uncertainties in the safety analysis. The acceptance level can be judged in a dialogue with the transport modelling and safety analysis teams. A tool for judgement of the quality in data is to use the model test samples as mentioned in section 5.1.2.

6.2 Preparation/update of retardation model

The retardation model is constructed as discussed in section 2.1–2.3 based on the latest geological model and the results of the laboratory investigations. Firstly, the retardation model is prepared or updated, i.e. that the different rock types, fracture types etc needed to describe the transport properties are defined. Next, the characteristics of the different types is analysed and interpreted, including composition and parameter values with variation width or uncertainty. The parameter variation width or uncertainty can be given as max/min values or using statistical measures (e.g. standard deviation) depending on the amount of available data.

A hypothetical example of a description of the rock units is given in Figure 6-2 and the parameterisation of fracture types and local fracture zones can be visualised as in Figure 6-3. For each rock unit, the parameterisation can be described as proposed in Table 6-1. At an investigated site there may consequently be a number of x tables for rock types, y tables for fractures, z tables for local minor fracture zones ending up with x+y+z tables as input for the modellers to deal with. It is then the modeller's choice how to incorporate retardation data in the transport model or safety analysis model.

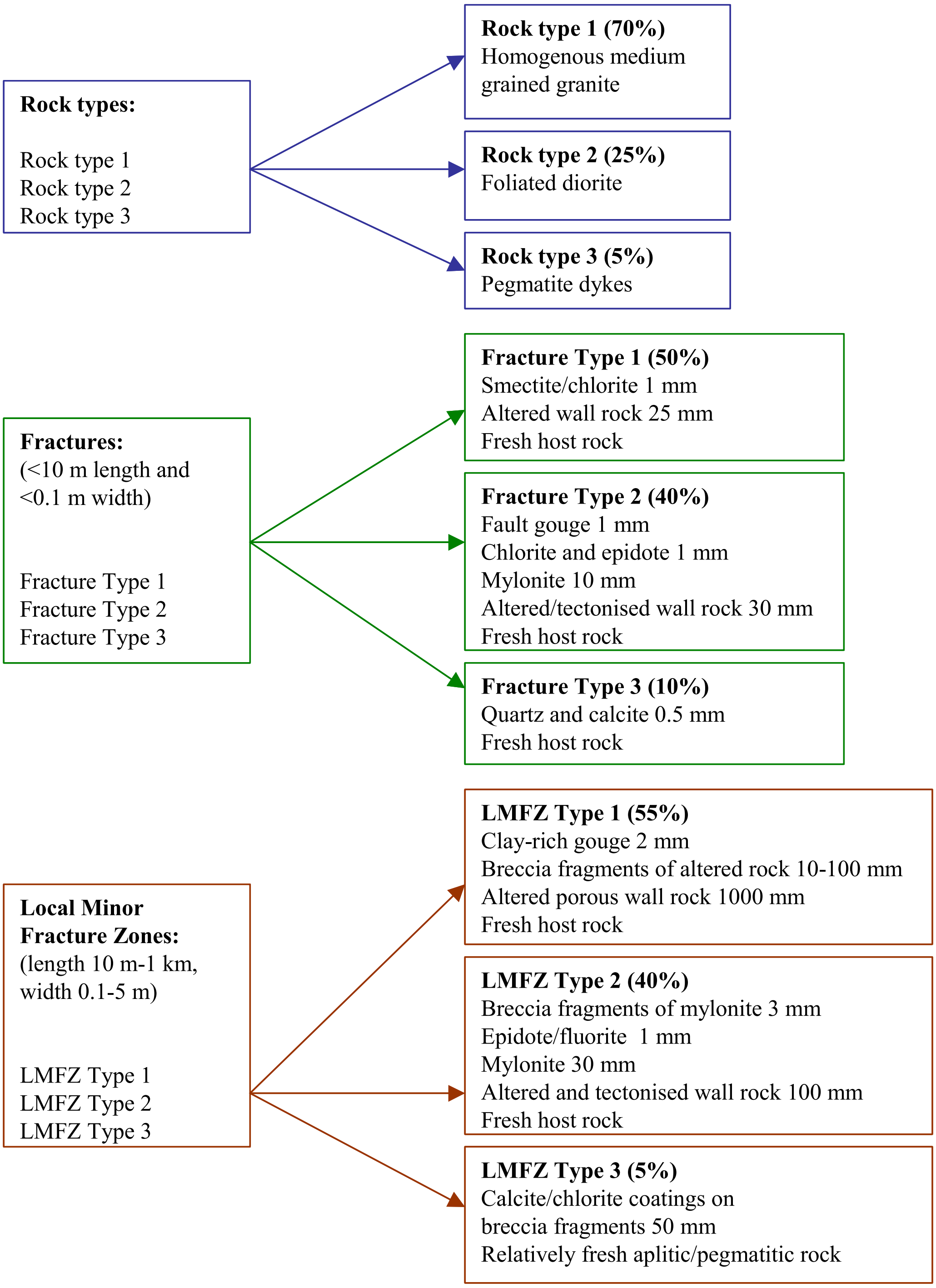


Figure 6-2 *A tentative description of the rock units along the flow paths. The %-values is an estimation of the proportion of a rock, fracture or local minor fracture zone type within a site.*

Table 6-1. Hypothetical example of a compilation of interpreted retardation properties for Fracture Type 2.

	Gouge	Fracture coating	Mylonite	Altered wall rock	Fresh host rock
Distance[1]	1 mm	0–1 mm	1–10 mm	10–30 mm	30 mm –
Porosity[2]	0.5 (estimated open fracture voids)	0.10 (estimated) No gradient	0.03±0.01 (mean±1s) Linear gradient from 0.05 to 0.01 Cross-sectional log-normal distribution $10^{(-2.4\pm0.5)}$	0.008±0.002 (mean±1 st.dev.) Linear gradient from 0.01 to 0.005 Cross-sectional log-normal distribution $10^{(-1.7\pm0.5)}$	Data available in the data description for the host rock
Diffusivity[3]	5E–10 m^2/s (calculated)	2E–10 m^2/s (calculated)	1±0.3E–12 m^2/s (mean±1s) Linear gradient from 3E–12 to 7E–13 m^2/s.	5±2E–13 m^2/s (mean±1s) Linear gradient from 7E–13 to 3E–13 m^2/s.	Data available in the data description for the fresh host rock
Mineral content and grain sizes[4]	–	–	–	–	–
Sorption capacity[5]	–	*K*d(Cs) for water type A: 5±2E–2 m^3/kg etc	*K*d(Cs) for water type A: 1±0.5E–2 m^3/kg etc	*K*d(Cs) for water type A: 8±3E–3 m^3/kg etc	Data available in the data description for the fresh host rock
Portion of conducting structure[6]	40%				
Transmissivity interval[7]	1E–6<T<1E–7 m^2/s				

1. Average/typical distance of e.g. the altered zone perpendicular to the fracture surface

2. Porosity can be given as estimated value, mean value with standard deviation or maximum variation width and as porosity distribution and porosity gradient.

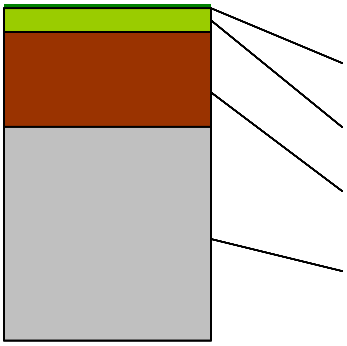
3. Diffusivity is given for HTO and calculated for sorbing species according to /Ohlsson and Neretnieks, 1997/. Surface diffusivity for sorbing species is also considered according to Ohlsson and Neretnieks.

4. Mineral contents should also include description of grain size distribution if possible.

5. The default value for species not listed in the table is the value given in the generic database. Data can be given for a certain species if this specie is interpreted to deviate significantly from the generic database. Correction factors may also be given for groups of elements according to the discussion in section 6.2.1 and 7.3.3.

6. Describes for how large portion of the entire fracture size class at the site the given description is valid.

7. Typical fracture transmissivity interval based on data from flow logging of the sampled fracture intersections. This value and the fracture frequency can be used in transport modelling to link retardation properties to fracture transmissivity.



Thickness	Mineral/rock	Mean Porosity (-)	K_d(Cs) (m^3/kg)	D_e(Cs) (m^2/s)
0-1 mm	chlorite	0.05	5E-2	5E-12
1-10 mm	mylonite	0.02	1E-2	1E-12
10-30 mm	altered rock	0.01	8E-3	5E-13
30 mm -	fresh host rock	0.005	5E-3	2E-13

Figure 6-3. *Hypothetical example of fracture layer description and interpreted data for some selected parameters for Fracture Type 2.*

6.2.1 Interpreted sorption data

It would be very impractical to determine individual sorption data for all sorbing species for all combinations of groundwater compositions and rock type. It is instead proposed that some sorption data will be calculated using well-established chemical analogies between different elements. This procedure is further discussed in section 7.3.3.

6.2.2 Judgement of retardation model

A tool for judgement of the quality in the description of retardation properties is to use the model test samples as described in 5.2.1. For a final acceptance of the site-specific retardation model, a general consensus in the understanding and confidence in the quality of the geological and hydrogeological models, the retardation database and the retardation model are required. It is also important that the remaining uncertainty in the retardation model is on an acceptable level in relation to other data uncertainties in the safety analysis. The acceptance level can be judged in a dialogue with the transport modelling and safety analysis teams.

7 Method specific strategies and recommendations

7.1 General conditions for the laboratory experiments

For tracer experiments aimed for determination of transport parameters in laboratory experiment (i.e. batch sorption experiments and diffusion experiments), the general conditions will be selected in order to resemble the conditions applied in the TRUE-1 laboratory experiment /Byegård et al, 1998/, i.e.;

- To obtain reducing conditions that resemble the natural oxygen-free prevailing in the groundwater, the experiments will be performed in glove boxes with a continuous flow of N_2 or Ar. It is of course not possible to obtain strict site-specific conditions with respect to the electrochemical conditions so the purpose is mainly to avoid as much oxidation of the rock material as possible.
- Since *in situ* sampled groundwater is suspected to be exposed for oxidation and/or formation of colloids, synthetically produced groundwater will be used instead. This synthetic groundwater will be produced on the laboratory by mixing distilled water with salts in order to obtain water according to the composition determined for the natural groundwater.
- The concentration of the tracer to be studied is selected in order to resemble the natural abundant concentration of that element in the natural groundwater. In order to fulfil this prerequisite and at the same time obtain a good dynamic measurement range, the use of radioisotopes (or possibly enrichment of a stabile isotope) is necessary. In the cases where this criteria can not be fulfilled (e.g. an appropriate radioisotope or a stable isotope enrichment is not available for the present tracer, the background concentration is too low to allow a satisfying dynamic range even when radioisotopes or stabile isotopes are used) the concentration is set as low as possible to allow measurement conditions that can fulfil the desired limits of uncertainty within the method.

7.2 Addresses of disturbances of the geologic material caused by sampling

A general problem with laboratory investigations of transport parameters on geologic material is the stress release caused by the sampling. It is suspected that this stress release may cause an increased porosity that is non-representative to the *in situ* rock material. These disturbances are most likely to be considered as irreversible; it is not likely that attempts to recreate the stress in the laboratory will restore representative conditions. Results and conclusions from sorption and diffusion experiment performed under *in situ* conditions within the site investigation programme must therefore continuously be compared and implemented in the laboratory experiments.

It is reasonable to assume that intact parts of drill cores are less influenced by sampling disturbances than what crushed rock material would be. One could therefore assume that sorption studied by a diffusion experiment instead of batch sorption experiment would be one way to decrease any artefacts caused by the pressure release. It has been shown /Johansson et al, 1997/ that in saline groundwater environment, through-diffusion curves of Sr^{2+} in 2 cm rock coupons can be obtained. Penetration profile studies of the stronger sorbing tracer Cs^{+} are possible if diffusion times of ~1 year are used /Johansson et al, 1998/. However, it has been indicated that evaluation of sorption coefficients from diffusion experiments are likely to be influenced by heterogeneity of the rock material /Johansson et al, 2000, Byegård and Widestrand, 2002/. Furthermore, indications have been obtained that mobility in the sorbed phase (surface diffusion) may give an increased mobility /e.g. Ohlsson, 2001/; i.e. the surface diffusion coefficient must be known in order to evaluate the sorption coefficients from diffusion experimental data. The impact of both these processes is that an increased diffusion will be observed compared to the situation of diffusion in a homogeneous medium and to the situation of only pore diffusion, respectively. Evaluation of the diffusion data without including any of these processes will cause an underestimation of the sorption coefficients.

Accordingly, batch sorption experiments are proposed to be the main technique for sorption coefficient determination. However, it is proposed to use a low number of diffusion experiments in order to have supporting data for a possible conservative approach, i.e. using diffusion data for evaluation of sorption coefficients by using only a homogeneous pore diffusion model.

Attempts are presently made to use electro-migration for a faster penetration of tracer into crystalline rock /Lövgren and Neretnieks, 2002b/. In the case that this approach turns out to be successful, sorption experiment influenced by electro-migration can be used as a valuable tool to address sorption on intact rock. However, further research is necessary in order to develop and implement this method to the site investigation programme.

7.3 Batch sorption experiments

7.3.1 Selection of tracers

In their review of sorption coefficients, /Carbol and Engkvist, 1997/ list 28 elements that have radionuclides with potential influence on the safety assessment of a repository of spent nuclear fuel. It is most probably not feasible to include all these elements in the sorption coefficient determinations within the site investigation programme. Instead, for a large number of the radionuclides, values of the sorption coefficients will have to be imported from other sources. A selection of elements that are appropriate to include in the present investigation therefore has to be done.

An identification of different classes of investigations using different methods and/or radionuclides has therefore been done, according to Table 7-1. The rationale with doing this classification is that a large number of rock material could be investigated using the level C or B, i.e. using less laborious methods to obtain a general view of the sorption capacity. Consequently, investigations according to level A should be reserved for a few numbers of combinations of groundwater compositions and rock materials.

Table 7-1. Selections of radionuclides within the different levels of batch sorption experiment to be used in the SKB site investigation programme.

Level	Selection type	Procedure/radionuclides
C	Determination of cation exchange capacity (CEC) combined with specific surface area BET measurement	Procedure according to ISO 13536 (CEC) and ISO 9277:1995 (BET)
B	Level C + Sorption experiment using Cs^{+}, Sr^{2+} and Am(III)	$^{134}Cs^{+}$, $^{85}Sr^{2+}$, $^{241}Am(III)^{A}$
A	Level B + Selection of radionuclides/elements representing different oxidation states, safety assessment perspective	$^{134}Cs^{+}$, $^{85}Sr^{2+}$, $^{226}Ra^{2+}$, $^{63}Ni^{2+}$, $^{241}Am(III)^{A}$, $^{234}Th(IV)$, $^{99}Tc(VII)O_4^{-}$, $^{233}U(VI)O_2^{2+}$, $^{237}Np(V)O_2^{+}$
in situ experiment tracers	Weakly and moderately sorbing tracers, possible use in *in situ* experiments	$^{22}Na^{+}$,$^{45}Ca^{2+}$, $^{83}Rb^{+}$, $^{85}Sr^{2+}$, $^{134}Cs^{+}$, $^{133}Ba^{2+}$, $^{54}Mn^{2+}$, $^{57}Co^{2+}$

A. ^{241}Am can be exchanged towards lanthanide isotopes, see text for details.

The basic concept is to perform a qualified judgement of which level (A–C) of batch sorption experiment the different sampled geologic material should be exposed to. The base for these predictions will be an attempt to quantify their relative importance in contribution to the total retention properties of the site. As a goal, it is proposed that as a first subdivision, 5% of the geologic materials will be placed in level A, 20% in level B and 75% in level C. However, parallel to the batch sorption experiment, prediction of the experimental results based on available sorption databases will be done. If strong deviations between the predictions and the measured data are observed for a particular geologic material, the geologic material will be subject for a re-classification. Further details concerning this selection process are given in Section 7.3.2.

Level C: Cation Exchange Capacity (CEC) and surface area measurement (BET)

Determination of cation exchange capacity (CEC) involves that the negatively charged sorption sites are saturated with one particular cation by contacting the material to a solution containing a high concentration (typically 0.1–1 M) of that cation. This amount of desorbed cations is then measured and defined as the cation exchange capacity of the rock material. CEC is often closely related to the specific surface area of the rock material, i.e. a property that is measured by gas adsorption measurement (BET). However, a full correlation of these parameters has not been demonstrated /Allard et al, 1983/ so the combination of these parameters are probably necessary in order to obtain a simplified estimation of the sorption capacity of the geologic material.

Accordingly, the determination of cation exchange capacity and specific surface area does not produce sorption coefficients (K_d or K_a), i.e. parameters that are used in the safety assessment calculation to determine the retardation of radionuclides due to adsorption on to mineral surfaces. However, the BET surface area and the CEC are good diagnostic parameters in order to give rough diagnoses of the sorption capacity of different geologic material. The strategy is therefore to use measurements of these parameters as a scanning tool to investigate a large number of geologic materials and thereby obtain general information of the sorption capacity of the material. If a geologic material originally decided to be in level C is showing an unexpectedly high or low value for these measurements, further sorption measurements in level B or A should be considered.

Level B: Batch sorption experiment using Cs^+, Sr^{2+} and Am(III)

In their review of sorption coefficients that can be used for a safety assessment, /Carbol and Engkvist, 1997/ consider Cs^+ and Sr^{2+} as the elements within the spent nuclear fuel that have sorption properties that are most sensitive to site specific parameters likely to vary within a site investigation programme, e.g. groundwater composition and mineralogy of the rock material. The lowest level of introducing studies addressing the influence of the groundwater composition would thus be to measure the sorption of Cs^+ and Sr^{2+} using site-specific conditions.

It is also proposed that to already in this level use a tracer that is influenced by hydrolysis and/or surface complexation. Thereby, one should already in this level obtain a general indication of the surface complexation properties of the geologic material. For investigations of geologic material with large availability (e.g. the major rock types) individual batches using Am(III) is proposed for this purpose. In cases where materials with very restricted amounts are available, a multi-tracer cocktail with γ-emitting radionuclides will be necessary to use. Since Am(III) does not have any isotope with good γ-ray characteristics from a multi-tracer measurement perspective, Am(III) will therefore be replaced by an analogous lanthanide, e.g. Eu(III) or Tb(III).

Level A: Batch sorption experiment using tracers representing different oxidation states

As been mentioned earlier, it is considered as non-realistic to perform batch sorption experiment using all the elements in the spent nuclear fuel that have radionuclides of interest for the performance assessment for all site specific conditions. However, certain situations can be identified in which the more general approaches of estimating the sorption capacities (Level B–C) need to be complemented with batch sorption experiment with involvement of tracers representing full coverage of oxidation states.

Level A of batch sorption experiments is a level where radionuclides representing elements with different oxidation states are selected. It is advised to use Cs^+, Sr^{2+}, Ra^{2+}, Ni^{2+}, Am(III), Th(IV), $Np(V)O_2^+$ and $U(VI)O_2^{2+}$. The reason for using three cations with oxidation state of II is that Sr^{2+} will represent cations sorbing mainly with cation exchange mechanism while Ni^{2+} is selected to represent cations with influences of surface complexation in the sorption mechanism. Since Ra^{2+} is considered to be much stronger sorbed than Sr^{2+} and is considered to have a considerable impact in the safety assessment, it will also be included.

As for the level B, any cases of restricted amount of geological material will demand use of multi tracer cocktails. In these cases, Am(III) will be replaced by Eu(III) or Tb(III) and the use of Ra^{2+} may need to be excluded.

In situ experiment tracers

In the site investigation programme for hydrogeological characterisation the possibilities are discussed of including sorbing tracers in the different tracer experiments that are proposed (e.g. single-well injection-withdrawal experiment, *in situ* sorption experiment and multi-well experiments). For the interpretation of these experiments, laboratory batch experiment for measurement of sorption coefficients may be needed that are determined using site-specific conditions. A level of laboratory batch experiments can therefore be identified in which the selection of tracers are done within the group of tracers that have been used within the TRUE-experiment, i.e. Na^+, K^+, Ca^{2+}, Rb^+, Sr^{2+}, Cs^+, Ba^{2+}, Mn^{2+} and Co^{2+} /Winberg et al, 2000; Andersson et al, 2002/. The results from the use of these tracers may therefore not be applied in safety assessment but only for interpretation of the results from the *in situ* experiments.

7.3.2 Strategy for selecting experiment level for the different geologic material

A proposed process for determination of sorption coefficients combined with batch sorption experiment programme is illustrated in Figure 7-1 and is described in details in the following sections.

The basic concept for this process is a hierarchic principle in which a large number (75%) of the geologic materials identified in a site investigation are investigated by a scanning method, i.e. determination of the cation exchange capacity and specific surface area. This method does not produce any sorption data (i.e. K_d or K_a) but gives a general estimation of the sorption capacity of the geologic material. If the value is within the expected range (defined below), no further investigation of the material is performed.

From the remaining (25%) geologic material selected for the investigation of sorption coefficients, experimental determinations of sorption coefficients should be performed. Since the sorption coefficients (opposite to the cation exchange capacity) are dependent on the water composition, the number of experimental cases is a result of the multiplication of the number of geologic material with the number of water compositions. From this total number of experimental cases, ranking should be performed with the respect to the estimated importance in the safety assessment. Although a material may be found on a place where a particular water composition has been found to dominate during the investigation phase, the safety assessment may address scenarios where other water compositions may come in contact with this geologic material.

The total number of combinations (geologic material – water compositions) will therefore be divided into two groups A, and B with respect to their estimated importance in the safety assessment. It is foreseen that this division should be done according to 25% A and 75% B. It should be noted that it is the combinations (geologic material – water compositions) that are divided and the division of the total number of geologic material do not have to follow the numbers given above. For example, if one type of fracture rock type from the site-investigation can be considered under natural conditions to be in contact with low-saline water, this combination may be placed in the category A. A scenario of the same fracture rock type coming into contact with a high saline groundwater may be considered as less likely to occur and, consequently, this combination may be given a lower priority, e.g. category B.

Selection of K_d (K_a) data for information database

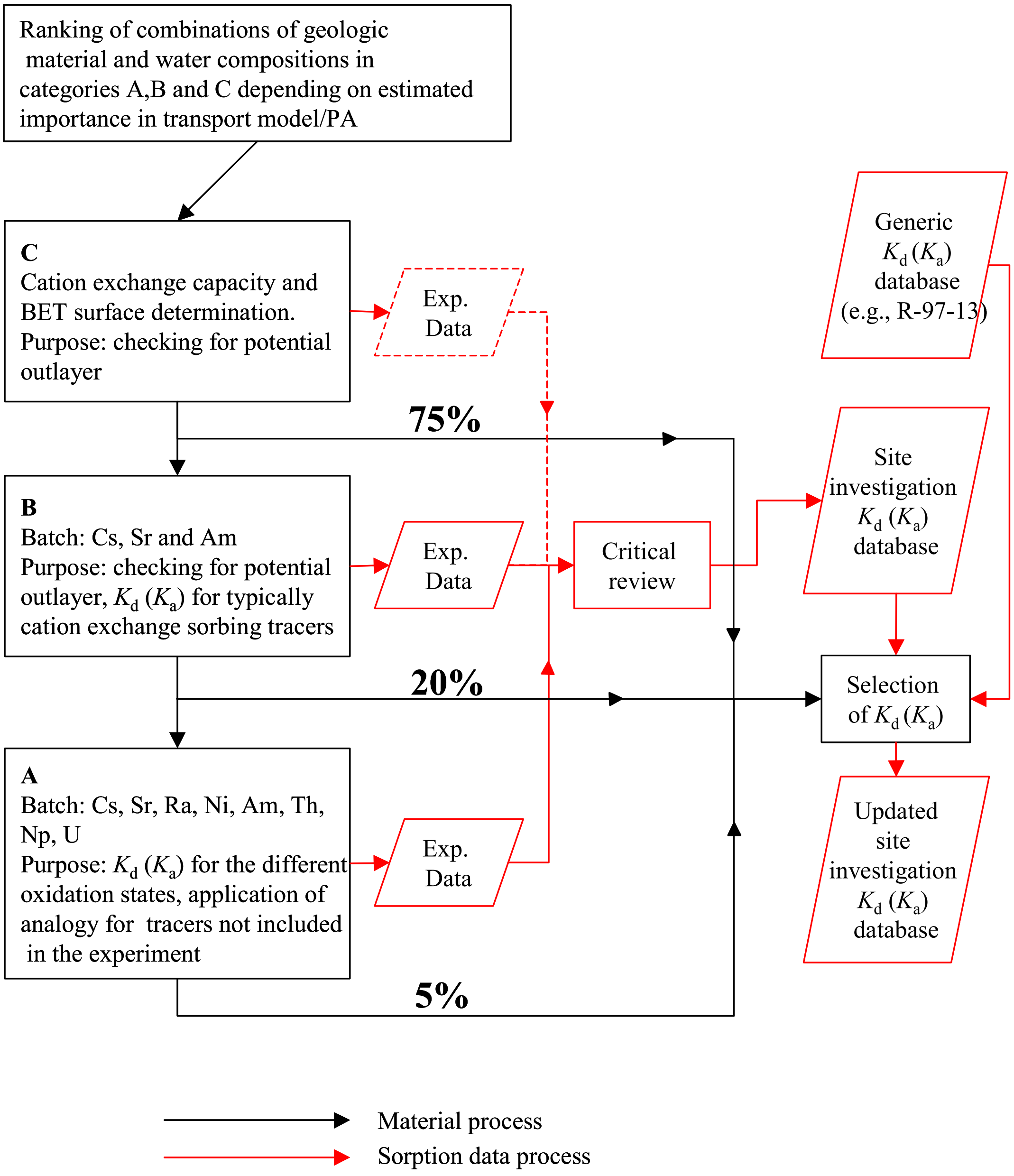


***Figure 7-1.** Process flow for the hierarchic principle of levels in the batch sorption experiments.*

The overall rationale for the selection should be a judgement from the pre-investigation of the site where the relative importance of the different combinations of geologic materials and groundwater compositions in the safety assessment for the site is estimated. One can also foresee an iterative process, i.e. safety analyses may in a later stage identify combinations of geologic materials and groundwater compositions as significant sources of uncertainty, which makes it necessary to revise the original selected level.

7.3.3 Strategy for assigning sorption data for the different combinations of geologic materials and groundwater compositions.

As been mentioned in Section 7.3.1, data for 28 different radionuclides can be involved in a performance assessment calculation. It can easily be foreseen that a site investigation laboratory programme involving experiments of each of these elements (i.e. sorption experiment with the all radionuclides in all possible combinations of geologic materials and water compositions) would expand to a non-feasible level.

For the site description process, it is considered advantageous that all the sorption data accounted for are summarized in a database exemplified in Table 2-2. Sorption data will therefore have to be included in this table that are not directly measured values. For the combinations of geologic materials and groundwater compositions for which a batch sorption experiment is not performed for a particular element, a numerical value should be obtained (in preferential order) from the following processes:

1. Selection from a numerical value for a chemical analogous element (cf. Table 7-2) for which an experimentally determined value using the same combination of geologic material and groundwater composition are available.
2. Selection from the site-specific database, i.e. selection of an experimentally determined value that originates from a combination of geologic material and groundwater that is considered to resemble the particular conditions.
3. Selection from measured sorption coefficients determined for materials that have shown similar cation exchange capacity and/or BET surface area compared to the present geologic material.
4. Selection of the best possible value from the generic database.

The process described in Figure 7-1 therefore also involves the possibility of a successive refinement of the site-specific sorption database. As the process proceeds, more and more site-specific data will be available which probably will be considered as more relevant than the original generic database used.

For the tracers considered as chemical analogous to these tracers (cf. Table 7-2), the sorption coefficients are calculated according to:

$$K_{\mathrm{x(an)}} = K_{\mathrm{x(m)}} \cdot R_{\mathrm{(an/m)}} \qquad (7\text{-}1)$$

where:

$K_{\mathrm{x(m)}}$ K_{d} (or K_{a}) for the tracer that has been used in the measurement

$K_{\mathrm{x(an)}}$ K_{d} (or K_{a}) for the tracer that is considered as an analog to the tracer that has been used in the measurement

$R_{\mathrm{(an/m)}}$ The ratio of K_{d} (or K_{a}) for the analog tracer and the measured tracer, derived from values found in the site-specific database or in a generic database.

Table 7-2. Sources for the sorption coefficients of the different elements included in a performance assessment calculation.

Group	Elements	Level C	Level B	Level A
Mono-valent cations	Cs, Ag	All: database import	Cs: Exp. result Ag: Analogy to Cs	Cs: Exp. result Ag: Analogy to Cs
Hard di-valent cations	Sr, Ra	All: database import	Sr: Exp. result Ra: Analogy to Sr	Sr: Exp. result Ra: Exp. Result
Soft di-valent cations	Co, Ni, Pd, Cd	All: database import	All: database import	Ni: Exp. result Other: Analogy to Ni
Trivalent cations	Sm, Eu, Ho, Ac, Am, Cm	All: database import	Am: Exp. results Other: Analogy to Am[D]	Am: Exp. result Other: Analogy to Am[D]
Tetravalent cations	Zr, Tc(IV), Sn, Pa[A], Th, U(IV), Np(IV), Pu[B]	All: database import	All: database import	Th : Exp. Result Other: Analogy to Th
Pentavalent cations	Nb, Np(V)	All: database import	All: database import	Np(V): Exp results Nb: database import
Hexavalent cations	U(VI)	database import	database import	Exp results
Other	C, Cl, Se[C], Tc(VII), I,	All: database import	All: database import	All: database import

A /Carbol and Engkvist, 1997/ list a recommended K_d for the entire element, i.e. no differentiation of sorption coefficients due to the possible oxidation states (III,IV) is performed.

B /Carbol and Engkvist, 1997/ list a recommended K_d for the entire element, i.e. no differentiation of sorption coefficients due to the possible oxidation states (IV,V) is performed.

C /Carbol and Engkvist, 1997/ list a recommended K_d for the entire element, i.e. no differentiation of sorption coefficients due to the possible oxidation states (–II, IV,VI) is performed.

D In the cases where Eu and Tb have been used instead of Am, the analogy is based on that measurement.

At the present level, $R_{(an/m)}$ is available from the ratios of the sorption coefficient given by /Carbol and Engkvist, 1997/. These values are recommended for "granitic rock" in "non-saline" groundwater ($[Cl^-] < 500$ mg/l) or in "saline" groundwater ($500 < [Cl^-] < 6500$ mg/l). A listing of the $R_{(an/m)}$ is given in Table 7-3, which is proposed to be used as a first database. This comprises a rather rough concept, e.g. no variation due to geological composition is indicated. It can therefore be assumed that future work (within or outside the site investigation program) will give reasons for revision and/or a more elaborate database with respect to the mineralogy. This "analogy database" should therefore be subject for a continuous and regular revision.

Table 7-3. $R_{(an/m)}$ coefficients, derived using K_d- values recommended in the /Carbol and Engkvist, 1997/ database.

Group	Measured tracer	Analogous tracer	$R_{(an/m)}$
Monovalent	Cs	Ag	1
Hard divalent	Sr	Ba	0.01
Soft divalent	Ni	Co, Cd	1
		Pd	1 (non-saline) 0.5 (saline)
Tri-valent	Am	Sm, Eu, Ho	0.67
		Ac, Cm	1
	Eu (Tb)	Sm, Eu, Ho	1
		Ac, Cm. Am	1.5
Tetra-valent	Th	Sn(IV)	0.0002
		Zr, Tc(IV), Pa(IV,V)	0.2
		U(IV), Np(IV), Pu(IV,V)	1

Level C

Parallel to the experimental determination of the CEC and the BET, a prediction is made from the mineralogical composition of the geologic material combined with a database containing the CEC and BET surface area for the pure mineral phases, i.e.

$$\mathrm{CEC}_{tot} = \sum_i n_i \cdot \mathrm{CEC}_i \tag{7-2}$$

where $\mathrm{CEC}_{\mathrm{tot}}$ is the CEC for the rock material, CEC_i is the CEC for a individual mineral, and n_i is the part of the mineral found in the composition of the rock material. and

$$\mathrm{BET}_{tot} = \sum_i n_i \cdot \mathrm{BET}_i \tag{7-3}$$

where $\mathrm{BET}_{\mathrm{tot}}$ is the surface area for the rock material and BET_i is the surface area for an individual mineral. If the predicted value deviates more than a factor 3 from the measured value, the priority of the rock is than changed to level B. This process is described in Figure 7-2. /Allard et al, 1983/ is proposed to be used as the initial CEC and BET database.

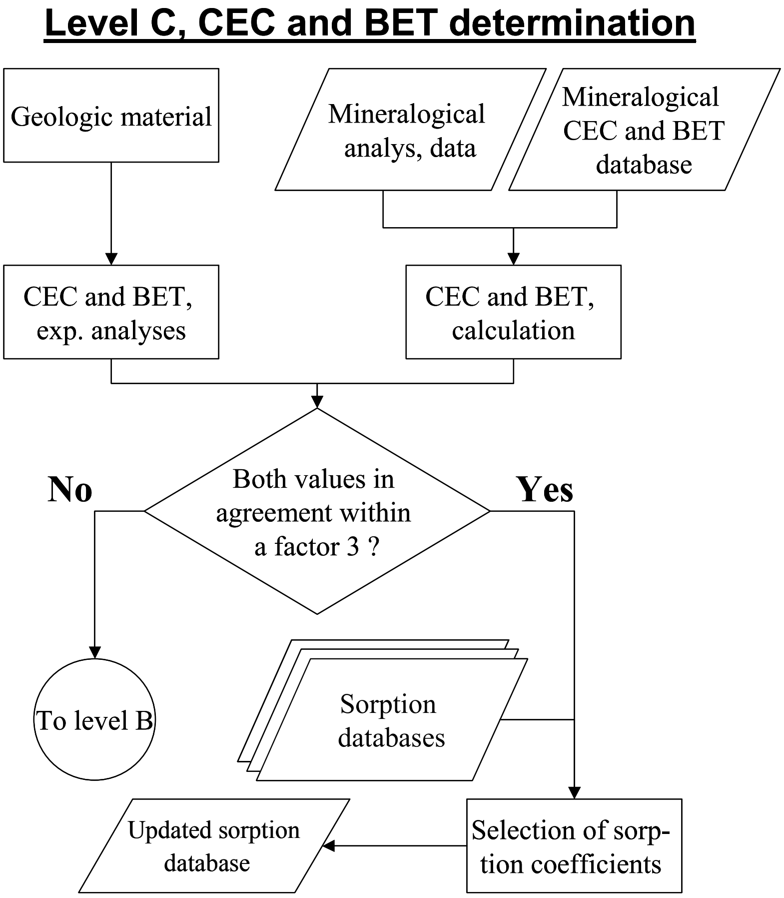


Figure 7-2. *Process flow for the determination sorption of coefficients for the geologic material given the priority D.*

Level B

Accordingly, the second selection is that 75% of the remaining rock/water combinations should only be exposed for batch sorption experiment using Cs^+, Sr^{2+} and a trivalent actinide/lanthanide as tracers. By this method, sorption coefficients (i.e. K_d or K_a) for Cs^+, Sr^{2+} and Am(III) are obtained which can be directly exported to the database.

Parallel to the experimental determination of sorption coefficients, a prediction is made based on the available sorption coefficient database. A value is selected that is derived from conditions (i.e. mineralogy and groundwater composition) that are considered to be similar to the conditions used in the particular experiment. If the experimentally determined K_d deviates more than a factor 10 from the predicted value, this particular rock/water combination is than given the priority of level A. This process is described in Figure 7-3.

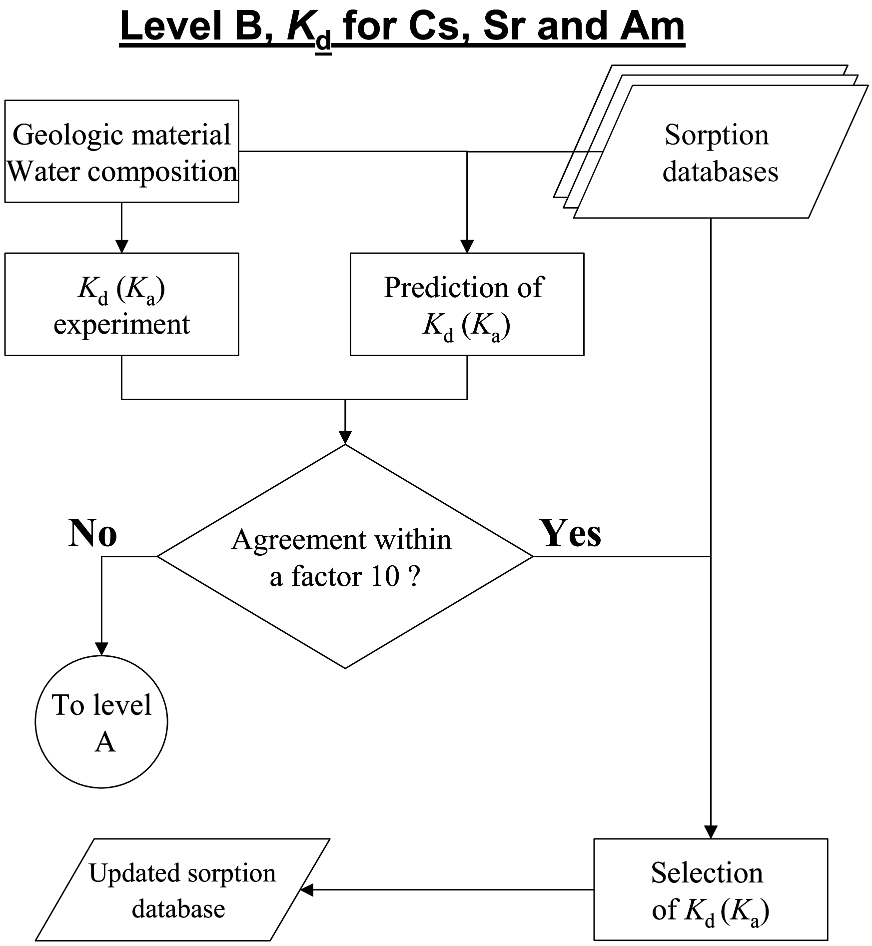


Figure 7-3. *Process flow for the determination sorption of coefficients for the geologic material given the priority B.*

Level A

The second selection is that 25% of the remaining rock/water combinations should be exposed for batch sorption experiments somewhat more elaborate compared to the C-level. Besides the Cs^+, Sr^{2+} and Am(III) that are included in the level B, the experimental programme for level B is extended with Ni^{2+}, Th(IV), $Np(V)O_2^+$ and $U(VI)O_2^{2+}$. Sorption coefficients (i.e. K_d or K_a) are obtained for each of these 7 tracers and can be directly exported to the database. By this tracer selection, a sorption coefficient (i.e. K_d or K_a) for each different oxidation state of the cations is obtained and analog calculations (Equation 7-1) can be performed for the tracers listed in Table 7-2. Using this concept, analogy based sorption coefficients for 16 tracers can be obtained using the level A.

Parallel to the experimental determination of sorption coefficients, a prediction is made based on the available sorption coefficient database. A value is selected that is considered as be derived from conditions (i.e. mineralogy and groundwater composition) that are considered to be most representative to the conditions used in the particular experiment. If the experimentally determined K_d deviates more than a factor 10 from the predicted value, this particular rock/water combination should be a subject for a special investigation. The process is described in Figure 7-4.

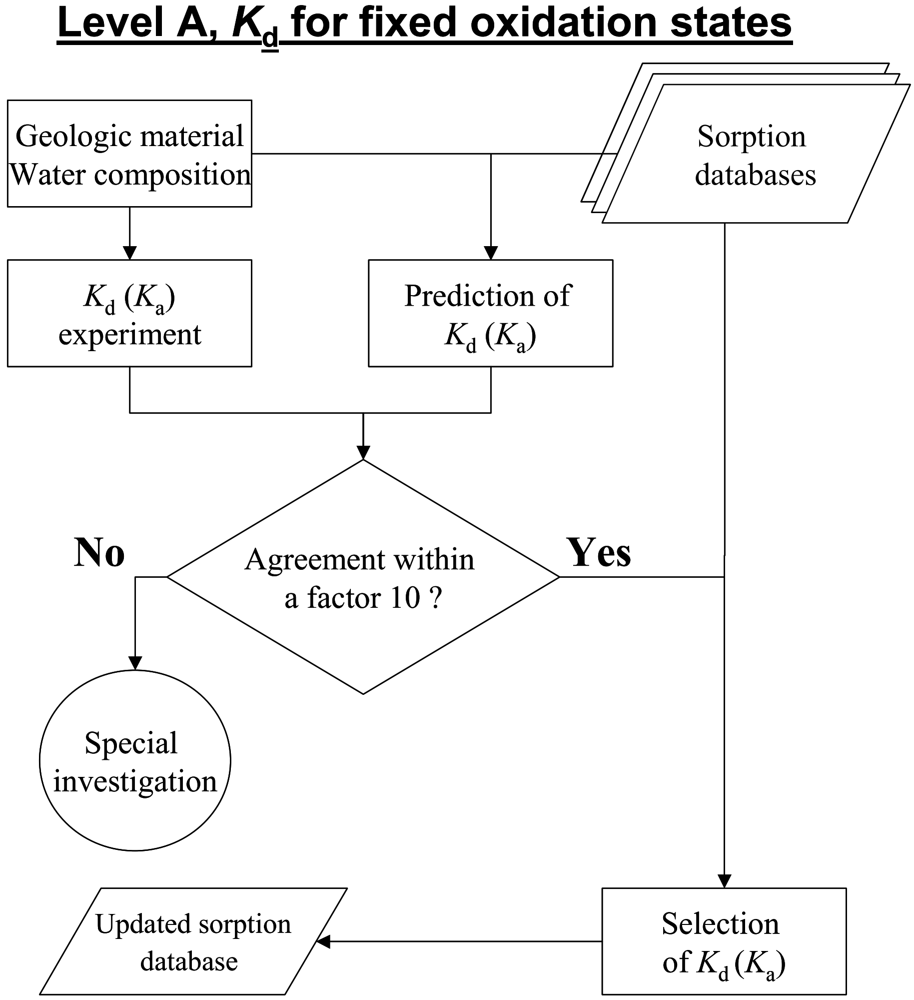


Figure 7-4. *Process flow for the determination sorption of coefficients for the geologic material given the priority A.*

7.3.4 Selection of size fraction of the geological material

Some investigations /e.g. Byegård et al, 1995, 1998; Eriksen and Locklund, 1987/ have indicated that sorption coefficients determined in batch sorption experiment varies with particle size of the crushed rock material as well as with the contact time of the batch sorption experiment. One possible explanation to this behavior is that the smaller size fraction material should consist of a large amount of outer surfaces. According to this model, the adsorption could be interpreted as the sum of two processes:

1. A fast sorption process consisting of the tracer interacting with the easy accessible outer surface of the rock material.
2. A slow sorption process consisting of the tracer diffusing in to the inner surfaces of the rock material followed by a sorption on these inner surfaces.

According to this model, it is included that the outer surfaces are artifacts created by the crushing of the rock material and, therefore, they are not representative for the intact rock material. In order to obtain results that are representative for the *in situ* rock matrix diffusion process, one should therefore do batch sorption experiment where the amount of outer surfaces are minimized. Accordingly, the most representative batch sorption experiment results should therefore be obtained using the large size fractions.

Alternatively, it has been proposed /Neretnieks, 2002a; Skagius et al, 1982/ that the inner surfaces are always dominating no matter what size fractions of the crushed rock material are used. Following this model, the batch sorption experiment results using the small size fractions should be the most representative for *in situ* matrix diffusion. The reason for that should be that only in the smaller size fractions can the tracers be able to penetrate through the rock and establish equilibrium within a reasonable time perspective. Support for this model was given by /Skagius et al, 1982/, in which the sorption of Sr^{2+} and Cs^{+} was studied. It was found that after one year of contact time, the sorption coefficients were very similar, no matter what size fraction of the rock material that had been used.

The best way to obtain a measure of the total amount of accessible surface area of a crushed rock material is gas adsorption measurements, i.e. BET-measurements. This method is normally carried out by letting N_2 adsorb on the solid phase, and since gas diffusion is far much faster compared with diffusion in water phase, equilibrium can be established within a reasonable time perspective. In the case of the outer surfaces being negligible compared to the inner surfaces, one would thus expect that the BET-measurements would give more or less the same results whatever size fraction was used. /Skagius et al, 1982/ reports the same surface area, 1 m^2/g, for the size fractions measured, 0.20–0.25 mm and 1.0–1.5 mm. These measurements were carried out using Finnsjön granite as the solid phase and using N_2 in the BET measurements. On the other hand, /Byegård et al, 1998/ investigated Äspö diorite and Fine grained granite using BET-measurements with Kr and found a very pronounced dependence of the surface area versus the particle size of the crushed rock material.

Within the site investigation program, the results of the BET-measurements will therefore decide which of the size fractions that should be used for batch sorption experiment, according to:

1. If it can be established that the largest size fraction (2–4 mm) has a surface area of >75% compared to the smallest size fraction (<0.063mm), the smallest size fraction is used for batch sorption experiment. The sorption coefficients determined using this size fraction could thus directly be input as the K_d for the rock material.

2. In the case where the BET-measurements show that the surface area of the largest size fraction (2–4 mm) has a surface area of <75% compared to the smallest size fraction used (<0.063mm), 3 size fractions of the rock materials are selected (0.045–0.090 mm, 0.25–0.5 mm, 1–2 mm). The sorption coefficients are thus studied as a function of the surface area and a sorption coefficient determining solely the interaction with inner surfaces can thus be determined, according to:

   $$R_{\mathrm{d}} = K_{\mathrm{d,i}} + K_{\mathrm{a}} \cdot \frac{6}{\rho \cdot \langle d_{\mathrm{p}} \rangle} \qquad (7\text{-}4)$$

   where R_d (m^3/kg) is the measured tracer distribution for a particular size fraction, $K_{d,i}$ (m^3/kg) is the sorption coefficient for the interaction with the inner surfaces, K_a (m) is the surface sorption coefficient describing the interaction with the outer surfaces, ρ (kg/m^3) is the density of the rock material and d_p (m) is the average particle size of the particular size fraction. Plotting K_d as a function of $1/d_p$ thus gives K_a from the slope and $K_{d,i}$ can be determined from the interception with the Y-axis.

7.3.5 Selection of contact time in the sorption experiment

An issue that is closely related to the selection of the size fraction of the geologic material in the batch sorption experiment is the selection of the contact time to be applied. The time dependence of the sorption (i.e. increased sorption with increasing sorption time) can be interpreted as the results of the following processes:

- Diffusion into the micro-pores of the crushed material.
- Sorption influenced by reaction kinetics.
- Degradation/weathering of the crushed material causing increased sorption capacity.
- A combination of the processes mentioned above.

For the two first processes, experiments done with long contact time should reach a sorption equilibrium that should be representative for a safety assessment time perspective. Ideally, one should therefore from this perspective do experiments with application of very long contact time, i.e. until the equilibrium is reached.

However, when strongly sorbing tracer is used it can be shown that the apparent diffusion into the micro pores will be extremely low. A realistic time perspective for laboratory experiments (e.g. 1 year) is probably not enough in order to reach a full equilibrium. From this perspective, one can foresee a conservative approach in which a maximum contact time has to be set, even if equilibrium will not have been reached. The sorption coefficient determined at this maximum contact time will therefore represent a maximum sorption that can be used in safety assessment calculation. It can also be foreseen that maximum experimental contact time can be further restricted because of a short half-life of the most appropriate radioactive tracer of the element.

Degradation/weathering of the geologic material in batch sorption experiment is likely a process that is speeded up by the applied experimental conditions, e.g. the use of crushed rock gives increased access to the inner surfaces. From this perspective (opposite to diffusion and or kinetics), the use of sorption data determined using short contact time would be the most representative the natural conditions.

Based on these facts, it is proposed that sorption data determined with long contact times, and/or cases when equilibrium has been obtained, will be the main source for data to be imported into the databases. However, sampling and measurement will also be performed at short and intermediate contact times. This approach will make it possible in the future to make a further conservative approach, i.e. to make a compensation of the sorption coefficients due to degradation/weathering of the geologic material. It will also enable that in the future go back to the original data and try to apply a dynamic interpretation of the sorption data, e.g. including diffusion and/or kinetics.

The different sampling times that are proposed are therefore 1 day, 7 days, 1 month, 3 months and 1 year. Based on the radionuclides that are proposed (cf. Table 7-1) exceptions will have to be made for ^{234}Th that due to the half-life (24 days) cannot be studied for more than 3 months.

7.4 Through-diffusion experiments

7.4.1 Selection of tracers

Non-sorbing tracers

The principal aim with the through-diffusion measurements is to determine the effective diffusivity (D_e) for tritiated water (HTO) in intact drill core material. By comparison of the effective diffusivity to the tabulated water diffusivity (D_w) of tritiated water, the rock type specific formation factor (F) can be determined, according to:

$$F = \frac{D_w}{D_e} \tag{7-5}$$

HTO can be considered as a good reference tracer in the determination of the formation factor since the measurement is performed with a minimum of interaction processes, such as sorption, anion exclusion, surface diffusion etc. This formation factor can then be used in calculations of the effective diffusivities for other dissolved species provided that the water diffusivities of those species are known. This concept was used as the basis for the tabulation of effective diffusivities for the determination of the water for the SR-97 /Ohlsson and Neretnieks, 1997/. HTO is therefore proposed as the major reference tracer in the determination of the effective diffusivities.

Sorbing tracers

Comparisons of sorption coefficients (K_d) determined in batch experiments using crushed rock material to K_d determined in diffusion experiments have shown some differences /e.g. Johansson et al, 1997, 1998/. It has been indicated that the differences can be explained by erroneously neglecting the heterogeneously distributed porosity distribution /e.g. Johansson et al, 2000; Byegård et al, 2001; Byegård and Widestrand, 2002/.

It cannot be excluded that the crushing of the rock material can cause an increase of the sorption capacity and that the K_d's determined in batch sorption experiments are suspected to be overestimated. It is therefore proposed to include a low number of diffusion experiments with sorbing tracers (preferentially Cs^+ and Sr^{2+}) and to evaluate K_d from these experiments. This concept enables a potential future downscaling of the batch sorption K_d for the case that it from a conservative point of view is considered that K_d determined in batch experiments cannot be motivated to be used in performance assessment.

Based on experiences of diffusion experiments using sorbing tracers /e.g. Ittner et al, 1990; Johansson et al, 1998, 2000/ it is not expected within realistic time perspectives to obtain a breakthrough for Cs^+. Penetration profile studies will therefore be necessary for that tracer. However, for Sr^{2+} it is expected that breakthrough curves can be obtained using saline groundwater environment /Johansson et al, 1998/ but that the apparent diffusion is very low in low saline groundwater environment /Ittner et al, 1990/. It is therefore recommended to use penetration profile studies for diffusion experiments with Sr^{2+} when the ionic strength is <0.1 M and to use through-diffusion experiment when the ionic strength is >0.1 M.

7.4.2 Selection of sample thickness

Different studies of the pore connectivity as a function of the sample length have not given consistent results. Experiments using the through-diffusion technique have in most cases shown a decreased diffusivity when using rock specimen with lengths up to some centimeter. Due to the low porosity/diffusivity of crystalline rock the use of lengths >4 cm is not possible when the maximum experimental time is set to 1 year. Measurements of the electrical conductivity show in most cases (similar to the through-diffusion technique) a decrease of the conductivity for the first centimeters. Using longer specimens, the conductivity seems to reach a constant value. However, in the investigation of /Ohlsson, 2000/ a relatively constant diffusivity was obtained for all of the lengths (1–15 cm) that were investigated.

The selection of a specimen length in diffusion experiments aimed for the determination of diffusivities for the safety assessment scale is related to the connectivity model that is used and also to the degree of conservatism. The maximum penetration depth used in the safety assessment together with heterogeneity of the rock material is also of importance. In the continuing discussion, it is presumed that diffusivity measurements using a range of different specimen lengths for all rock types and samples are not a subject for site investigation measurements. Furthermore, it has been assumed that the maximum experimental time for a diffusivity measurement of a sample has been set to 1 year.

The most conservative approach would be to assume a generally decreasing diffusivity with increasing specimen length, which, however, is contradicted by the electrical resistivity measurements of rock samples /Ohlsson, 2000/. If the maximum length that can be used from a realistic experimental time perspective is 3–4 cm, the diffusivity for stronger sorbing species (shorter penetration depths) may be underestimated while the diffusivity for non- or slightly sorbing tracers will be overestimated in a longer time perspective (for deeper penetration depths than 3–4 cm). The selection of 3–4 cm long specimen can be regarded as a compromise for the diffusivity determinations. For extremely low porous and dense rock material, it can be suspected that breakthrough will not be obtained in a one-year time perspective. If so, only the maximum diffusivities will be reported which will be based on the detection limit for the tracer.

A less conservative approach would be to assume that the porosity is fully connected over the entire rock and that the measured diffusivity will be independent of the specimen lengths used in the experiments. In that case, attention will only have to be paid to the heterogeneity (based on the average grain size) of the rock material. Specimen lengths of 1–2 cm would therefore be a representative length for the most fine- and medium grained rock materials.

Independently of what standard specimen length that is selected for the through diffusion experiment, comparative measures will be obtained between the different rock materials included in the investigations. Using longer specimen length decreases the risk of overestimation of the diffusivity deeper into the rock material. However, the "price" for this conservative approach is a risk of underestimation of the diffusivity in the shorter penetration depths, i.e. the penetration depths to which the diffusion of the strongest sorbing tracers is restricted. The proposal of this report will therefore be to select 3 cm as the standard specimen length of the through-diffusion experiments for major rock types within the SKB site investigation program. This proposal is based on the prerequisite that the measurements should be possible to perform within a reasonable experimental time and the selection is reasonably conservative for use in performance assessment calculations. However, as is discussed in section 3.1.3, the diffusivity as a function of sample length will be studied for the major rock types found in the site investigation. The results of such studies may be used as the basis for scaling laboratory determined diffusivities to the safety assessment scale.

For the measurements of diffusivity in altered layers of fractures or fracture zones it is necessary to investigate specimen lengths that are adjusted to the specific sample properties. The selection of sample lengths and geometry for such experiments will therefore have to be determined arbitrarily based on the fracture-specific conditions.

7.4.3 Rock sample replicates

Because of the variation of the natural composition of the rock samples on the cm scale, a number of replicates for each drill core sample should be used in the determination of the diffusivities. The minimum number of replicates for each drill core sample is proposed to be 3 and the average and standard deviation should be calculated from the results from these replicates. A larger number of replicates would of course give a better basis for the determination of the diffusivity but is not considered as necessary compared to the other sources of uncertainty involved in the diffusivity determinations. For calibration of electrical conductivity measurements, however, only one sample is needed, since these measurements focus on the repository-scale variability and not on the sample scale variability (see section 7.5.1).

7.4.4 Evaluation procedure

For the evaluation of the diffusion measurement it is proposed that main objective will be to use homogeneous diffusion models. It is the authors' opinion that other mechanisms, such as heterogeneous diffusion caused by spatial variation in porosity and mobility in the sorbed phase (surface diffusion) cannot at this stage be justified for application. However, it is possible that in the future the experimental results can be re-evaluated involving other mechanisms, such as heterogeneity and surface diffusion.

For the results of the through-diffusion data, the effective diffusivity, D_e, and the capacity factor, α, is calculated with a fit of the experimental data to the equation /Crank, 1975/.

$$C_r = \frac{D_e t}{l^2} - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left\{ -\frac{D_e n^2 \pi^2 t}{l^2 \alpha} \right\} \qquad (7\text{-}6)$$

The fitting calculation is done by minimizing the error square sum, *ESQ*

$$ESQ = \sum_{i=1}^{n} (C_{r,meas} - C_{r,calc})^2 \qquad (7\text{-}7)$$

A minimization of the total error square sum (contrary to the use of the sum of the relative errors) involves a relatively larger impact of the later part of the breakthrough curve. This will minimize the impact of the very early breakthrough, which has been indicated to be a result of the restriction of the homogeneous model to describe the diffusion /Johansson et al, 2000/.

Sorption coefficients, K_d, can be calculated for a sorbing tracer that has been used simultaneously with a non-sorbing tracer in the same diffusion cell. The relation between the capacity factor and sorption coefficient is described as $\alpha = \varepsilon_p + K_d\rho$, where ρ is the density of the rock. For a non-sorbing tracer ($K_d = 0$) the matrix porosity is obtained by $\alpha = \varepsilon_p$. The sorption coefficient for a sorbing tracer can thus be calculated from

$$K_d = \frac{\alpha_s - \alpha_i}{\rho} \qquad (7\text{-}8)$$

where α_s and α_i are the capacity factor for the sorbing and the non-sorbing tracers, respectively.

7.5 Laboratory electrical conductivity measurements

7.5.1 Samples and replicates

The method is fast and not so labour intensive, which gives an opportunity to obtain some statistics on the variability in rock diffusivity within the investigated rock volume. Based on the observed variability in diffusivity in the investigations of /Ohlsson, 2000/, /Johansson et al, 1997/ and /Xu and Wörman, 1998/ we suggest measurement of electrical conductivity for one sample at approximately every 20th m of the first three deep cored boreholes. This sampling frequency gives about 50 samples per borehole, which should be sufficient to provide information on the spatial variability of the matrix diffusivity. These data may also be used in the future for inter-calibration or interpretation of *in situ* electrical resistivity data, if that method is successfully implemented in the investigations. No extra sample replicates (i.e. single measurements) are recommended for the electrical conductivity method since the focus is on the repository-scale spatial variability. The sample scale variability is measured by using sample triplicates in the through-diffusion measurements.

7.5.2 Sample length

For consistency with the through-diffusion measurements, the same sample length as proposed above (see section 7.4.2) should be used for major rock types, i.e. 3 cm. Accordingly, a flexible sample length is required for measurements of fracture materials.

In experiments aimed for verification of rock pore connectivity, longer samples can be used. The length is then only limited by capability of the measuring equipment.

7.5.3 Calibration of method

A calibration of electrical conductivity data can be done by measurement of identical samples using the through-diffusion method in liquid phase with tritiated water tracer /SKB, 2003a/. We suggest that this calibration should be carried out for every 10th electrical conductivity sample. For samples for which no calibration is possible, diffusivities evaluated from electrical conductivity measurements should be multiplied by a factor of 0.5. This factor is based on the results of the method comparison in Appendix A.

7.6 Gas diffusion measurements

The gas diffusion method is based on using He-gas as a tracer in a nitrogen gas phase. The main advantage of the method is that the diffusion in the gas phase is much faster than in the liquid phase, i.e. that the experimental time requirement for a measurement is much lower than for diffusion in the liquid phase. Inversely, a longer specimen can be measured in the same time as by using e.g. HTO diffusion in water. Since the main quantification of matrix diffusivity is proposed to be done using through-diffusion of HTO, the diffusion investigations can be complemented by He-gas diffusion measurements for verification of pore connectivity for longer sample specimens. In the diffusion method comparison (Appendix A), through-diffusion of He was verified in 10 cm samples. The proposal is to use the He-gas method as a support for the extension of the pore connectivity by measurements of at least one 10 cm sample per major rock type. Gas diffusion measurements using He are performed according to the methodology used by /Maaranen et al, 2001/.

7.7 Porosity measurements using water saturation technique

Matrix porosity measurements of rock types are primarily managed within the geology program. However, measurement of matrix porosity is included in the method description for through-diffusion measurements of matrix diffusivity as a basic material characterisation and supporting parameter. It is also desired from the safety analysis to be able to correlate matrix diffusivity with matrix porosity. For the same reasons, it is beneficial if matrix porosity is measured for the samples used for electrical conductivity measurements. Consequently, matrix porosity measurements using standard techniques are recommended for all samples used for diffusion measurements. The matrix porosity measurements are done for identical samples used in the diffusion methods, consequently the 3 cm size will be used. Matrix porosity measurements for the fracture specific materials are an important part of the characterisation of fracture-type specific retardation properties. For fracture materials, the 3 cm standard length will probably be difficult to maintain in measurements of the porosity in fracture specific rock samples (e.g. mylonites, cataclasites and/or altered rock materials). As for the diffusivity measurements of fracture materials, the specimen length in this case will have to be determined arbitrarily based on the fracture specific conditions. The measurements are performed according to standardised methods (SS-EN 1936 or ISRM 1979).

7.8 PMMA porosity studies

For consistency with the diffusivity measurements, 3 cm is proposed as the standard specimen length for the rock samples used in water PMMA porosity measurements. The average porosity together with the standard deviation should be analysed for a minimum of 3 evaluation points per sample. The measurements are performed according to the method description /SKB, 2003c/.

The 3 cm standard length will probably be difficult to maintain in measurements of the porosity in fracture specific rock samples (e.g. mylonites, cataclasites and/or altered rock materials). As for the diffusivity measurements, the specimen length in this case will probably have to be determined arbitrarily based on the fracture specific conditions.

7.9 *In situ* tracer borehole sorption/diffusion experiments

The method is under development and therefore the implementation of it in the characterisation programme will have to be done at a later stage. The preliminary study suggests that the method can be used for scanning of variability in surface sorption or CEC along borehole surfaces. The possibilities to indirectly or directly measure K_d and diffusivity by the *in situ* method are subjects for the present investigation.

7.10 *In situ* formation factor logging

The method is under development and therefore the implementation of it in the characterisation programme will have to be done at a later stage. The previous study suggests that the method can be used for *in situ* determination of the variability in formation factor based on borehole resistivity logging and detailed fracture groundwater chemistry data /Lövgren and Neretnieks, 2002a/.

7.11 Electro-migration

Electro-migration is currently being developed as a method for the measurement of sorption coefficients in intact rock samples by using electro-migration to obtain a faster transport and equilibration with the internal rock surfaces /Neretnieks, 2003/. The method is under development and therefore the implementation of it in the characterisation programme will have to be done at a later stage.

8 Final comments

The laboratory measurement programme as described in this document should be regarded as a tool and a guide, rather than as a strict instruction, for the practical performance of the laboratory measurements within the site investigation of transport properties. It is a complex task to describe the site-specific transport properties, therefore collaboration with the geology, hydrogeology and hydrogeochemistry programmes are of essential importance in order to achieve the goals as defined in Chapter 1.

The core of the laboratory investigations can be seen as to provide data and support for the understanding of processes occurring at different time perspectives: from short term tracer tests to long-term safety assessment. Of overshadowing importance is the data requirement for the safety analysis. However, the safety assessment rests on a confidence and understanding of the complex processes that occurs in the heterogeneous system that a deep repository for spent nuclear fuel constitutes. Hence, it is important to achieve an understanding of processes occurring also at shorter time perspectives (e.g. tracer tests performed to build confidence in transport models) to be able to understand the longer time perspectives.

Acknowledgement

The constructive review criticism from the following persons is gratefully acknowledged:

Sten Berglund, Anders Winberg, Johan Andersson, Ivars Neretnieks, John Smellie, Kristina Skagius, Fred Karlsson, Yngve Albinsson, Anna-Maria Jakobsson, Mats Jonsson, Trygve Eriksen, Olle Olsson, Ignasi Puigdomenech and Jan-Olof Selroos.

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Appendix A

Comparative study of methods for laboratory diffusion measurements

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2002-07-22

Summary

Matrix diffusion is generally studied by liquid diffusion experiments. Due to the long experimental times involved, other methods such as the electrical conductivity (EC) and the He-gas diffusion method have been developed. In this study, these methods are described and compared with each other, using experimental data from experiments performed on the same samples using all three methods. The liquid diffusion experiments were carried out with tritiated water, HTO, as diffusing specie, and the relative relationship in formation factors between the samples (Äspö diorite and fine grained granite), He:HTO:EC, was roughly 0.25:1:2. The study shows that there is a good correlation between the three methods, however with a better agreement for the Äspö diorite than for the fine grained granite.

The applicability of the methods is discussed, and a strategy to chose method depending on the purpose of the experiment is proposed in the paper. Generally, the EC-method was found to be the simplest and most economical method and especially suitable when handling large amounts of samples. Through-diffusion with HTO is valuable for calibration of the other methods and is the most physically significant method, but unfortunately time consuming and thereby limited to short samples. The He-method is faster, and may be an alternative to both of the others in some cases.

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A1 Background

There are a number of experimental methods for studies of diffusion in low porosity crystalline rocks. The most important methods are diffusion measurements in liquid or gas phase and electrical conductivity measurements. Only a small number of comparative studies of methods are available in the scientific literature. Usually, the focus has been on the properties and variability in the rock types and not on the measurement methods. There is a need for a basis for assessment of laboratory diffusion methods that are of interest within the SKB site characterisation programme /SKB, 2001/.

The objective of this work is to make a comparison between rock formation factors determined using the methods

- Through-diffusion in liquid phase (HTO tracer in water).
- Through-diffusion in gas phase (He tracer in nitrogen).
- Electrical conductivity measurements.

In the first two methods, diffusion through a rock disc is measured using a tracer in liquid or gas phase. The liquid phase is usually water and the soluble tracers are usually dyes or radioisotopes of metal ions or water itself. In gas phase experiments, the sample is dried and nitrogen is used as carrier gas and helium as tracer. The formation factor in both liquid and gas phase measurements is obtained by relating the diffusion coefficient of the sample to that of the diffusion of the tracer in the bulk phase. In electrical conductivity measurements, the electrical conductivity in the rock disc is measured in an electrolyte saturated sample. The formation factor is obtained by relating the electrical conductivity of the sample to the electrical conductivity of the electrolyte that the sample was saturated with.

A number of samples (13) have been measured by the three methods, but the results have only been reported partly and no comparison between the methods has been done. Through-diffusion measurements using tritiated water, HTO, was done at Chalmers University of Technology /Johansson et al, 1997/, electrical conductivity measurements by Yvonne Ohlsson, Royal University of Technology (results presented in this work), and gas-diffusion at University of Jyväskylä /Maaranen et al, 2001/. In addition to a comparative study of the results of the three methods, a limited literature study of other comparative studies was also done.

A2 Theory

Fick's first law of diffusion states that a substance diffuses in the direction of decreasing concentration:

$$J = -D\frac{dC}{dx} \qquad \text{A2-1}$$

J (mol/m^2,s) is the rate of transfer per unit area, D (m^2/s) is the diffusivity and C (mol/m^3) the concentration of the diffusing species.

When the transport is instationary and the solute accumulates or is depleted from the system, Fick's second law describes the transport and accumulation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad \text{A2-2}$$

The solutions to problems described by Fick's second law may often be found in /Crank, 1975/ and /Carslaw and Jaeger, 1959/.

A2.1 Diffusion in liquid filled porous media

In porous media dissolved solutes move by diffusion in the pore water. The tortuosity of the pores increases the diffusion path. The diffusion is also hindered by the constrictivity of the pores. Therefore the pore diffusivity will be less than that in unconfined water:

$$D_p = D\frac{\delta_D}{\tau^2} \qquad \text{A2-3}$$

δ_D is the constrictivity, τ^2 the tortuosity and D_p the pore diffusivity.

The porosity, ε (m^3 pore volume/m^3 rock), of a porous medium is made up of a transport porosity, ε_t, and a storage porosity, ε_d. The transport porosity consists of the pores that are utilised in transporting the substance. Storage porosity refers to pores that have a dead end, and therefore contribute little or nothing to the transport, but can affect the capacity to hold the dissolved species.

$$\varepsilon = \varepsilon_t + \varepsilon_d \qquad \text{A2-4}$$

Fick's first law for transport through porous media can then be described as follows:

$$J = -D_p\varepsilon_t\frac{dC_p}{dx} \qquad \text{A2-5}$$

where C_p is the solute concentration in the pore water. $D_p\varepsilon_t=D_e$, and is often called the effective diffusivity. The porosity, constrictivity and tortuosity can be lumped into an entity, F_f, known as the formation factor. The effective diffusivity can then be expressed as the product of the formation factor and the diffusivity in the free bulk solution, D_w:

$$D_e = D_w \varepsilon_t \frac{\delta_D}{\tau^2} = D_w F_f \qquad \text{A2-6}$$

The same theory applies to diffusion in the gas phase, exchanging D_w for the diffusivity in the free bulk carrier gas. It should be noted that in the literature the formation factor is sometimes described as the inverse of that described by Equation A2-6. The definition used here is, however, widely used in the nuclear waste management community.

A2.1.1 Diffusion and electrical conductivity

In a non-conductive porous material *electrical conduction* will only occur in the fluid in the pores. The tortuosity and constrictivity of the pores cause the electrical conductivity to be smaller than in an unconfined liquid. A relation between these properties is then given by:

$$\frac{\kappa_p}{\kappa_w} = \frac{R_w}{R_p} = \frac{\varepsilon_t \delta_D}{\tau^2} = F_f \qquad \text{A2-7}$$

where κ_p and κ_w (S/m) denote the electrical conductivity in the fluid in the pores and in an open liquid-filled space respectively. In the same manner R (Ω-m) denotes the resistivity. Combining this expression with Equation A2-6 gives:

$$\frac{D_p \varepsilon_t}{D_w} = \frac{\varepsilon_t \delta_D}{\tau^2} = \frac{R_w}{R_p} = \frac{\kappa_p}{\kappa_w} = F_f \qquad \text{A2-8}$$

A3 Experimental

A3.1 Rock material used in the comparison

Äspö diorite and fine-grained granite collected at the Äspö HRL were selected for the laboratory diffusion experiments, since these represent the most coarse- and fine-grained crystalline rock types at the site, respectively. The Äspö diorite is a medium-grained, porphyritic monzo/grano diorite containing centimetre sized K-feldspar phenocrysts. The Äspö diorite is slightly foliated, but the foliation could not easily be observed in the drill cores used for the diffusion experiments. The porosity of Äspö diorite was determined to be ~0.5% using water saturation technique and ~0.4% using ^{14}C-PMMA technique /Johansson et al, 1998/. The fine-grained granite is a more homogeneous, fine-grained alkali granite with a porosity of about 0.2% (^{14}C-PMMA) to 0.25% (water saturation). The drill cores of the fine-grained granite were foliated in approximately a 45-degree angle to the studied diffusion direction. Cutting of the drill cores was done by water-cooled diamond sawing followed by careful grinding. Examples of pictures of polished rock surfaces are shown in Figure A3-1. The mineralogical composition of the two rock types is given in Table A3-1 and a more detailed description of the materials can be found in /Byegård et al, 1998/.

Table A3-1. Major mineral composition and densities of the rock samples /Johansson et al, 1998/.

Mineral	Äspö-diorite (%)	Fine-grained granite (%)
Plagioclase	45	23
Biotite	15	-
K-feldspar	15	38
Quartz	14	31
Epidote	6	-
Chlorite	-	3
Muscovite	-	2.5
Density	2740 kg/m^3	2630 kg/m^3

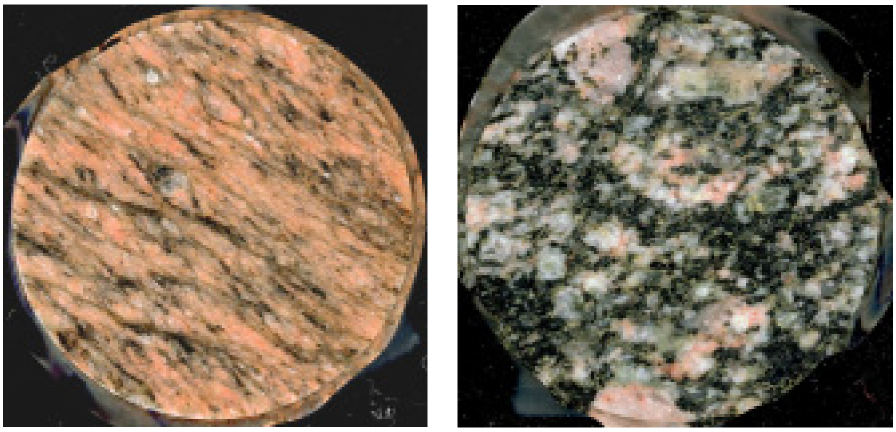

Figure A3-1. Photograph of fine-grained granite (left) and Äspö diorite (right).

A3.2 Through-diffusion in the liquid phase

1, 2 and 4 cm long rock discs with epoxy resin mantling were fixed between 20 ml containers (Figure A3-2). The containers were filled with a solution of synthetic "Äspö water" with an ionic strength of 0.25 M. The rock samples had before assembling been cast in the epoxy resin. After grinding of the end surfaces, the dry samples were saturated with the synthetic water by evacuating the pores from air using vacuum and finally contacting the samples with the water for 1 month. One side of the cell, the high concentration side, was then spiked with the diffusing species, i.e. HTO. The concentration increase on the low concentration side was monitored by collecting samples and analysing them with liquid scintillation counting.

The effective diffusivity was evaluated from the break-through curve by fitting a solution of Fick's second law (Equation A3-1) using the boundary conditions constant inlet concentration C_1, and outlet concentration $C_2 << C_1$ throughout the experiment /Crank, 1975/:

$$C_r = \frac{C_2 V_2}{C_1 A l} = D_e \frac{t}{l^2} - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left\{ -\frac{D_e n^2 \pi^2 t}{l^2 \alpha} \right\} \qquad \text{A3-1}$$

C_r is the scaled ratio of the concentration in the low concentration cell, $\alpha = \varepsilon + K_d \rho$ and ρ is the dry density of the rock (m^3/kg) and K_d the sorption coefficient (kg/m^3). t is the time (s) and l is the sample length (m). V is the container volume (m^3) and A the sample cross-sectional area (m^2).

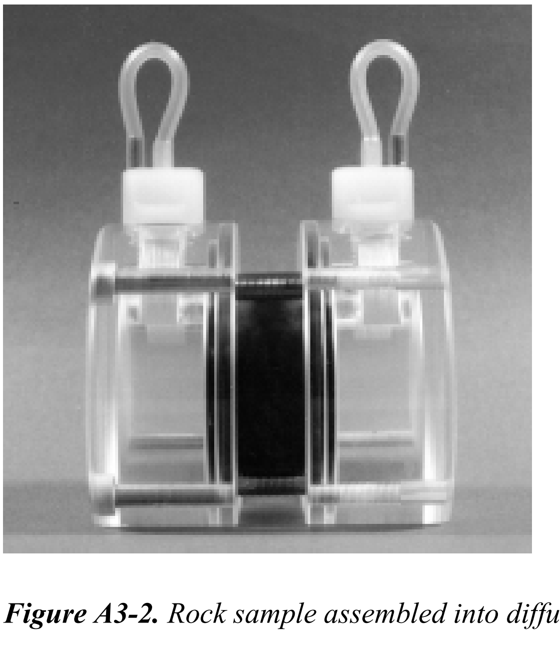

Figure A3-2. *Rock sample assembled into diffusion cell.*

A3.3 Electrical conductivity measurements

The rock electrical conductivity, due to the conducting liquid in the pores, was measured by attaching copper electrodes to each side of the samples, with a thin porous filter between rock surface and electrode, and applying an AC current. The filter was soaked in the same solution that the rock had previously been saturated with, and assured liquid contact between rock and electrodes. The samples had beforehand been vacuum saturated with an electrolyte and kept in the solution for saturation. The temperature was in most experiments kept at 25°C. The method is also described by e.g. /Shopper, 1982/.

The samples were fixed in plastic frames, Figure A3-3, in order to make sure that there could be no short circuit in liquid films on the mantle area of the sample, which can lead to substantial errors if care is not taken. The outer surfaces of larger samples (larger than 2cm) were covered with a layer of silicon glue, Figure A3-3. The covering of the surfaces, both for the samples in frames and those with only a layer of silicon, also prevented evaporation of pore liquid from these surfaces during the measurements. To examine if the silicon glue itself could conduct current and thereby affect the measurements, one of the plastic frames was filled only with silicon glue, and the conductivity through it was measured. The conductivity was less than 0.01 μS/cm. This low conductivity would not affect any measurements, especially since no or very little silicon is in contact with the copper electrodes.

To determine the influence of electrical conductivity through the dry solid rock matrix, an attempt was made to measure the conductivity through 1 cm thick pieces of Äspö diorite. No conductivity could be measured with the equipment used. This means that the conductivity is less than 0.1 nS/cm, which is the lower measuring limit of the equipment.

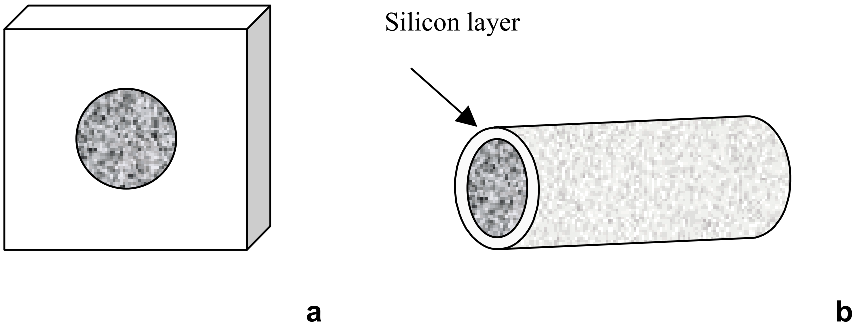

__Figure A3-3.__ Rock sample a) glued into plastic frame b) covered with layer of silicon.

A3.3.1 Formation factor

When determining the formation factor the rock pieces were saturated with a high concentration salt solution (1 M NaCl) and the samples were then kept in the bulk solution for equilibration. Thereafter the conductivity of the rock (due to the pore solution), as well as that of the bulk solution, was measured and the formation factor determined (Equation 2-7). The high concentration is necessary to diminish the influence of the surface conductivity in formation factor determinations /Ohlsson, 2001/.

The electrical conductivity is somewhat frequency dependent. /Kumpulainen and Uusheimo, 1989/ found that at low frequencies (50-1000 Hz) it is almost constant and the impedance is mainly resistive for the granite rock sample. The rock conductivity used for the determination of the formation factor was measured at 375 and 2930 Hz. Some samples could also be measured at 94 Hz, but only those with very low formation factor since the measurement range of the instrument limited measurements at higher conductance at this frequency. As can be seen in Table A3-2, the difference in formation factor is generally small between the frequencies used.

Table A3-2. Formation factors determined at different measuring frequencies.

	ÄD24	ÄD25	ÄD26	ÄD31	ÄD33	ÄD36	ÄD46
94 Hz	-	-	-	3.26E-5	-	1.41E-5	-
375 Hz	1.15E-4	1.43e-4	9.00E-5	3.29E-5	8.02E-5	1.43E-5	9.02E-5
2930 Hz	1.17E-4	1.44E-4	9.11E-5	3.29E-5	8.06E-5	1.46E-5	9.19E-5

A3.4 Helium gas through-diffusion experiments

Diffusion and migration properties are usually determined in the liquid phase. Measurements on low porosity rock samples in the liquid phase are, however, time consuming because the diffusion processes are relatively slow. Diffusion in the gas phase is generally about four orders of magnitude faster than in the liquid phase. The gas diffusion technique was therefore developed at the University of Jyväskylä /Väätinen et al, 1993; Hartikainen et al, 1994, 1995, 1996, 1997/ in order to provide a fast method for studies of migration phenomena. In the He-gas diffusion technique nitrogen is used as the carrier gas and helium as the tracer. An accurate and sensitive determination of helium concentration is possible by using standard techniques such as helium leak detectors.

In the gas phase method, helium is used as tracer. The injection cell at one end of the sample is initially filled with helium, and the surface at the other end of the sample is continuously flushed with nitrogen. The helium concentration of this nitrogen is then measured as a function of time. The experimental set-up for drill core samples is shown in Figure A3-4. The porosity and effective diffusion coefficient ($D_e(He/N_2)$) is then obtained by fitting the analytical solution of the diffusion equation in one dimension to the breakthrough curves /Hartikainen et al, 1996/. The formation factor for the rock sample is then obtained by

$$F_f = \frac{D_e(He/N_2)}{D(He/N_2)} \qquad \text{A3-2}$$

where $D(He/N_2) = 6.75\text{x}10^{-5}$ m^2/s is the diffusion coefficient of helium diffusing in free nitrogen gas at 22ºC /Seager et al, 1963/. An estimate of diffusion coefficients for other tracers in a water saturated rock sample can be done by multiplying the formation factor with the diffusion coefficient in unconfined water. Thus, a scaling factor of about 1/32000 can be applied for estimates of the effective diffusivity of HTO based on the measured effective helium gas diffusivities ($D(HTO/H_20) \sim 2.1\text{x}10^{-9}$ m^2/s at 22ºC, /Mills and Lobo, 1989/).

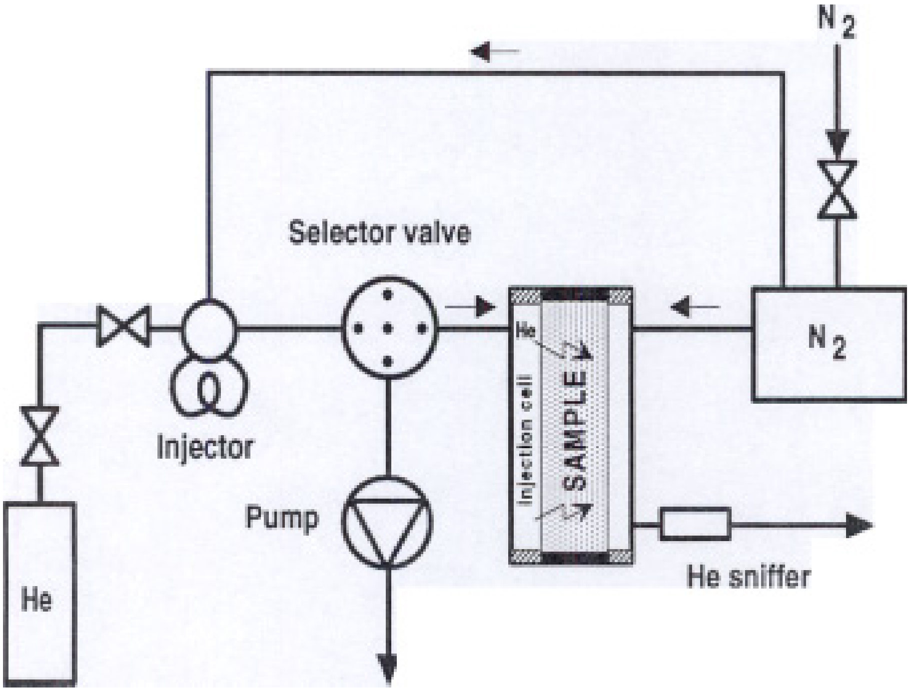

Figure A3-4. *The experimental set-up for drill core samples in the He-gas through diffusion measurements /from Hartikainen et al, 1996/.*

A4 Results and method comparison

A4.1 Results

A summary of the data obtained from the three methods is presented in Table A4-1. The sample variation in diffusivity and porosity is generally larger than the individual experimental errors, therefore the individual experimental errors are excluded from the table. In the electrical conductivity measurements, sample number 26 may have been affected by poor gluing and samples 1 to 4 may have been affected by a too short equilibration time. The effective diffusivity for sample 6 and 7 was measured using the tracer $^{22}Na^+$ in water phase. For these samples, the formation factor was calculated using the water diffusivity of Na^+, which gives a comparative value to that based on HTO diffusion. Ratios of formation factors between the methods are included in the table.

Table A4-1. Results from the through-diffusion experiments using He/N2 gas diffusion, HTO diffusion in water and electrical conductivity (EC) measurements.

Cell #	Type	$D_e(He/N_2)$[1] $[m^2/s]$	$D_e(HTO/H_20$ est. from $He/N_2)$[2] $[m^2/s]$	$D_e(HTO)$[3] $[m^2/s]$	F(He)[4] [1]	F(HTO)[5] [1]	F(EC)[6] [1]	ε(He)[1] [%]	ε(HTO)[3] [%]	F(EC)/F(He) [1]	F(EC)/F(HTO) [1]	F(HTO)/F(He) [1]	Comment
1	FGG 1 cm	2,4E-10	7,5E-15	1,0E-13	3,6E-06	4,9E-05	7,1E-05	0,13	0,47	20,0	1,4	13,8	1 week eq. for el.cond.
8	FGG 1 cm	6,5E-10	2,0E-14	1,2E-13	9,6E-06	5,8E-05	1,6E-04	0,14	0,34	16,6	2,7	6,1	
14	FGG 1 cm	3,6E-09	1,1E-13	4,1E-13	5,3E-05	1,9E-04	4,0E-04	0,33	0,86	7,5	2,1	3,6	
26	FGG 1 cm	9,4E-10	2,9E-14	7,2E-14	1,4E-05	3,4E-05	1,9E-04	0,2	0,49	13,6	5,5	2,5	El.cond. poor gluing?
2	FGG 2 cm	2,0E-10	6,3E-15	7,4E-14	3,0E-06	3,5E-05	6,6E-05	0,17	0,44	21,9	1,9	11,8	1 week eq. for el.cond.
6	FGG 4 cm	1,9E-09	6,1E-14	[7]6.3E-14	2,9E-05	[7]4.7E-05	1,8E-04	0,19	n.m.	6,3	3,8	1,6	F from $^{22}Na^+$-tracer
3	ÄD 1 cm	1,4E-09	4,4E-14	1,4E-13	2,1E-05	6,9E-05	7,5E-05	0,28	0,44	3,6	1,1	3,3	1 week eq. for el.cond.
10	ÄD 1 cm	1,1E-09	3,4E-14	1,9E-13	1,6E-05	9,3E-05	1,0E-04	0,25	0,98	6,1	1,1	5,7	
15	ÄD 1 cm	1,2E-09	3,8E-14	1,2E-13	1,8E-05	5,9E-05	7,9E-05	0,24	0,55	4,4	1,3	3,3	
27	ÄD 1 cm	1,3E-09	4,1E-14	1,4E-13	1,9E-05	6,7E-05	9,5E-05	0,3	0,77	4,9	1,4	3,5	
4	ÄD 2 cm	1,2E-09	3,8E-14	1,2E-13	1,8E-05	5,8E-05	9,3E-05	0,21	0,43	5,2	1,6	3,3	1 week eq. for el.cond.
5	ÄD 4 cm	9,6E-10	3,0E-14	3,1E-14	1,4E-05	1,5E-05	6,6E-05	0,29	0,09	4,6	4,4	1,0	
7	ÄD 4 cm	1,2E-09	3,8E-14	[7]1.6E-14	1,8E-05	[7]1.2E-05	6,1E-05	0,26	n.m.	3,4	5,1	0,7	F from $^{22}Na^+$-tracer

FGG = fine-grained granite
ÄD = Äspö diorite
n.m. = not measured

[1] Evaluated from breakthrough curve in helium gas diffusion experiment

[2] Estimated HTO diffusivity based on $D_e(He/N_2)/32000$

[3] Evaluated from breakthrough curve in HTO diffusion experiment

[4] $F(He) = D_e(He/N_2)/D(He/N_2)$, $D(He/N_2) = 6.75E-5\ m^2/s$

[5] $F(HTO) = D_e(HTO)/D_w(HTO)$, $D_w(HTO) = 2.1E-9\ m^2/s$

[6] $F(EC) = \kappa_{sample}/\kappa_w$

[7] D_e measured for $^{22}Na^+$. $F(HTO) \sim F(Na) = D_e(Na)/D_w(Na)$, $D_w(Na) = 1.33E-9\ m^2/s$

A4.2 Method comparison and discussion

A general observation is that the methods give systematically increasing values of the formation factors in the order helium gas diffusion (He) < HTO diffusion (HTO) < electrical conductivity (EC) measurements. This can clearly be seen in Figure A4-1 for 11 of 13 samples. Including all samples, the relative relationship in formation factors between He:HTO:EC is roughly 0.25:1:2. However, as can be seen in Table A4-2, the ratio between the formation factors for different samples varies, especially for the fine-grained granite. For Äspö diorite, the ratios F(EC)/F(He) is ~4, with only a small variation between the samples. The ratios of F(EC)/F(HTO) and F(HTO)/F(He) show a similar behavior with only a small variation, except for the 4 cm Äspö diorite samples that seem to be too low in the HTO measurement (there is also a very slight indication that the 4 cm fine-grained granite sample is low in the HTO/$^{22}Na^+$ measurement). A possible reason for the "possibly" low values for these thicker samples in the HTO diffusion experiment may be that the homogeneous diffusion model is erroneous in the pre-steady state region of the breakthrough curves. Heterogeneous porosity effects may cause a faster breakthrough than expected from the model. When the model is fitted to data from the pre-steady state region only, as is the case for the 4 cm samples, it may lead to an underestimation of the diffusivity and porosity. Unfortunately, the model is still able to give a very close and unique fit to the data, which makes it impossible to distinguish such an error by lack of model fit. A check of the evaluation of samples 5 to 7 indicates that this kind of error may have occurred for sample 6 and 7, but not for sample 5. It is thus not clear if the data for the 4 cm samples in the HTO/$^{22}Na^+$ measurement are correct or not, which implies that those data should be regarded as possibly underestimated.

Counting only the 1 and 2 cm samples for Äspö diorite, the relative relationship between the methods is now roughly 1/3:1:4/3 (He:HTO:EC). It may thus be so that the results of different methods are dependent on the rock characteristics. This is evaluated further below. The reason for the larger spread in formation factor ratios for fine-grained granite is not known. The variation in formation factor for fine-grained granite could however be interpreted as an effect of micro fractures that occur in some samples. The occurrence of micro fractures in some samples leads to a larger variation in porosity and thereby in diffusivity. It could also be speculated that the lower porosity of the fine-grained granite makes it more sensitive to sample disturbances such as pore clogging from handling etc.

The correlation of formation factor measurements with the different methods is evaluated by plotting the formation factors versus each other (Figure A4-2–Figure A4-4) and by calculating a correlation coefficient, see Table A4-3. Generally, the methods show a good positive correlation. The best correlation is obtained for the fine-grained granite, primarily because the interval over which data exists is larger for fine-grained granite than for Äspö diorite. The plot of F(EC) versus F(He) in Figure A4-2 indicates that there may be a rock type dependency in at least one of these methods, since the data for the two rock types seems to be separated. The two other comparisons (Figure A4-3 and Figure A4-4) indicate more separation between the rock types in F(EC) versus F(HTO) than in F(HTO) versus F(He), especially when the two smallest data points for HTO are considered as possibly underestimated by a factor of two to three. Thus, there is a slight indication that the EC measurement gives higher formation factors for fine-grained granite relative to the other methods. This is an observation that is difficult to explain.

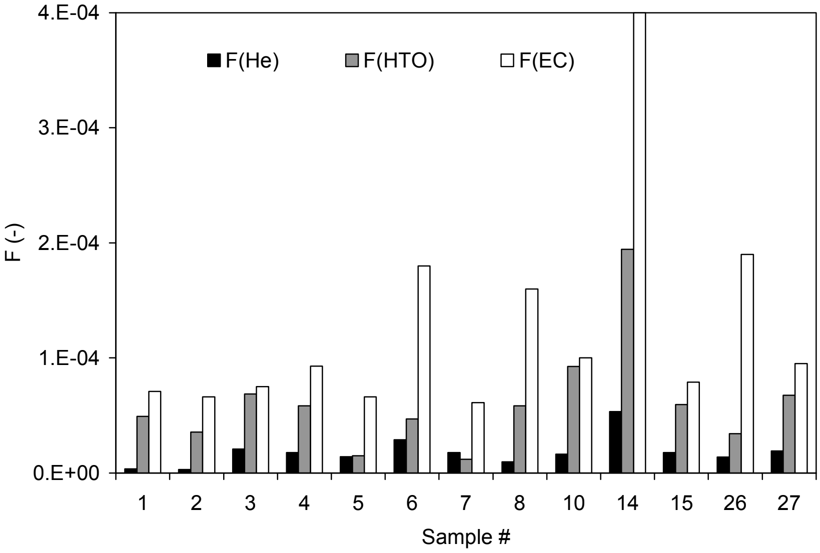

Figure A4-1. *Plot of formation factor obtained using the different methods for all samples.*

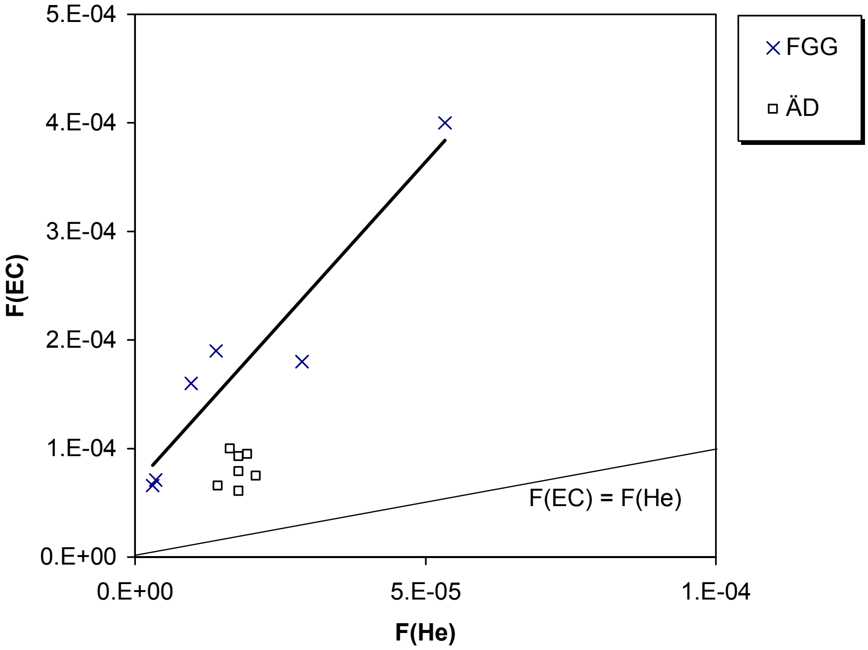

Figure A4-2. *Plot of formation factors for fine-grained granite and Äspö diorite obtained using electrical conductivity versus helium gas diffusion measurements.*

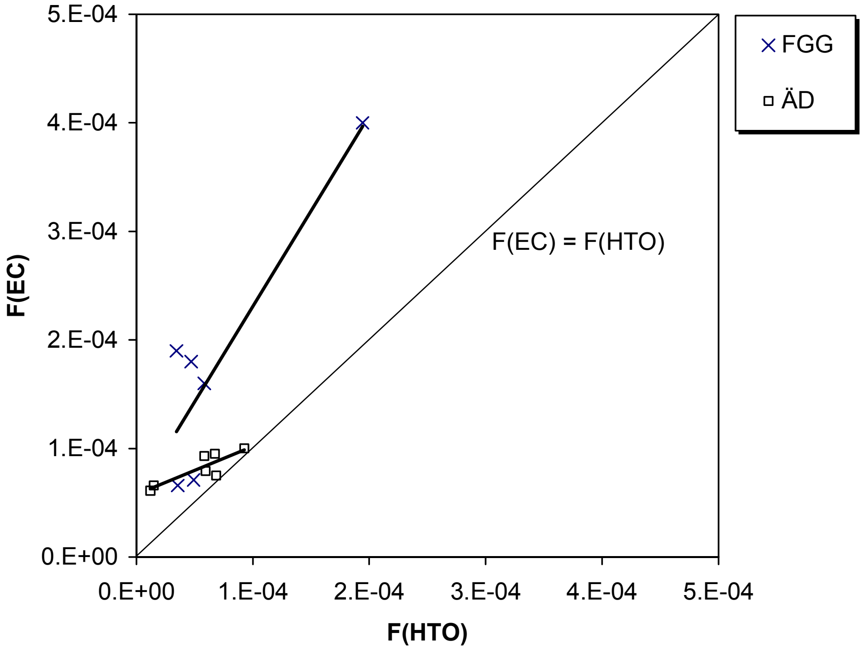

Figure A4-3. *Plot of formation factors for fine-grained granite and Äspö diorite obtained using electrical conductivity versus HTO diffusion measurements.*

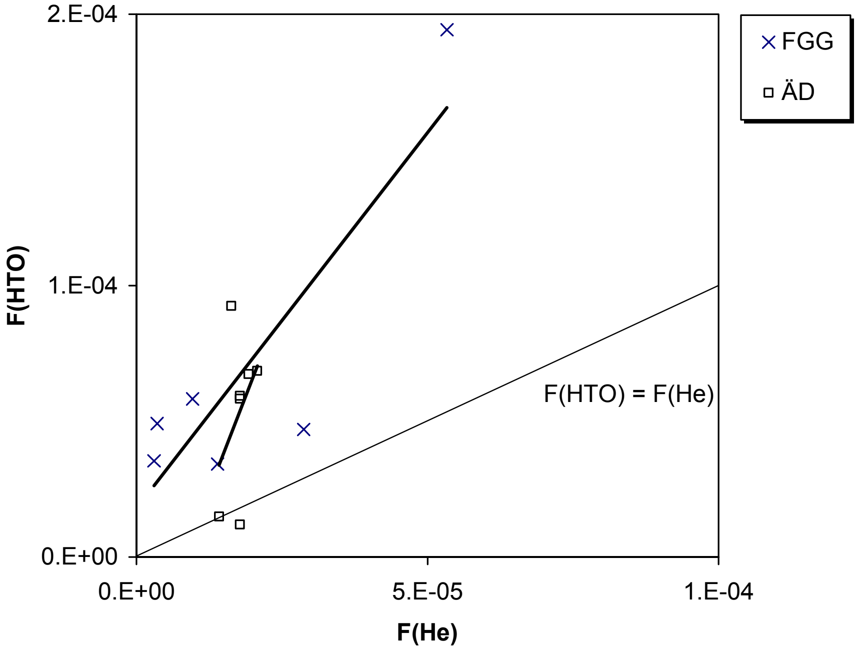

Figure A4-4. *Plot of formation factors for fine-grained granite and Äspö diorite obtained using HTO diffusion versus helium gas diffusion measurements.*

Table A4-2. Correlation coefficients between formation factors and porosities (from HTO and He experiments) for fine-grained granite and Äspö diorite samples. The correlation coefficient is the covariance of two data sets divided by the product of their standard deviations. A value of 1 means a perfect positive correlation and a value of 0 means that the data are uncorrelated.

FGG all samples

	F(EC)	*F(HTO)*	*F(He)*	*e(HTO)*	*e(He)*
F(EC)	1.00				
F(HTO)	0.89	1.00			
F(He)	0.95	0.87	1.00		
e(HTO)	0.86	0.91	0.93	1.00	
e(He)	0.93	0.88	0.92	0.95	1.00

ÄD all samples

	F(EC)	*F(HTO)*	*F(He)*	*e(HTO)*	*e(He)*
F(EC)	1.00				
F(HTO)	0.86	1.00			
F(He)	0.15	0.39	1.00		
e(HTO)	0.86	0.92	0.29	1.00	
e(He)	-0.27	-0.19	0.07	-0.10	1.00

One explanation may be that there is a “background” of rock mineral conductivity in the fine-grained granite. This has not been found, but cannot be entirely ruled out. It is however important to remember that the relatively small number of samples gives a poor statistical basis for detailed evaluations of the results.

The general observation is that the results of the methods correlate well, however with the observed systematic differences between the methods as mentioned above (F(EC) / F(HTO) ~ 1.3 to 2 and F(HTO) / F(He) ~ 3-4). There may be several explanations for these systematic differences. The lower formation factors in the helium gas experiments may be an effect of that the smaller and uncharged helium atom can reach smaller pores and therefore will experience a more tortuous pore network than charged ions or a water molecule can. Secondly, pores may be slightly clogged by salt when the sample is dried prior to gas diffusion measurement. Even though the effect on porosity would be small, it may have an effect on diffusivity depending on how the salt crystals form inside the pores. This effect may be enhanced when electrical conductivity measurements have been performed prior to gas diffusion measurements, since in the EC measurement the samples are saturated with 1 M NaCl (~6% salt by weight). Thirdly, uncertainties in the bulk phase diffusivities contribute to systematic errors for the diffusion methods, although these errors can be expected to be less than ±10%. An advantage with the electric conductivity method is that the conductivity of the bulk solution is measured directly in the bulk phase.

The correlation with porosity is positive and relatively strong as indicated by the values of the correlation coefficients between formation factors and porosity in Table A4-2. One exception occurs in Äspö diorite though, for which the correlation with helium porosity is poor owing to a narrow range of the helium porosity data for Äspö diorite. A positive correlation between formation factors and porosity is expected simply due to the definition of the formation factor. In this respect, the results are satisfying for all methods.

In Figure A4-5 the formation factor for varying sample thickness is shown. It is indicated that there is a larger variation among the one cm samples, however too few two and four cm samples have been measured to be able to draw any conclusions. The diagram also indicates that there is no difference between the two and four cm samples in the helium gas and electrical conductivity methods. Considering that the four cm HTO samples may be too low, no difference between two and four cm samples can be found with this method either.

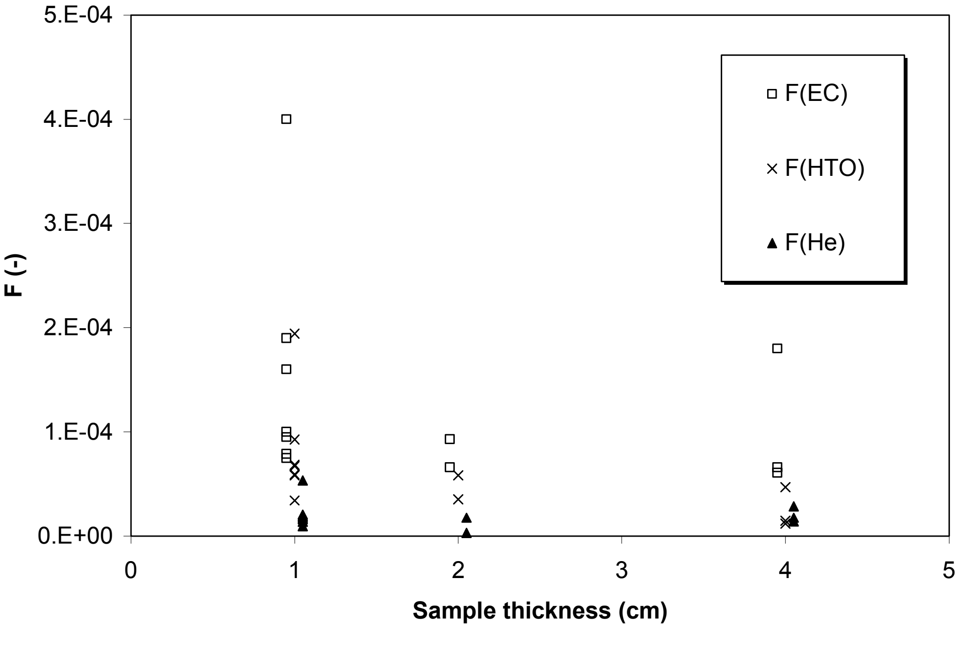

Figure A4-5. *Plot of formation factors versus sample thickness for all three methods.*

4.3 References to other comparative studies

A comparison between electrical conductivity measurements and through-diffusion measurements with uranine as diffusing species was carried out by /Ohlsson, 2001/, also on Äspö diorite samples that were 0,5 – 1 cm thick. The result is shown in Figure A4-6 together with the data for 1-4 cm Äspö diorite samples obtained in the current study. The two studies gave similar results with generally larger formation factors for the electrical conductivity measurements. A clear correlation between the methods is, however, found.

In another study /Siitari-Kauppi et al, 1994/ He-diffusion experiments were compared with through-diffusion experiments in liquid phase. The He-diffusivity was recalculated to HTO-diffusivity using a conversion factor (section A3.4). In Figure A4-7 the apparent diffusivity ($D_a=D_e/(\varepsilon+\rho K_d)$) for HTO determined by the two methods is shown, together with a line for D_a(He-diff)=D_a(liquid-diff).

The He-method correlated well with the liquid through-diffusion measurements, with somewhat lower diffusion coefficients than for HTO-diffusion in the liquid phase. One of the data points differs in magnitude from thee others, however, and very much affects the appearance of the diagram.

No other study has been found that compares the He-method with the EC-method.

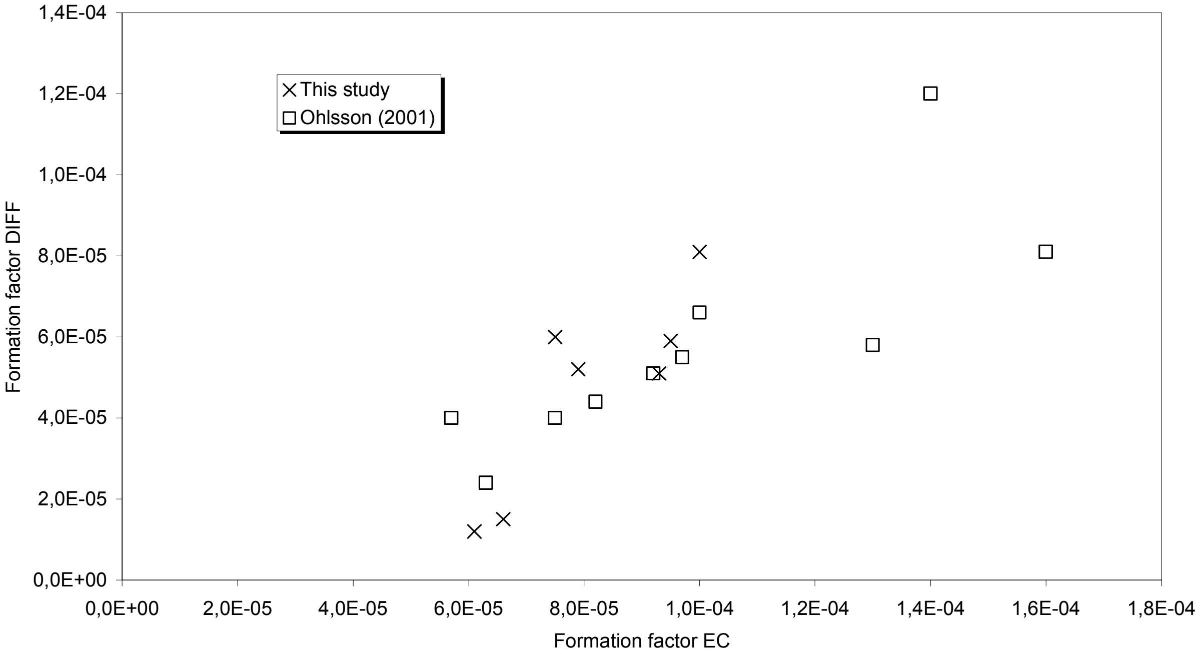

***Figure A4-6.** Results from two studies comparing electrical conductivity and through diffusion measurements using samples of Äspö diorite.*

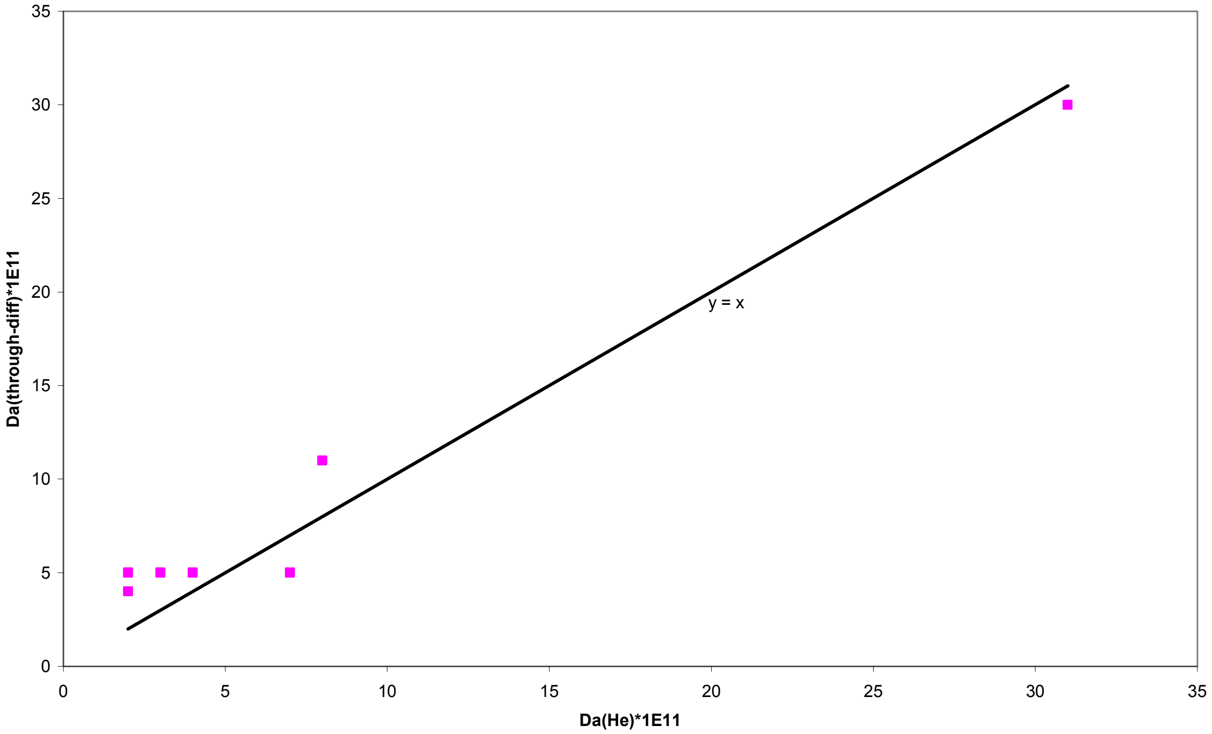

Figure A4-7. *Apparent diffusivity for HTO measured by liquid diffusion versus the HTO-diffusivity calculated from gas diffusion measurements.*

A5 Summary and discussion about the applicability of the methods

A5.1 Through-diffusion in aqueous phase (HTO)

Through-diffusion is the most common method for diffusivity measurements. It is unfortunately rather slow when used for dense rock samples and one is limited to rather short samples. However, it has the advantage of being the only one of the three methods that is measuring throughput of the actual molecule of interest (HTO) in the phase that is of interest in the bedrock, i.e. the water phase. It is thus the technique that best reflects the real situation in the bedrock.

For obvious reasons, diffusion in aqueous phase is also the technique that is used for sorbing tracers. An advantage of using radioactive tracers for these purposes is that identification of diffusion pathways or preferential mineral sorption can be done by autoradiography. Evidence of matrix diffusion not only by the through-diffusion itself, but also by observations of tracers within the rock matrix can thus be obtained with aqueous diffusion methods.

The experimental technique is rather simple, but the experimental analysis requires qualified personnel, at least when using radioactive tracers. The pre-treatment requirements are similar to the other methods. Sample analysis and data analysis is more costly and time consuming than electrical conductivity measurements since the method requires manual sampling. Some benefit in costs and work are however made when several experiments are run at the same time, since sampling can be performed simultaneously and sample analysis is made automatically for a series of samples. Thus, the cost and work per sample decreases with increasing number of samples for this method.

The method is the only one that indicates continuously decreasing formation factors even for samples longer than a few centimeters (although very few long samples have been measured with the He-gas through-diffusion technique). However, too few samples have been measured to confirm this indication. The low diffusivities for longer samples may also be affected by the evaluation using a model for homogeneous porous material as discussed above. The uncertainty in the evaluation of longer samples is partly an effect of the slow diffusion in the liquid phase. The data were evaluated before steady state was finally reached due to the long experimental times involved. If the model then is poor in the pre-stady state region there is a risk that the diffusivity will be underestimated. Monitoring of the breakthrough curve until steady state is reached would solve the problem. However, in the case of 4 cm samples this means monitoring for a few extra years.

Regarding the different aspects discussed above, through-diffusion measurements in the aqueous phase is recommended when quantitative data are required and primarily for shorter samples for which steady state can be obtained within the time available for the experiment.

A5.2 Electrical conductivity measurements

The electrical conductivity method is a fast method even for large rock samples. The time and work required for pre-treatment of samples is similar to that of the other methods. With this method, the pre-treatment of the samples constitutes most of the work and time needed for the experiments, since the actual measurement is done almost instantly. Electrical conductivity measurements are easy to carry out, has a good repeatability and is probably the most practical and economical method when handling a large amount of samples. The disadvantage is that electrically conducting minerals may lead to an overestimation of the formation factor. In comparison with the other methods it gives a somewhat higher formation factor. The reason for this is not clear.

A promising electrical conductivity method for *in situ* measurements is under development /Ohlsson et al, 2001/. By using this method, borehole scans of the variation in formation factor are possible, that could be combined with laboratory measurements on the corresponding drill cores for calibration of the *in situ* data. What is determined with this method is the formation factor for the fresh rock surfaces.

The laboratory electrical conductivity method is recommended when handling a large quantity of samples, and when there is no need to prove that there is actual through-put of diffusing molecules. Through-diffusion experiments can be used for calibration of the method.

A5.3 Helium gas through-diffusion

Since diffusion takes place in the gas phase this method is much faster than the liquid phase through-diffusion method. The experimental time is only a few days, or even hours, instead of months as in liquid phase experiments. Still, there is a need for data analysis and the method is more complicated than the electrical conductivity method. The concentration of the He breakthrough is continuously measured on-line and is automated which is an advantage compared to the liquid diffusion measurements. The pre-treatment (drying) requirements are similar in time and work needed as for the other methods. The method generally gives lower formation factors than the electrical conductivity method, and in this study also lower formation factors than the liquid phase through-diffusion method. This could be due to that the samples had been saturated with a high concentration salt solution before the helium diffusion experiment was carried out. Precipitated salt crystals may have clogged some pores and hindered the diffusion somewhat. However, repetitive measurements on a couple of samples showed only around 20% difference in the formation factor between the measurements when He-diffusion was carried out before and after the samples had been saturated with the salt solution. This suggests that other effects cause the low formation factors. Another reason may have been that the samples were not completely dry and that residual water in the micro pores hindered the diffusion.

A disadvantage with this method is that the experiments are performed in the gas phase, which may lead to errors when data are recalculated to liquid phase. The transformation of data from gas to liquid phase using known bulk diffusivities requires that the diffusing species have experienced exactly the same pore system in the experiments. If this is the case is not known, although it can be assumed that the difference would be small and likely negligible.

The helium gas through-diffusion method is suitable for measurements of samples up to 10 cm thickness within reasonable times (months). However, one experimental equipment setup is needed for each sample. Therefore samples cannot be run in parallel unless several experimental setups are available. Thus, He gas through-diffusion experiments are well suited for large numbers of short samples. Although the technique enables measurements for longer samples than using liquid diffusion, measurements on a large number of long samples will be either costly (if run in parallel) or time consuming (if run one after the other).

Other experimental setups that are available with He gas diffusion techniques are channel flow experiments on long samples and an *in situ* version of the channel flow measurements. These measurements are based on evaluation of breakthrough curves from a pulse injection of He in a nitrogen gas flow along the outer surface of a drill core or the borehole surface. The flow channel is formed between the sample surface and the inner surface of a metal tube or the outer surface of a metal dummy in the *in situ* version. In these measurements, interaction with a large surface area is created which is then observed as a matrix diffusion signal in the breakthrough curves. The advantage of this setup is that finite sample variation effects are avoided in the large sample used. However, the disadvantage is that all of the diffusion takes place in the pore network near the drill core/borehole surfaces and that dispersion effects must be well controlled in order not to influence the evaluation of the breakthrough curves. Thus, these techniques are well suited for scanning purposes, but in order to obtain matrix diffusion data for use in the repository performance assessment, through-diffusion geometry is recommended.

The helium gas through-diffusion method is recommended mainly for demonstration of through-put of molecules in large samples.

A5.4 Summary of method characteristics

A summary of the benefits and drawbacks with the different methods is given in Table A5-1. The summary is based on the discussion in 5.1–5.3 and the judgments should be viewed in relation to the other methods.

Table A5-1. Summary of relative advantages and disadvantages for different method properties.

	Physical significance	Repeat-ability	Time req.	Cost	Simp-licity	Exp. analysis req.	Data evalution req.	Pre-treatment	Avail-ability	Appl. to larger samples	In- situ possibility
HTO	+	+	-	-	-	-	-	a	+	-	-
EC	a	+	+	+	+	+	+	a	+	+	(+)
He	a	+	a	-	-	a	-	a	-	a	+

+: advantageous

a: average

-: disadvantageous

The parameters comprise different kinds of considerations. Some aspects suggested to be considered are the following:

- Physical significance

  This factor takes into account what is actually measured. Only in the HTO-diffusion method an actual molecule is transported in the phase of interest, i.e. the water phase.

- Repeatability

  All methods have shown a good repeatability.

- Time requirements

  Total evaluation and experimental time requirements.

- Cost

  Includes equipment, analysis, personnel requirements etc.

- Simplicity

  Need for qualified personnel, complicated equipment etc.

- Experimental analysis requirements

  Analysis equipment.

- Data evaluation requirements

  Complicated evaluation process? Special evaluation tools needed?

- Pretreatment

  Need for drying, leaching, vacuum saturation etc?

- Availability

  Availability of qualified personnel? Is method developed or in investigation phase? Can the method be used now? Is the method commercially available?

- Application to larger samples

  Can measurements be carried out within reasonable time?

- *In situ* possibility

  It may be advantageous to use the same method in laboratory as *In situ*.

These aspects are merely examples, and further aspects to be considered could be added to the table. The suggested table is meant as a rough aid in choosing methods, and gives an overview of the advantages and disadvantages of each method.

A6 Conclusions and recommendations

The comparison of 13 rock samples measured with electrical conductivity, helium gas diffusion and HTO diffusion in aqueous phase generally indicated a good correlation, however with systematic differences between the methods. The agreement was better for the Äspö diorite than for the fine-grained granite. The relative relationship between the methods was roughly 0.25:1:2 (He:HTO:EC) for all samples and about 1/3:1:4/3 for the one and two cm thick Äspö diorite samples. The ratio of 1.5 to 2 between the EC and HTO methods is consistent with findings in other studies. The lower formation factors found for the helium gas method in this study is however not in agreement with what was found in another study that indicated a 1:1 agreement for gas and liquid diffusion. One possible cause of the systematic differences in this study may have been that pores were clogged by salt crystals from previous equilibration of the samples with 1 M NaCl used in the EC measurement. This explanation was however contradicted by repetitive measurements performed on a couple of samples before and after they were saturated with the 1 M NaCl-solution.

The choice of method should depend on the purpose of the study. Below in Table A6-1, we have suggested the method we recommend for some examples of purposes, based on the summary of method characteristics in Table A5-1. For the SKB site characterisation program, both quantitative data and knowledge of the spatial variation within a site is of interest. In the first phase, we recommend that a practical and cost efficient method is used to obtain information on the spatial variation in formation factors within a block or a site. Ideally, the *in situ* EC method, which is now under development, could be used for borehole logging of variations in the formation factor. If this method does not prove to be useful, laboratory measurements using the EC method is recommended in order to scan a larger number of selected samples with different rock characteristics (rock types, alteration, deformation, foliation etc). In a second phase, samples are selected for which quantitative data is of interest, based on the results of the logging or scanning. These samples are then measured using aqueous phase diffusion, preferably with HTO as a tracer, which gives a "calibration" of the larger data set. In this way, aqueous phase diffusion data and electrical conductivity data can be combined to obtain quantitative data and variability in formation factor within the site.

Table A6-1. Recommendations for the choice of methods for determination of formation factors in crystalline rock within the SKB site characterisation program (PLU).

Purpose of study	Governing concideration	1st choice	2nd choice	Comment
Variability	-Scanning of a large amount of samples	EC	He/(Aq.)	He/Aq. possible if automated process is developed.
	-Scanning of long samples (>2-3 cm)	EC	He	
Pore connectivity	-Verification of pore connectivity	He	Aq.	Choice depends on time available for experiment and if tracer breakthrough is critical or not.
	-Scanning of long samples	EC	He	
Sorbing tracers		Aq.	-	-
Quantitative laboratory data/PA	Physical significance	Aq. HTO	-	When quantitative data are required aqueous phase measurements are recommended. Limitation to short samples.

EC = electrical conductivity

He = He-gas through-diffusion in nitrogen gas

Aq. = through-diffusion of suitable tracer in aqueous phase

Aq. HTO = through-diffusion of HTO in aqueous phase

A7 Recommendations for further studies

The findings from this study are based on measurements on a very limited number of samples. Furthermore, some factors that may have affected the results were not considered in the experiments. For increased credibility in the comparison between the methods further investigation would be valuable. With thorough planning of a comparative study using the three methods the factors that may have affected the measurements can be avoided. For example, the samples are saturated with a highly saline solution in the EC-measurements, which may cause some erosion of the samples. To avoid possible *clogging* of pores by precipitated salt crystals, samples containing highly saline solutions should in a future study be leached before they are allowed to dry.

When comparing the methods for larger samples, > 2 cm, care should be taken in the evaluation of the HTO-experiments. If steady state has not been reached when the experiment is evaluated, there is a risk of underestimating the formation factor.

A careful examination of the rock sample mineralogy would be valuable in the evaluation, to judge whether mineral electrical conductivity could influence the measurements. Another way of testing how the three methods compare is to use a manufactured porous material as a reference material in the measurements. In this way factors like a possibly electrically conducting matrix could be avoided by using only non-conducting material. Furthermore, in this study rock material was used within a very narrow range of porosities. This may have the effect that deviations that would seem small in a wide range cause a seemingly huge deviation for a number of samples in a narrow range. To further study the correlation between the methods samples with a larger range of porosity, and maybe also a variety in rock material would be desirable.

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Appendix B

An attempt to quantify a laboratory programme conducted according to the proposed strategy

General

Based on the strategy for the selection of sampling of the geologic material and the strategy proposed for the different laboratory methods, an attempt has been made to estimate the number of samples that will have to be measured. The basic boundary condition given in this case is the tentative description of rock units along a pathway (Figure 5-2 in the report) together with the tentative rock characterization matrix (Table 2-2). Using these data, a realistic extent of a site investigation transport laboratory program has been estimated for a one individual site.

Batch sorption experiment

Combining Figure 5-2 with Table 2-2 gives the numbers of geologic materials that will be sampled for batch sorption experiment, cf. Table B-1. These samples will be distributed between the defined categories of batch sorption experiment levels A-C, as described in Section 6.3.2. Furthermore, the rock materials given the priority A and B will be exposed to the different water compositions identified at the site. In this tentative example, three different water compositions are identified.

Together with the total number of 24 rock materials given higher priority than C, a total number of 3x24=72 different rock/water combinations will be defined. These 72 different rock/water combinations will be distributed between the sorption levels A-B, i.e. 18 (25%) rock/water water combinations will be given the priority A and 54 (75%) will be given the priority B. It should be emphasized that the judgment of the priority should be done based on the relative importance of the rock/water combinations and not solely on the rock material.

For the level B, 3 tracers are used ($^{85}Sr^{2+}$, $^{134}Cs^{+}$ and ^{241}Am(III)). It is foreseen that two batches will be used for each investigation; one with one where simultaneous γ-spectrometry measurement of $^{85}Sr^{2+}$ and $^{134}Cs^{+}$ are made and one batch which is used for ^{241}Am(III) measured with liquid scintillation with Pulse Shape Analyses (PSA). For geologic material with limit availability (e.g. material associated with fractures) ^{241}Am(III) will be exchanged to ^{152}Eu(III) (possibly ^{160}Tb(III)) and thereby all measurements will be done using only one batch. However, one can also foresee that individual batches have to be prepared for $^{85}Sr^{2+}$ in some cases where the sorption of this isotope is expected to be very low (e.g. use of groundwater with high salinity), cf. SKB MD 540 002. In this estimation of the quantity of a laboratory program, it has been assumed that all measurements in level B can be made using two batches; one for γ-spectrometry measurements and one for liquid scintillation counting.

For the level A, 8 tracers are used which will be divided in 4 different batches according to:

- $^{85}Sr^{2+}$, $^{134}Cs^{+}$ and $^{234}Th(IV)$, tracers measured with γ-spectrometry. In the same batch, $^{237}Np(V)$ and $^{233}U(VI)$ are also used but are measured using ICP-MS. Since these measurements do not interfere with each other, these tracers can be used simultaneously in the same batch.
- $^{63}Ni^{2+}$, measured using liquid scintillation.
- $^{241}Am(III)$, measured using liquid scintillation with PSA.
- $^{226}Ra^{2+}$, measured using liquid scintillation with PSA.

$^{63}Ni^{2+}$, $^{241}Am(III)$ and $^{226}Ra^{2+}$ are likely to interfere with each other during liquid scintillation counting and should therefore be used in individual batches. In cases where there will be limited availability of the geologic material, the isotopes $^{63}Ni^{2+}$ and $^{241}Am(III)$ can be replaced by the γ-emitting isotopes $^{63}Ni^{2+}$ and $^{152}Eu(III)$ (possibly $^{160}Tb(III)$), respectively, and thereby be used in the first batch. In such cases, $^{226}Ra^{2+}$ will have to be excluded. As described above for level B, it may also be necessary in some cases to set up individual batches for $^{85}Sr^{2+}$ when very low sorption is expected. In the calculation of the estimated quantity of the laboratory program, it has, however, been assumed that 4 bathes will be used for each sample measured with level A; one with combined γ-spectrometry/ICP-MS and three batches for liquid scintillation measurements.

This will result in the number of batch sorption experiment described in Table B-2. In Table B-1, an estimation is also given to what extent the batch sorption experiment program would increase if there is a need to identify an additional geological unit, i.e. an major/minor rock type or a fracture type or a local minor fracture zone.

Table B-1 Description of the origin and the total number of geologic material that will be used in batch sorption experiments

	Unaltered rock	**Breccia fragment**	**Gouge**	**Fracture coating**	**Mylonite/ Cataclasite**	**Altered wall rock**	**Sum**	**Increase*) (%)**
Rock type 1 (major)	15	-	-	-	-	-	15	7
Rock type 2 (major)	15	-	-	-	-	-	15	7
Rock type 3 (minor)	3	-	-	-	-	-	3	0.1
Fracture type 1	-	-	-	3	-	5	8	3
Fracture type 2	-	-	3	3	5	5	16	8
Fracture type 3	-	-	-	3	-	-	3	0.1
LMFZ type 1	-	3	3	-	-	5	11	5
LMFZ type 2	-	3	-	3	5	5	16	8
LMFZ type 3	-	3	-	3	-	-	6	2
							93	

*) The increase (in %) of the total number of batch experiment measurements that will be obtained by adding an additional rock type/fracture type/LMFZ to the program.

Table B-2 Estimation of the size of batch sorption experiment program.

Priority	A		B		C		Total#
# rock samples	<------ 24 ------>					71	95 rock samples
# combinations (water/rock)	(*3)	18	(*3)	54	*1	71	
# tracers	*8	144	*3	162	*1	71	306 K_d-values (+ 71 additional CEC and BET-surf.)
Reduction due to use of multi-tracer cocktails [1]	*4/8	72	*2/3	108	*1	71	251
# repetitions per experiment	*3	216	*3	324	*3	213	753
# size fractions used per experiment	*3	648	*3	972	*3	639	2259 experiment batches
# samplings	*5	3240	*5	4860	*1	639	8739 samplings
# γ-spectrometry measurements [2]	*1/4	810	*1/2	2430			3240 γ-spectrometry measurements
# liq. scint. measurements [2]	*3/4	2430	*1/2	2430			4860 liq. scint. measurements
# ICP-MS measurements [2]	*1/4	810					810 ICP-MS measurements

1) For the level A, the use of multi-tracer cocktail enables that the 8 tracers used can be studied using 4 batches. Similarly, for the level B, 3 tracers are studied using 2 batches.

2) For the level B, one of the batches is used both for γ-spectrometry measurements and ICP-measurements and three of the batches are used for liquid scintillation counting. For the level C, one of the batches is used for γ-spectrometry measurements and one of the batches is used for liquid scintillation counting.

Use of intact rock material as an alternative to batch sorption experiment

An explanation that has been presented for the different sorption characteristics observed in diffusion and batch sorption experiment is that the use crushed rock material gives an overrepresentation of available outer surfaces and may therefore give an overestimation of the sorption capacity. A possible alternative laboratory program would therefore be to do the sorption experiment by using intact rock material in as many cases as possible. For samples consisting of drill cores sampled in fractures and local minor/major fracture zones, the intact rock samples is likely to consist of several layers of rock material, e.g. fracture coating, mylonite, cataclasite and altered wall rock. Using an intact rock approach, it cannot be considered realistic to obtain sorption coefficients for all individual materials that are involved. Instead, values will only be obtained as an average of the integrated samples; i.e. a less detailed conceptual model will be obtained by this approach. However, the non-consolidated material in the fracture (e.g. the gouge material and the breccia fragments) will still have to be investigated using batch sorption experiment.

Using a tentative description of the rock units in a site investigation (Figure 5-2) and combining this with the tentative rock characterization matrix (Table 2-2), the following extent is proposed for a program with intact rock material:

- 3 drill core samples for each rock type, i.e. a total number of 9 samples of the major rock types that will be used for diffusion experiment.
- 5 drill core samples for each fracture type, i.e. a total number of 15 samples of the major rock types that will be used for diffusion experiment.
- 5 drill core samples for each local minor/major FZ type, i.e. a total number of 15 samples of the major rock types that will be used for diffusion experiment.

A total number of 39 diffusion samples are thus foreseen in this experimental approach. Analogous to the batch sorption experiment approach, it is proposed that the diffusion experiments should be used with the tracer level B, i.e. diffusion studies with $^{134}Cs^{+}$, $^{85}Sr^{2+}$ and $^{160}Tb(III)$ as tracers in the same cocktails.

Nevertheless, the non-consolidated materials involved in the investigation (i.e. breccia fragments and gouge materials) are not suitable for diffusion studies and therefore have to be studied using the batch sorption measurement technique. The amount of this material can be summed up as:

- 3 samples of gouge material from each fracture type 2 and also 3 samples of gouge material from the local minor/major FZ of type 1, i.e. a total number of 6 gouge material samples that will be used for batch sorption experiment.
- 3 sample of breccia fragments from each local minor/major FZ type, i.e. a total number of 9 breccia fragment samples that will be used for batch sorption experiment.

This total number of 15 non-consolidated materials is proposed to be treated as the rock materials described in the previous section, i.e. given the priority A, B or C depending on their relative importance. This can be compared to the number of 95 rock materials studied for the concept when batch experiments is proposed as the major source for sorption data which gives a total number of 2259 total experimental batches. Given the same relative proportions, it can be foreseen that these total number of 15 materials will give approximately 15/95*2259 = 357 experimental batches.

Diffusivity determinations

The determination matrix diffusivity in the for the rock matrix is proposed to be performed according to:

- 50 determinations per borehole using electrical conductivity measurements; i.e. in a 1000m long borehole a sample will be taken each 20m. Using the assumption that 3 boreholes are set at each site investigation, a total number of 150 samples will be used for laboratory electrical conductivity measurements.
- 15 of these samples are selected for comparative verification measurement using through diffusion technique with HTO as tracer.
- 2 sets of rock samples (, 0.5, 1, 3 and 5 cm) from each rock type are used for study of the diffusivity versus sample length. These samples are used for study of
  - The diffusivity versus sample length (pore connectivity study).
  - The homogeneity of the major rock type in the sample scale (by using triplicates from the same rock sample).
  - The homogeneity of the major rock type within the repository volume (by using 2 different rock samples per major rock type).

  Using the tentative description of a site investigation in Figure 5-2, this task will give a total number of 48 additional diffusion cells.
- 3 integrated samples from each fracture type and 3 integrated samples from each local minor/major fracture zone type are exposed for diffusion experiments. It is estimated that 20% of these samples are large enough to isolate >1cm thick samples of pure mylonite/cataclasite and altered wall rock to be used for individual diffusivity determination of these materials. According to the tentative description of a site investigation in the report, this concept will then give additionally 25 diffusion cells. (Comment: it is doubtful if so much fracture material will be available for diffusion experiments)

The total extent of the diffusivity determination in the laboratory program will thus consist of 150 experiments using the electrical conductivity method and 88 experiments addressing through diffusion technique. For the case that the sorption investigation is done using intact rock material (see above) an integration of these investigations can be foreseen which will reduce the total number of batch sorption samples significantly.

Porosity

Matrix porosity is a parameter that is dealt with in the geology program. However, quantitative and qualitative information of the porosity is produced as supporting data in the diffusion experiments. An estimation of the number of porosity determinations in the diffusion program is done below:

- 223 porosity measurements on intact rock using the water saturation technique. This consists of all samples exposed for through diffusion experiment (88 samples) plus 150 samples exposed for the electrical conductivity measurements. A correction has to be made since 15 of the samples are measured both with electrical conductivity and through-diffusion (for comparative purpose).
- 285 porosity measurements of crushed (or naturally non-consolidated) rock material, i.e. supporting measurements for the materials used in the batch sorption experiments. This consists of the 95 different rock materials, each material measured in 3 different size fractions. For the concept of addressing sorption measurement by the use of intact rock samples, it will only be necessary to do these type of porosity measurements on naturally non-consolidated material, i.e. fault gouge and breccia. On can therefore foresee a total number of 15 rock materials that has to be exposed for this type of porosity measurements; using 3 size fraction will thus give a total number of 45 porosity measurement on non-consolidated rock material.
- 15 measurements of porosity using the PMMA method (1 sample per rock type/fracture type/local major or minor fracture zone type).

Surface area determinations

BET surface determinations are proposed as a supplement to the batch sorption experiment. Depending on the extension of the batch sorption experiment program, the following number of BET surface measurements can be foreseen:

- Batch sorption experiment; 95 different rock materials that will be measured with using 3 different size fractions, i.e. 285 BET determinations.
- Addressing sorption coefficients by the use of intact rock; 45 BET surface determinations (the same rationale as described above for the porosity measurement of non-consolidated rock material).

Pore connectivity verification

Experiments in order to verify the hypothesis of unlimited pore connectivity are done by gas diffusion experiment using one 10 cm rock sample for each major rock type. This will lead to a total number of 2 gas diffusion experiments.

Summary

A summary of the extent of the different proposed laboratory concepts are given in Table. B-3. As a comparison, the extent of the TRUE-1 laboratory program studying the diffusion and sorption in Äspö HRL rock material /Byegård et al, 1998/ in combination with the program with electrical conductivity measurement of Äspö diorite /Ohlsson, 2001/.

Table B-3. Summary of the extent of the different proposed concepts of the laboratory program of the transport parameters of a site investigation. As a comparison, the extent is given for the laboratory determination of transport parameters done for the Äspö Hard Rock Laboratory (investigation done at the Department of Nuclear Chemistry, Chalmers University of Technology and at the Department of Chemical Engineering and Technology, Royal Institute of Technology.

Concept	Batch sorption experiments using crushed rock material	Preferential use of intact rock	TRUE-1 laboratory program
# Batches used in sorption experiment	2259	357	57
# Through diffusion cells	96 (only non-sorbing tracers)	96 (sorbing and non-sorbing tracers, combined)	31(sorbing and non-sorbing tracers)
# Electrical conductivity measurements	150	150	87
# BET surface area determinations	295	45	18
# Rock samples exposed for PMMA porosity measurements	18	18	3
# Porosity determinations (intact rock material)	231	231	107
# Porosity determinations (crushed or non-consolidated rock material)	295	45	0
# Pore connectivity verification (Gas diffusion measurements)	2	2	17